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EDITORIAL

Dear colleagues!

We have the honour to introduce the 30th issue since Ukrainian Food Journal formation.

The Journal was founded in 2012 to promote the publication of young scientists, but during this time it became a good assistant in research, a professional platform for publication and, consequently, discussion of important questions of food science.

We are proud of the Journal's recognition of the global scientific community. Wide geography of authors, including scientists from Bulgaria, Belarus, Romania, Lithuania, Moldova, Turkey, Iran, Czech Republic, Nigeria, Macedonia, Brazil, China, Poland, USA, Kazakhstan, Bangladesh, India, Japan, Georgia, France, Croatia, United Kingdom, Croatia, Ireland, Algeria, South Africa, Indonesia, Austria, Pakistan, Australia, and, of course, Ukraine, and the advisory support of partners from Poland, Bulgaria and Romania contribute the development of our Journal and make it interesting.

The quality of the Ukrainian Food Journal is confirmed by its indexation by EBSCO, CABI, DOAJ, ERIH PLUS, Chemical Abstracts Service Source Index, Food Science and Technology Abstracts and others. Since 2015, all journal articles have been indexed by the Emerging Sources Citation Index, which is part of the Web of Science Core Collection.

However, the achieved successes don’t decrease, but also require greater responsibility for preparing the next issue. Currently, the journal is facing even more challenges and complicated tasks. We need to follow the requirements of science bases, which include the widening of the geography of authors, increasing the scientific level of articles and their citation. But we are convinced that the high potential and creativity of the authors of the articles will take our publication to a new level, provide it with even greater authority in professional circles.

Today's anniversary of the Ukrainian Food Journal is the result of the hard work of scientists and the editorial board. We are sincerely grateful to all those who have made efforts to create, develop our journal and, above all, to the authors who are responsible for the preparation of articles that are really relevant and actively cited.

We wish the authors, the editorial board and our readers good health, enrichment of scientific achievements and the fullest realization of scientific potential!

Sincerely,

Editor-in-Chief

Valerii Mank
Effect of high pressure processing on meat and meat products. A review

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Abstract

Abstract. High pressure processing of meat is considered the best non-thermal processing technology to prolong the shelf life and safety of meat, semifinished meat and ready-to-eat meat products preserving sensory and nutritional properties.

Material and methods. The object of the paper is properties of meat, minced meat products, gel and protein conformation of myofibrillar proteins treated with high pressure. The research method is the analysis and synthesis of the latest study of the world’s leading scientific journals.

Result and discussion. During high pressure processing, pressure level is 100–1000 MPa and temperature range is -20 °C to 90 °C. The relevance and perspectiveness of the research of the use of high pressure technology in the meat industry have been proved on the basis of the analysis of the principle of high pressure processing of meat and meat products, the impact of high pressure on: muscle features (pH, colour, texture, tenderness and water-holding capacity); minced meat products (water- and fat- holding capacity, texture); quality features of gel and protein conformation of myofibrillar proteins (water- and fat- holding capacity of myofibrillar proteins, covalent and noncovalent bonds, protein conformation of myofibrillar proteins).

High pressure processing improves features of muscle, minced meat products and myofibrillar proteins. The application of moderate pressure treatment to prerigor meat maintains the colour and tenderness. High pressure treatment can increase water-and fat holding capacity and texture of minced meat. High pressure also affects on covalent and noncovalent bonds and protein conformation of myofibrillar proteins, develops water-holding capacity, improves texture of myofibrilla proteins.

Conclusion. The use of high pressure processing technology in the meat industry is important and promising. However, the effect of factors on muscle properties, minced meat and myofibrillar proteins when using high pressure is very complex and it should be studied further.
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Conclusion.

Introduction

High pressure processing (HPP), can be referred to as ultra high pressure technology or hydrostatic technology, the water or other incompressible fluid mediums often act as mediators of pressure. During the high pressure processing, the pressure levels generally not less than 100 MPa, the commonly used range is 100–1000 MPa and can work in the temperature range of -20 °C to 90 °C. After the food is sealed in an elastic container or placed in a pressure system, the non-covalent bonds (hydrogen bonds, ionic bonds and hydrophobic bonds, etc.) are been destroyed or formed at a certain temperature for the appropriate processing time and pressure level, which cited the enzyme in food, protein, starch and other biological high molecular substances are deactivated, denatured and gelatinized respectively, and kill the microorganism in food biological, so as to achieve the purpose of food sterilization, preservation and processing.

The ability of high pressures to inactivate micro organisms and denature proteins has been known for over one hundred years. Food high pressure processing technology was began at the end of the 19th century, and the first application of high pressure technology in the field of food is started in food sterilization. In 1895, H. Rouer had carried out the research on killing bacteria with high pressure technology. Hite used high pressure to treat and process milk and meat products in 1899, found that 450 MPa or beyond could prolong the storage life of milk, and put forward the possibility that high pressure can be used as food processing method for the first time. Due to the difficults of technology, the commercial application of high pressure processing in food until to the 1980s with the development of rigs capable of processing reasonably large volumes. Initial success was with fruit based products such as orange juice and avocado paste (guacamole) could be stored for several weeks at refrigeration temperatures with no discernable loss of quality after around 500 MPa treated, because of both bacteria and enzymes were fully or partially inactivated. Since that time many more products have appeared on the market with varying degrees of success.
1. Relevance and prospects of using high pressure technology in the meat industry

High pressure processing is basically a physical process and using a liquid media. Which has the advantages of pressure uniform transmission, instantaneous, efficient, low energy consumption, pollution little dyeing, and no obvious effects of low molecular compounds such as Vitamins, pigments and flavor substances, etc. Therefore, high pressure technology can develop the appearance and new types of meat with different textures will be available in meat processing and storage. At present, the application of high pressure technology in meat processing mainly includes improving meat quality, sterilization and freezing and thawing meat, such as improve meat tenderness, water- and fat- holding capacity, fat oxidation, gel properties. However, in order to realize the large-scale application of high pressure technology in meat processing, there are still many problems worthy of in-depth discussion, and the research on these problems may be the key consideration in the future. Firstly, the high pressure equipment needs a high investment, which has to solve the problem of high cost, which seriously restricts the promotion of industrialization. Secondly, the affecting factors of high pressure processing is complex and diverse, including pressure levels, time, temperature, pressure and the characteristics of raw materials (such as chemical composition, water activity, pH, meat types and quantity, additives, microbial pollution), and so on. The effects of high pressure processing current research is not much, need a lot of researches for a long term.

2. Principle of high pressure processing and high pressure process equipment

Basic Governing Principles. As with heat, pressure is a basic thermodynamic variable. Strictly speaking, during HPP the effects of temperature cannot be separated from the effects of pressure. This is because for every temperature there is a corresponding pressure. Thermal effects during pressure treatment can cause volume and energy changes. However, pressure primarily affects the volume of the product being processed. The combined net effect during HPP may be synergistic, antagonistic, or additive.

Mathematically, the impact of pressure ($p$) and temperature ($T$) can be quantitatively related using Gibbs’s definition of free energy $G$:

\[ G \equiv H - TS, \quad (1) \]

where $H$ and $S$ are the enthalpy and entropy, respectively. Further,

\[ H \equiv U + pV, \quad (2) \]

where $U = \text{internal energy}$ and $V = \text{volume}$.

It can be deduced from Equations 1 and 2 that

\[ d(\Delta G) = \Delta Vdp - \Delta SdT. \quad (3) \]

Therefore, reactions such as phase transitions or molecular reorientation depend on both temperature and pressure and cannot be treated separately. The following are some basic governing principles behind HPP.

The fundamental principles of hyperbaric technique are pascaline law and Le Chatelier principle. Pascaline law takes advantage of the compression effect of high pressure on liquids, which means that the pressure applied to the liquid can be transmitted to all parts of
the system instantaneously at the same size. Therefore, dry food, powdery food or granular food should not be used high pressure treatment. According to Pascaline law, the effect of high pressure processing is independent of the size, shape and volume of the food. In the process of high pressure processing, the whole food will be treated uniformly, the pressure transfer speed is fast, there is no pressure gradient. Therefore, the high pressure processing of food is simpler, and the energy consumption is also significantly reduced. According to Le Chatelier principle, the external pressure reduces the volume of the pressurized system and vice versa. Therefore, the physical and chemical reactions in food ingredients will be carried out in the direction of the maximum compression state under the pressure treatment of food. The increase or decrease of the reaction rate constant \( k \) depends on whether the “active volume” of the reaction is positive or negative. This means that high pressure processed food will force the reaction system to reduce the volume, affecting not only the reaction balance in the food, but also the reaction rate, including chemical reactions and possible changes in molecular conformation. It is well known that the mechanism of meat proteins unfolded, denaturation and formed gel caused by heat and high pressure is difference. High pressure processing induced meat gels are based on the protein volume decline, while the thermal meat gels is caused by the violent movement of molecules and destruction of non-covalent bonds.

Principle of microscopic ordering. At constant temperature, an increase in pressure increases the degree of ordering of molecules of a given substance. Therefore, pressure and temperature exert antagonistic forces on molecular structure and chemical reactions.

Arrhenius relationship. As with thermal processing, various reaction rates during HPP are also influenced by thermal effects during pressure treatment. The net pressure-thermal effects can be synergistic, additive, or antagonistic.

High-pressure processing of muscle based products is paying more and more attention in the meat industry, which could prolong the shelf life of meat products, inactivate vegetative micro-organisms and enzymes near room temperature, because of the processing allows the decontamination of muscle based products with minimal impact on their nutritional and sensory features. Therefore, The application of high pressure offers some interesting opportunities in the processing of muscle-based food products, such as, the high pressure can affect the texture and gel-forming properties of meat batter and myofibrillar proteins, the tenderize, color and other properties of muscle. The processing effects on muscle based products are highly dependent on the primary effects of pressure, time and temperature on the relevant thermodynamic and transport properties of meat systems. However, the pressure-labile nature of some meat protein systems, such as myosin or myoglobin often limits the range of attractive commercial applications to prefermented and cooked meat products.

Pressure Generation Means. Unlike straight processes such as thermal processing, the high-pressure process is independent of the equipment and processed food size and shape. The reason is that the pressure transmission is not mass/time dependent. Hence, reducing the processing time and scaling up the equipment from the laboratory to commercial size will not touch the efficiency of HPP. In contrast, it helps the HPP applications to develop faster. Two types of the compression processes, direct (piston) or indirect (pump) compression can achieve generation of high pressures in the pressure vessels (Figure 1).
Figure 1. Schematics of high-pressure food processing techniques direct (left) and indirect (right) compression:
1 – Top closure; 2 – Pressure medium; 3 – Pressure vessel; 4 – Product; 5 – Piston; 6 – Low-pressure pump; 7 – Tank; 8 – Intensifier pump.

1. **Direct compression.** This technique uses the vessel ends closure/s to act as a piston to build/release the pressure. This happens by reducing the specific volume inside the vessel until the desired pressure is reached. Although, the direct system can achieve a rapid compression, the restrictions of the dynamic seal between the piston and the vessel obstruct the applications of this technique for a small-scale laboratory.

2. **Indirect compression.** Indirect compression is the method used in the application of much high pressure processing equipment in the food industry. It employs a high-pressure intensifier pump to compress a pressure fluid from its reservoir tank into a pressure vessel, transmitted through high-pressure tubes. This technique is more appropriate for solids and high viscous liquid food.

   This method also allows pressure to be released or kept constant at the required level during the treatment time for several minutes.

3. **Effects of high pressure processing on the properties of muscle**

   3.1 **Effects of high pressure processing on the pH of muscle**

   The effects of high pressure processing on the pH of meat was depended on pressure levels, treatment time and temperature, meat temperature, muscle type and so on. The fresh meat had a rapid pH decrease and an intense contraction after high pressure treatment. The mainly reason is that pressurization induced contraction causing calcium release stimulating glycolysis, the changes of activity of phosphorylase, phosphorylase kinase and phosphorylase phosphatase, whose were breakdown the regulation of glycogen during the
high pressure processing. The pH of red meat, such as ovine and bovine muscles were decreased 0.6–0.8 unit after 100–150 MPa, 1–5 min at 35 °C. However, the pH of white meat, such as longissimus dorsi from rabbit had a larger decrease than the musseter after 10 min pressurisation (Cheftel, Culioli, 1997) [1]. The high pressure treatments also affected the ultimate pH of meat. The ultimate pH of pre-rigor pork longissimus increased by 0.48 after high pressure treatments at 215 MPa [2] (Souza et al., 2011). Simonin et al. (2012) [3] showed that the HPP treatment of post-rigor muscles increased the ultimate pH of the meat [4]. MacFarlane (1973) found that the ultimate pH of muscle strips reduced from 5.31 to 5.26 with application of pressure up to 150 MPa. The differences were caused by the different meat type and pressure conditions.

The post-rigor meat had a slight pH increase after high pressure treatment, and the pH increased with the pressure levels increasing. The reason might be that the exposure of acidic groups were decrease due to conformational changes of proteins associated with denaturation during the high pressure processing [5] (Poulter et al. 2010). The pH of porcine and bovine M. semimembranosus muscles slightly increased from 5.6 to 5.8 after 400 MPa, 20 °C, 10 min. The pH of the post-rigor bovine M. semitendinosus muscle slightly increased from 5.4 to 5.6 after high-pressure treatments at 100 and 400 MPa, 15 °C, 5 min, respectively [6–7] (Kwiatkowska et al., 2002; Kim et al., 2007). Ma et al. (2019) [8] reported that the pH of yak meat (thigh muscle) increased with pressure levels increased from 0.1 MPa to 450 MPa. Morton et al. (2017) [9] found that the mean pH of the prime and bull were caused a significant increase, and the cow meat had a significant decrease after high-pressure treatments at 175 MPa, and the mean pH of meat from all the animal classes were significantly increased (P<0.05) by 250 MPa treatment.

3.2. Effects of high pressure processing on the color of muscle

Meat color is one of the most important quality properties for the consumers in a purchase situation, which is determine to the consumers purchase it or not. For example, the consumers usually like a bright red color of beef meat, and a stable reddish/pink color of cured pork products, these were perceived as a sign of freshness (Schulte et al., 1995; Sikes Tume, 2014) [10,11].

Myoglobin is the most important meat pigment, making up 90–95% of the total pigment content. Its concentration and chemical-physical state has a key step of the color of fresh and processed meat (Carlez, Veciana-Nogues, Cheftel, 1995) [12]. The color changes of meat induced by high pressure are basically dependent on three main mechanisms: 1) denaturation of myoglobin, 2) modification or disruption of the porphyrin ring, and 3) changes in the myoglobin redox chemistry (Bak et al., 2017) [13]. These were connection with the meat type, pressure conditions, pH, and so on. High pressure conditions and myoglobin redox form prior to high pressure treatment are the main reasons for the color changes of pressurized meat. At low temperature, below 300 MPa treatment have minor effects on color than the higher pressures. But the myoglobin is not stable, the denaturation had been found to take place at low pressures (Bak et al., 2012) [14]. Korzeniowski et al. (1999) [15] found that the 28% of myoglobin was denatured after 100 MPa treatment, increasing to 66% denaturation of myoglobin after 400 MPa treatment. Souza et al. (2011) [2] found that the high pressure treated longissimus dorsi, triceps brachii, and psoas major muscles had L* values that were 3.87, 6.37, and 2.71 units higher (lighter) (P < 0.05) than controls. The a* values for treated longissimus dorsi muscles were 0.94 units lower (less red) than controls, while treated triceps brachii muscles were 0.67 units higher (more red) than controls. Due to the denaturation of myoglobin, some researchers have reported that high pressure possible gives the fresh meat
a cooked appearance which does not visually appeal to consumers. Carlez et al. (1995) [12] found that the color minced beef meat was changed into “whitening” when the pressures over 200 MPa, the main reason is that a whitening effect due to myoglobin denaturation and/or to haem displacement or release and oxidation of the ferrous myoglobin to ferric myoglobin above 400 MPa. Bolumar et al. (2012) [16] showed that the beef color changes caused by high pressure was similar in appearance to the color change upon cooking, such as lightness increased, redness decreased and yellowness remained more or less unchanged, although the color changes induced by cooking and high pressure have different mechanisms. The oxidation state of the iron in myoglobin is a key factor on the meat color treatment by high pressure. Due to the light reflection and scattering increased, L* value of pork increases at pressures up to 400 MPa. The other reason is possible that the myofibrillar proteins was decreased the solubility and formed of larger insoluble protein aggregates during the high pressure treatment, which may affect the meat surface and the light reflectance (Olsen and Orlien, 2016) [17]. Wackerbarth et al. (2009) [18] studied the effect of high pressure processing on structural changes of pork myoglobin by resonance Raman spectroscopy, found that the oxy-myoglobin was changed into the formation of met-myoglobin and further denatured ferric Mb species, the structural transition could cause a colour change and initiate unwanted oxidative side reactions involving further components of meat. High pressure treated meat samples have a high ultimate pH, that led to their color became darker. Brewer et al. (2001) [19] reported that higher pH of high pressure treated is correlated with lower L* values causing the meat to appear darker. The chicken meat has low content of myoglobin, is considered “white meat”. Therefore, the color of raw breast is slightly pinkish, the appearance is bluish-white to yellow. Therefore, the effect of high pressure on color is not different from beef and pork meat. The lightness, redness and yellowness of whole chicken breast fillets were increased after 300–600 MPa treatment. The increase of redness was caused by the reversible renaturation of pressure-denatured myoglobin (Kruk et al., 2011; Del Olmo et al., 2010) [20–21]. Overall, high pressure treatment of meat has a great impact on meat color, generally, the lightness was increased and the red of pork and beef was decreased, which is an interrelationship the modifications of myoglobin molecules.

### 3.3. Effects of high pressure processing on the water holding capacity of muscle

The effects of high pressure processing on the water holding capacity of meat was depended on pressure levels, treatment time and temperature. Ma et al. (2019) [8] reported that with increased time and pressure, the water holding capacity of the yak meat increased first and then decreased. At 250 MPa, 15 min, the water holding capacity had a increase of 10.50% and the meat turned white. The reason is that high pressure processing caused by reduced exposure of acidic groups and increased the pH levels of meat, which could improve the water holding capacity. When the high pressure and time were exceed, the meat has an excessive contraction and the water holding capacity decreased [22] (Hong et al., 2005). Souza et al. (2011) [2] also reported that the cooking loss of pork was decreased by 17.35% after being exposed to 215 MPa at 33 °C for 15 s. If the pressure lever is too high, the activity of calpain, such as desmin, is been inhibited by high pressure and prevents the degradation of cytoskeletal proteins, and reduces the water-holding capacity of muscle (Campus, 2010) [23]. The high pressure and heat combined could improve the water retention in muscle, depending on the process parameters. When pressure treatment at 100 to 200 MPa, the drip loss and free water of pork meat were increase from 4% to 7%, and at 300–400 MPa these were decreased to 4%. The cooking yield of pork meat by previously high-pressure-treated at 300 to 400 MPa was significantly higher than that found for heated-only samples; they
were no difference between heated-only samples and high-pressure-treated at 300 to 400 MPa (Korzeniowski et al., 1999) [15]. These different results for water holding capacity were caused by the different temperatures and pressure levels. Some researches have reported the high pressure processing could use to improve the quality of heterogeneous meat. The pale, soft, and exudative (PSE) meat has lower muscle pH is associated with lower water holding capacity. The high pressure processing may improve the water holding capacity of PSE meat. Chan et al. (2011) [24] found that the expressible moisture of PSE-like turkey breast meat was decreased at 50 and 100 MPa, and the lowest level occurring at 100 MPa (18.7%), the result in that the water holding capacity was increased at these pressure levels. However, the water holding capacity was decreased significantly (P < 0.05) at 150 MPa for 5 min at 4°C, because of the less hydrophobic interactions and lower protein surface hydrophobicity at 150 MPa. In addition, the effects of water characteristics in meat treated by high-pressure have been researched. Bertram (2004) [25] studied the effect of water characteristics in cooked beef by nuclear magnetic resonance, found that the T2 values were lower in pressure-heat treated meat revealing alterations in water characteristics of pressure-treated, cooked meat compared with cooked meat, and the shear force of pressure treated samples were lower. The high pressure treatment is affected the myofibrillar organization, which changes the properties of water in the meat and improved the tenderness of meat (Bertram, Purslow, Andersen, 2002) [26].

3.4. Effects of high pressure processing on the tenderness of muscle

Tenderness is identified as the primary eating quality factor, which is the key determinant of whether consumers are repeat buyers or not Miller, Carr, Ramsey, (Crockett, Hoover, 2001; Platter et al., 2003) [27,28].

The tenderness of meat are depend on the myofibrillar and connective tissue proteins. The mechanisms of meat tenderisation that occurs in high pressure processing of pre-rigor muscles and chill ageing of post-rigor muscles are differences. High pressure treatment could cause changes in the muscle microstructure, sarcomere contraction, muscle fiber damages, and myofibril fragmentation, such as hydrolyzed the proteins in the muscle fibers, weakened the cell structure, released the ions and activated calcium activating enzymes (Lowder et al., 2014) [29]. Calpains are a large family of cytoplasmic cysteine Ca2+ dependent proteases in skeletal muscle, some papers found they are contact with the post-mortem proteolysis and meat tenderization, which are able to degrade myofibrillar proteins including nebulin, titin, troponin-T and desmin (Hufflonergan et al., 1996; Kristensen Purslow, 2001) [30,31]. Homma et al. (1996) [32] found that the calpain activity of muscle was increased by pressure up to 200 MPa caused by Ca+, which was released from the sarcoplasmic reticulum and to the inactivation of the inhibitor calpastatin during the pressure treatment. Morton et al., (2018) [33] reported that high pressure processing could direct physical disruption of the sarcomeres, destroyed the organised structure of the sarcomere Z discs, M lines and A bands. Bouton et al. (1977) [34] obtained that high pressure processing is a clean technology that can tenderise post-rigor meat with the appropriate pressure levels and temperatures. Souza et al. (2011) [2] found that the shear force of pork were decreased by 30% after 215 MPa for 15 s at 33 °C. The similar results was reported that after 300 MPa for 20 min at 20 °C treatment, the shear force of goose breast were decreased by 34.78% (Gao et al. 2014) [35].

The shear force of hot-boned beef was decreased after 175 MPa treatment and improved the eating quality. Thus, the moderate pressure levels treatment of pre-rigor meat seems to have potential since the meat was tender and looked normal (Morton et al., 2017) [36]. Ma and Ledward (2013) [37] reported that the tenderness of pre-rigor meat after subjected to
pressures of about 100-150 MPa was significantly improved compared to the untreated counterpart, and this method have become a commercially viable process, which given the decreasing cost of high pressure machines. Up to 60 °C, the shear force of post-rigor meat was significantly reduced after subjected to pressures of 100–200 MPa. Some authors have reported that the post-rigour beef muscle treatments by high pressure had no beneficial effects, such as combined pressure-heating treatments, which result in brown discoulouration (Ma Ledward, 2004; Ma et al., 2007) [38,39].

The connective tissue proteins is an important factor of the tenderization of meat, such as the state of linking myofibrils to the sarcolemma and other filaments from the cytoskeletal netwrok (Cheftel Culioli, 1997; Taylor et al., 1995) [1,40].

The thermal solubility of collagen was changed caused by 200–500 MPa, 20°C, 10 min, the thermal stability of thermally undenatured collagen was improved, and the thermal stability of partial collagen denaturation before pressurization might be reduced. Ichinoseki et al. (2007) [41] found that the thermal stability and surface hydrophobicity of beef collagen fibrils was decreased treatment by high pressure processing, caused the structural weakening of intramuscular connective tissue. The intramuscular connective tissue was benefit of improving the tenderness. Kim et al. (2007) [7] showed that the shear force of the bovine M. semitendinosus muscle was decreased significantly treated by 100–500 MPa, 15°C, 5 min, after cooking to an internal temperature of 75 °C.

4. Effect of high pressure on the comminuted meat products

For years, the demand of comminuted meat products is increasing, which have enjoy widely consumer acceptance in certain sections of the global population (Delgado-Pando et al., 2010; Kang et al., 2017) [42,43]. The tradition comminuted meat products contain higher salt and fat, overtake the salt and fat could increases the risk of obesity, hypertension and cardiovascular disease (Jeon et al., 2015; Yalcin Seker, 2016) [44,45]. However, the salt and fat content have a key factor in the solubilization of the myofibrillar proteins, as it is these proteins that determine the binding and textural characteristics of the product, they are also contributes to flavor of comminuted meat products (Pietrasik Li-Chan, 2002; Tobin, O'Sullivan, Hamill, Kerry, 2013; Kang et al., 2014) [46–48]. For declining the animal salt and fat content of emulsion meat products, high pressure processing has caught the interest of emulsion meat products because it meets consumer's requirements for low fat and salt content, which has been renewed as a best non-thermal intervention for extending the shelf-life and safety of comminuted meat products without altering the sensory and nutritional properties (Hygreeva Pandey, 2016; Chen et al., 2018) [49,50].

4.1. Effect of high pressure on the water and fat holding capacity of comminuted meat products

The water and fat holding capacity expresses the ability of comminuted meat products to hold water and fat, which is an important indicator of products quality. In the gelation process proteins undergo unfolding and denaturation followed by protein association, forming a three dimensional network which entraps water molecules and thus produces a gel. The pressure intensity, salt content, meat type, composition, temperature and others factors independently affected both the water and fat holding capacity of comminuted meat products. Carballo et al. (2000) [51] found that the post-rigor pork gel structures had better water binding properties but were weaker than non-pressurized meat batters and batters pressurized prior to heating. Zheng et al. (2017) [52] reported that the cooking loss was not decrease.
caused by addition of salt with high pressure treated chicken meat batters, this suggested that high pressure was much more effective than salt in reducing water loss during the cooking. Rospolski et al. (2015) [53] studied the effects of high pressure processing parameters and NaCl concentration on the physical properties chicken meat batter, showed that water became slightly more tightly bound to the meat matrix after high pressure processing treatment, main reason is the high pressure processing could increase the solubility of muscle proteins, thus increasing water and fat holding capacity and decreasing mechanical water loss (Chan et al., 2011; Sikes, Tobin, Tume, 2009) [54,5 5]. Villamonte et al. (2013) [56] also observed an increase in water holding capacity due to the interaction of high pressure processing and salt in pork meat batter, this may be because increasing sodium chloride causes increasing denaturation of muscle proteins in high pressure treated meat batters and favors the solubilization of proteins and the formation of a gel network that retains water and fat.

The high pressure processing and heating (>40 °C) combinations limits the gelling process of meat systems. The pork and chicken meat batters had better water binding properties after 200–400 MPa treated for 30 min, at 60–80 °C, however, the gel structures were weaker than gels made by heating (non-pressurized) or pressurized prior to heating (Fernandez, 1998; Colmenero, 2002; Yang et al., 2015) [57–59]. Marcos et al. (2010) [60] also reported that the higher cooking yield was observed at 40 °C compared to 60 °C in ostrich meat sausage by pressurization before heating.

Under adequate conditions, application of high pressure treatment modifies the functionality of non-meat protein and polysaccharide molecules and significantly promotes the emulsifying activities and stability [61].

Moreover, some researches have reported a synergistic effect of dietary fibre, soy protein isolate, starch, hydrophilic colloid, and others material and high pressure processing on water and fat holding capacity in high pressure processing treated comminuted meat products. Grossi et al. (2011) [62] investigate the synergistic cooperation between high pressure treatment and carrot dietary fibre, found that high pressure treatment and carrot dietary fibre markedly improved emulsion strength resulting in firm pork sausages. Moller et al. (2011) [63] found that the significant effects of pressure temperature, holding time, and addition of carrot fibre on the distribution and mobility of water, and the T2 relaxation times were able to explain more than 90% of the variation in water holding capacity for both non-pressure and pressure-treated sausages, combined high pressure treatment and addition of fibre caused non-coherent changes in T2 NMR relaxation times. Chun et al. (2014) [64] used of the soy protein isolated, wheat flour (WF), and κ-carrageenan as binder, showed that the addition of binders improved water-binding properties of pressure or non-pressure-induced restructured pork, but lowered the hardness. Hong et al. (2004) [65] investigate the effect of high pressure and the addition of non-meat proteins on the physico-chemical and binding properties of restructured pork, found that high pressure and added isolated soy protein, sodium caseinate, whey protein concentrate and egg white powder improved the water binding capacities and binding strength of the restructured pork, respectively. However, due to the excessive protein damage reflected as increased surface hydrophobicity, less protein-water interactions and thus lower water-binding properties of sodium caseinate and whey protein concentrate, added sodium caseinate and whey protein concentrate were no effect on water binding properties under high pressure. Thus, the application of high pressure had more significant effect on restructuring meat than binders (Uresti et al., 2004) [66].

The high pressure treated whey protein isolate showed a continuous fine stranded network, while egg albumen had a porous aggregated network. The heated mixtures of whey protein isolate:egg albumen (7.5:7.5) showed large dense aggregates whereas high pressure treated mixtures produced smaller aggregates (Ngarize, Adams Howell, 2005) [67].
Trespalacios and Pla (2009) [68] used the dried egg white as fat replacement to obtain a low-fat chicken gel by means of high pressure, the water binding properties and hardness were improved, suggested their participation in the network structure coupled to the myofibrillar proteins, and noted that the modifying certain functional characteristics of chicken meat gels with low fat content by means of high pressure and the addition of dried egg white.

4.2. Effect of high pressure on the texture of comminuted meat products

The texture of comminuted meat products is an important factor to determine the consumers purchased or not. The high pressure treatment was affected the hardness, springiness, adhesiveness, gumminess and chewiness of emulsion meat products. High pressure processing induced texture modifications have been used to affect myofibrillar proteins and their gel-forming properties, raising the possibility of the development of processed comminuted meat products. Over 200 MPa treatment, the protein extractability was decreased significantly in meat batters, and caused protein denaturation and/or aggregation, which limited their functionalities (Oflynn et al., 2014; Sazonova et al., 2019) [69,70].

The M-line and Z-line of the chicken myofibril in 0.2 M NaCl were disrupted, and the thin and thick filaments were dissociated by high pressure treatment. The microstructure of pressure--heat-induced chicken myofibrillar gel was composed of three-dimensional fine strands. Pressurization, at 200 MPa, prior to heating, increased the apparent elasticities of chicken myofibrillar gel; however, pressure treatment above 200 MPa decreased it (Iwasaki, Noshiroya, Saitoh, Okano, Yamamoto, 2006) [71]. Yang et al. (2015) [52] have studied that the use of high pressure processing for enhancing the functional properties of reduced-fat (20%) and reduced-salt (1%) pork sausages without the need for additives, found that the textural properties of hardness, chewiness, springiness, cohesiveness and resilience were significantly ($P < 0.05$) increased at an interval of 100 MPa and 200 MPa, except the textural property of adhesiveness up to 200 MPa, but no changes of hardness, chewiness, springiness and resilience were observed up to 300 MPa and 400 MPa. Hwang, Lai, and Hsu (2007) [72] shown that the sausages had a harder texture after 200 MPa treatment, mainly because of partly depolymerized, unfolded, aggregated and denatured the extracted proteins under 200 MPa, which caused the changes of water distributions, formed new protein components, and solubilization or denaturation of myofibrillar proteins [73].

Some researchers have study the use of high pressure treatment to reduce the salt or phosphate content of comminuted meat products. Oflynn et al. (2014) [74] found that high pressure treatment is a potential technology to manufacture sausages maintaining organoleptic and functional properties, and could decrease the salt levels in reduced-phosphate breakfast sausages, improve the juiciness and cohesiveness.

Sikes et al. (2009) [48] reported that the myofibrillar proteins, such as myosin and actin, were more salt soluble when low-salt beef sausage batters were subjected to high pressure at 200 MPa than the untreated batter.

Hygreeva et al. (2016) [75] study the effects on quality characteristics of precooked chicken patties were subjected to high pressure at 200, 400 and 600 MPa for 10 min, the result indicated that the textural properties of chicken patties were improved after treated at 200 and 400 MPa. Crehan et al. (2000) [76] found that the hardness, cohesiveness, gumminess and chewiness of frankfurters were improved after 150 and 300 MPa treatment at low salt content (1.5%). Therefore, the texture properties of comminuted meat products with low salt content could be improved at moderate pressure levels (100–300 MPa).
The changes of texture properties also are related to the pressure temperature and processing, the possible is that the modified conformation, slowed heat-denaturation, together with disrupted myofibrillar eventually led to the different batter structures. The cooking of meat batters either before or after high-pressure treatment results in varying effects on meat product texture. Mor-Mur and Yuste (2003) [77] found that the textural properties of vacuum packed cooked sausages were treated at 500 MPa and 65°C, 5 or 15 min improved cohesiveness and increased fracture force of the product. Zheng et al. (2017) [52] studied the effect of heating under high pressure conditions (0 to 400 MPa, 75°C, 30 min) and sodium chloride (0 to 2.0 g/100g) on the texture, the results showed that the physical properties of batters were subjected by high pressure depended on the pressure intensity. The chicken meat batters treated at 200 MPa exhibited desirable qualities, having a smooth appearance and rigid texture, while those treated at 400 MPa had undesirable qualities, being coarse and watery in appearance, with a weak texture. The structural changes induced in proteins of meat batters were partially reversible at low temperatures when Increasing the pressure from 100 to 300 MPa, however, these changes were irreversible when the pressures beyond 300 MPa (Rastogi, Raghavarao, Balasubramaniam, Niranjan, Knorr, 2007) [78].

Carballo et al. (2000) [79] reported that the pork batters treated by high pressure prior to heating decreased the hardness, springiness and chewiness, formed a coarse, irregular, loose protein matrix and favoring weaker gel structures, because pressure could limit protein-protein interaction (Carballo,FernaÁndeze JimeÁnez-Colmenero, 1996) [51].

Some researchers had reported that high pressure induced muscle protein gels form a firmer texture. Yang et al. (2016) [80] reported that compared with the values of 0.1 MPa treated sausages, the 200 MPa for 2 min at 10 °C were significant (P < 0.05) increased in all the textural values. Zheng et al. (2015) [81] showed that high pressure treatment before heating sausages had significantly higher values for hardness, springiness, cohesiveness, chewiness and resilience than did the only-heat sausages.

It is well known, that high pressure causes protein denaturation with increasing the pressure and temperature (Tintchev et al., 2013; Rastogi et al., 2007) [78, 82]. The myosin protein have completely denaturation by 200 MPa, at 50 °C and 60 °C, the reason is the pressure and heat combined could be improved the efficient of protein aggregation and gelation, and form a heat induced helix-coil transition (Buckow, Sikes Tume, 2013) [83]. Which indicated that excessive temperature resulted in the weakening of molecular interactions and the destruction of the network structure in gels (Colmenero, 2002) [84]. In addition, the temperature with high pressure treatment was affected the state of moisture in the pork batters, which in turn affected the texture of the gel (Cando et al., 2014) [85].

Other factors also affected of the texture properties, such as added non-meat proteins, hydrophilic colloid. Hong and others (2008) [86] have studied the effects of high pressure processing and κ-carrageenan on cold-set binding in restructured pork meat, found that the breaking force and tensile strength of restructured pork meat treated by 200 MPa combined with κ-carrageenan were increased, and the pressure above 200 MPa and addition of 1.5% κ-carrageenan has potential use in cold-set meat restructuring.

Grossi et al. (2012) [87] reported that the use of carrot fibre and potato starch had more impact on textural properties in pork sausages with low salt content (1.2%) treated by high pressure processing, and water binding capacity of low salt pork sausages was improved, which produced sausages with better sensory properties.

Lee et al. (2018) [88] also the use of sea tangle powder and high pressure treatment combinations to reduce the phosphate in emulsion-type sausage, the result indicated that due to the pH and protein solubility were increased after was subjected to high pressure treatment, the water holding capacity and instrumental hardness of sausages treated with a combination...
of sea tangle powder and high pressure treatment were similar as the sausages with 0.2% sodium pyrophosphate, and greater inhibition ability against lipid oxidation and bacterial growth.

5. Effect of high pressure on the gel properties and protein conformation of myofibrillar proteins

Myofibrillar proteins accounts for 50%~55% of the total protein content in muscle, mainly composed of myosin and actin. Myofibrillar proteins are salt-soluble proteins, which are soluble in high ionic strength solution (> 0.3 M), it is decide to the gel properties, such as water holding capacity, texture, shelf life, and so on [89]. During the gel form, the helix-coil transitions of myosin tails and subsequent aggregation of myosin heads through intra- and intermolecular interaction, and then a three dimensional and crosslinked network is formed after partial unfolding or denaturation of myofibrillar proteins [90]. There is no doubt that high pressure induces certain alterations in myofibrillar proteins which influence their functional properties [91]. Myofibrillar proteins is sensitive to high pressure. The high pressure treatment is able to variable alterations on protein conformational structures, the quaternary structure of dissociates at 100~200 MPa, the tertiary structure is significantly affected above 200 MPa, and secondary structure changes take place at 300~700 MPa, which could improve the gelation properties of myofibrillar proteins [92,93].

5.1. Effect of high pressure on the water holding capacity of myofibrillar proteins

The water holding capacity of myofibrillar proteins gel was affected of the level, time and temperature of high pressure. When the pressure levels was low (≤ 200 MPa), which could improve the solubility of myofibrillar proteins; over 300 MPa, which could reduced solubility of myofibrillar proteins and form the large aggregates [24,94] observed that the denaturation of myosin of bovine occurred owing to the release of myosin light chain at 200 MPa, and the rate of myosin denaturation increased rapidly at pressures above 300 MPa because of the aggregation of myosin heavy chain. Actin were released at 200 MPa and the denaturation of actin might have been accelerated by the aggregation of released actin at pressures above 300 MPa. The solubilization of myofibrillar proteins also was affected by temperature during high pressure processing. The solubilization of myofibrillar proteins increased with increasing temperature, especially from 40 °C to 60 °C, and a regular trend of protein solubilization was found when isolated myofibrils were subjected to high pressure at different temperatures, an increase was observed with increasing pressure up to about 400 MPa, solubility then decreasing to 600 MPa [95]. Barriosperalta et al. (2012) [96] found that myofibrillar proteins from abalone and starch interaction increases the emulsifying capacity at pressures over 350 MPa applied for 3~5 min, myofibrillar proteins and egg white interactions at pressures higher than 450 MPa for 5~10 min formed coagulation, decreasing the emulsifying capacity. The reason is that myosin of pressure-induced surimi gelation denaturation and concomitant disulfide bond formation at 300 MPa, 5 °C for 30 min. During heating the pork myofibrillar proteins, aggregation of meat proteins caused the meat protein matrix to shrink, which reduced the amount of water that could be bound by the matrix, causing the cooking loss to increase [97]. Yang et al. (2015) [98] found that high pressure processing (200 MPa for 2 min) significantly decreased (P < 0.05) the cooked loss of reduced-fat and reduced-salt pork sausages, and changed the P2 peak ratio of the four water components in raw pork sausages. Therefore, the high pressure has an important commercial and health benefit of the altered properties of myofibrillar proteins, which is their ability to
form gels that have very high cook yields even in the presence of low salt [48]. Zhang et al. (2015) [99] showed that the myofibrillar proteins of chicken breast meat were treated at 100, 200, 300, 400, 500 MPa and kept for 10 min, the centrifugation loss increased gradually from 36.59% (0.1 MPa) to 37.28% (200 MPa) and decreased sharply from to 30.82% (300 MPa) as the pressure increased from 200 MPa to 300 MPa, then decreased slowly to 30.12% (500 MPa); the relaxation time of T_20 decreased from 2.31 ms to 1.32 ms, T_21 had no significant changes, and T_22 increased from 2477.08 ms to 3274.55 ms, that means bound water had lower water mobility, immobilized water had no significant changes and free water had a higher water mobility.

5.2. Effect of high pressure on the texture of myofibrillar proteins

The texture is an important characteristic of myofibrillar proteins gel, which decides the quality of meat product. The solubility of myofibrillar proteins affects the texture of myofibrillar proteins gel, because of the functional properties of myofibrillar proteins requires the solubilization of the proteins. High pressure is an important thermodynamic parameter that can profoundly influence molecular systems. The high pressure treatment could induce the depolymerisation of myofibrillar proteins with a consequence of increasing solubility. Iwasaki et al. (2006) [100] found that the elasticity of chicken myofibrillar gels were apparent increased by 2- or 3-fold at 200 MPa (10–20min), prior to heating at 70 °C. Cando et al. (2015) [101] showed that the surimi gel had higher breaking force after 150 MPa treatment, but decreased the breaking force after 300 MPa treatment. It is well known that high pressure processing is an important thermodynamic parameter that can profoundly influence molecular systems. When the high pressure over 400 MPa can readily denature proteins, and 200 MPa only affects their quaternary structures, leading to the dissociation of oligomeric proteins [102]. Zhang et al. (2017) [92] reported that the gel hardness of myofibrillar proteins increased from 20.25 (0.1 MPa) to 46.6 g (200 MPa), then decreased gradually to 33.3 g (500 MPa). The main reason is the high pressure treatment could affect molecular interactions (hydrogen bonds, hydrophobic interactions and electrostatic bonds) and protein conformations, which lead to denaturation, dissociation, aggregation of myofibrillar proteins, then resulting in modified functional properties [103]. Angsupanich, et al. (1999) [104] found when isolated myofibrillar protein from turkey was pressure treated at 200 MPa, there was no change in any of the peaks of DSC, up to 400 MPa and above caused loss of the myosin peak and major loss of actin structure and a ‘new’ peak (peak N ≈ 53–54 °C). Ko et al. (2003) [105] reported that the increase of the surface hydrophobicity of myosin with the improving the pressure levels, which caused the structural changes of myosin, would compensate for the decrease in the gel strength of myosin, this would cause the decreases in G’ values.

Textural properties of protein gel greatly depended on its microstructure. Ma, et al. (2011) [95] reported that myosin light chains and actin thin filaments of beef muscle were sensitive to pressure, they were released from myofibrils subjected to 100 MPa. Suzuki et al. (1991) [106] found that the proteins of actin, tropomyosin, troponin C as well as M-protein were solubilized at 100 MPa, whereas solubilization of myosin heavy chains over 300 MPa. Therefore, the muscle type, pH, temperature, and salt type and concentration were effect on the solubility and texture during the high pressure treatment. Cao et al. (2012) [107] observed by scanning electron microscopy that the network structure of rabbit myosin thermally induced gel was small and uniform after 200 MPa treatment, while the gel holes became larger above 200 MPa, and the G’ and G” values were decreased with the pressure levels increased. Zhang et al. (2017) [92] found that due to the myofibrillar proteins were
partial unfolded, the gels contained many filaments and irregular cavities at 100 MPa; the smallest particle size of myofibrillar proteins was formed at 200 MPa, the gels had denser and homogeneous network, and the hardness had a largest value; the myofibrillar proteins denatured excessively, interior hydrophobic and sulfhydryl groups exposed above 300 MPa, the gel cavities became larger and heterogeneous, and the hardness was decreased. Overall, myofibrillar proteins gels with higher hardness had smaller, denser and homogeneous gel microstructure, while gels with lower harness had larger cavities and coarse microstructure.

5.3. Effect of high pressure on the non-covalent, covalent bond and protein conformation of myofibrillar proteins

High pressure processing can affect myofibrillar proteins molecular interactions (hydrogen bonds, hydrophobic interactions, sulfydryl and electrostatic bonds) and protein conformation (secondary and tertiary structures), leading to protein denaturation, aggregation, or gelation that presents altered functional properties [108,109]. Which could be to improve the gel-forming properties of muscle proteins, a crucial factor in processed muscle-based food. The pressure-induced aggregation involved the dissociation of myosin heavy and light chains followed by aggregation of the heavy chains [110]. The proteins from the thin filament such as actin, tropomyosin, troponin C as well as M-protein were solubilized at 100 MPa, and myosin light chains also was sensitive to pressure, and were released from myofibrils subjected to 100 MPa, whereas solubilization of myosin heavy chains required up to 300 MPa [95,106]. Some authors had reported that the high pressure processing affects chemical forces of myofibrillar proteins [24,99,108]. Due to more tryptophan hydrophobic residues and phenolic hydroxyl groups of tyrosine residues tended to be buried in a hydrophobic microenvironment and generated hydrogen bonds with protein molecules, the hydrogen bonds appeared to be strengthened under pressure [1,99]. The intermolecular H-bonds between proteins was formed and caused the aggregation, which could decreased the solubility of myofibrillar proteins when the pressure up to 400 MPa and above, due to the protein-protein interaction at pressure 400 MPa is formed at the expense of protein-water interactions, and the intermolecular H-bonds between proteins are stronger than the H-bonds between protein and water [103]. Ansgupanich, et al. (1999) [104] studied the effect of isolated myofibrillar protein and myosin of cod or turkey (pH ≈7) were subjected to pressures up to 800 MPa for 20 min, found that high pressure-induced denaturation of myosin led to the formation of structures that contained hydrogen bonds and were additionally stabilized by disulfide bonds. It is well known that the breakdown of a disulphide bond requires an energy of 213.1 kJ/mol, but the high pressure treatment at 10,000 MPa only provides only 8.37 kJ/mol. Thus, the increase of the reactive sulphydryl groups content might cause by a change of myosin structure involving the active sites of myosin, which could lead to changes in actomyosin formation and enzymatic properties of myosin. The surface hydrophobicity was significantly positive with pressure level.

The myofibrillar proteins protein became more unfolded with the pressure increased, more buried hydrophobic residues were exposure, and more hydrophobic sites or pockets of protein molecules could bind to the ANS (1-anilinonaphthalene-8-sulphonic acid), then large protein aggregates was formed. Zhang et al. (2015) [99] found the surface hydrophobicity of myofibrillar proteins from chicken breast meat increased slowly from 0.1 MPa to 100 MPa, and then a sharp increase when treated by high pressure above 200 MPa. Cao et al. (2012) [107] showed that a clear positive relationship between pressure level applied and hydrophobicity, and increased significantly (P < 0.05) above 200 MPa, that means an increased denaturation and unfolding of myosin and greater exposure of amino acid residues.
with increased pressure. Chapleau and de Lamballerie-Anton (2003) [111] studied the effect of pressure (0–600 MPa) and time (0–1,800 s) on the surface hydrophobicity, and reactive sulphydryl groups content of bovine myofibrillar proteins in solution at 10 g/L, the results found that high pressure treatment induced a threefold increase of the surface hydrophobicity of myofibrillar proteins between 0 MPa and 450 MPa. The same upward trend was obtained on the reactive sulphydryl groups, which increased from 40% to 69%. The increasing linked with the change of the secondary structure and the destruction of the α-helices present in the heavy chains of myosin. Due to 100 or 200 MPa is too low to affect the exposure of buried sulfhydryl groups, the SH content of myosin was not significantly differences (P > 0.05), at 300 MPa and above, the SH content was significantly increased (P < 0.05), the increase of sulphydryl groups might be explained by the change of myosin structure [107, 112].

The secondary structures of meat protein is sensitive to changes in the hydrogen bonding scheme involving the peptide linkages of amide I band, which is attributable to α-helice, β-sheet, β-turn and random coil structures, respectively. Berhe et al. (2014) [113] had reported that the meat protein cooked above 60 °C were positively correlated to the high intensity of bands at the amide I regions. The results indicated that it was a significant (P < 0.05) increase in the β-sheet and β-turn structure content acco MPanied by a concomitant decrease in α-helice content. Zhang et al. (2017) [92] found that increased the pressure levels, α-helix and β-sheet changed into random coil and β-turn, and the surface hydrophobicity and formation of disulfide bonds were strengthened. Compared with the only-heat, when high pressure at 200 MPa, 15 min, the contents of β-sheet and β-turn were a significant increase (P < 0.05) from 20 °C to 40 °C, and there were no significant different (P > 0.05) from 50 °C to 60 °C, because of the myofibrillar protein had completely denaturation.

The high pressure treatment was significantly effect of the gel properties and protein conformation of myofibrillar proteins gel. The high pressure treatment could provide great potential for myofibrillar proteins structural modification, such as lead to protein denaturation, solubilization, aggregation or gelation, thereby creating innovative functional properties. A moderate pressure (< 200 MPa) can enhance water holding capacity and texture of myofibrillar proteins gel.

**Conclusion**

It is well established that high pressure processing will improved the properties of muscle, comminuted meat and myofibrillar proteins. The use of moderate pressure treatment of prerigor meat seems to have potential since the meat will be tender and look normal color. Reasonable high pressure processing could enhance the water holding capacity and texture of comminuted meat, but the products lacked the cooked appearance and potential for accelerated loss of flavour. Which also affected the non-covalent bond, covalent bond and protein conformation of myofibrillar proteins, the water holding capacity and texture of myofibrillar proteins will be increased produced by moderate pressure treatment. However, the affecting factors on properties of muscle, comminuted meat and myofibrillar proteins by high pressure processing is complex, still need a lot of research in the future.

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Comparison of fatty acids, lipid quality index and amino acid profiles of whiting (Merlangius merlangus euxinus Nordman, 1840) meat and roe during fishing season in Black Sea

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Keywords:
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EPA
DHA

Abstract

Introduction. The aim of research is to determine the fatty acid and amino acid composition of the whiting meat and roe caught in different months in Black Sea.

Materials and methods. The whiting (Merlangius merlangus euxinus Nordman, 1840) caught from the Sinop region of the Middle Black Sea Region. Sampling were carried out twice a month. And the whiting meat and roe were compared in view of its fatty acid (FA) and amino acid (AA) composition during fishing season in Black Sea.

Results and discussion. During the six months, the length and weight of whiting used in the study varied between 14.15–16.60 cm and 24.49–29.68 g, respectively. Minimum length and weight were determined in March. Maximum crude protein values of fish meat and roes was determined in May (18.61g/100g) and in April (16.30g/100g), respectively. SFA’s (saturated fatty acids), MUFA’s (monounsaturated fatty acids) and PUFA’s (polyunsaturated fatty acids) of fish meat and roes had been varied during the season. The minimum and maximum EPA, DHA contents were found as 7.42–10.72, 3.39–22.67g/100g in meat and 0.03–0.37, 3.79–4.76 g/100g in roe, respectively. The maximum and minimum n3/n6 values were found to be 14.01 in April and 4.47 in March in the fish meat, respectively.

Lysine was the highest EA (essential amino acids) in both meat and roe in whole months’ write values. The amounts of lysine and glutamic acid in fish meat were higher than in roe write values. The content of glutamic acid in fish meat was found higher than in fish roe during the study write values. The ratio of EA/non-EA were found to be max. 0.9 at March in meat. The fish roe’s EA/nonEA ratio were found between 0.7–0.9 in fishing season.

It has been found that whiting meat and roe contains high amounts of essential FA and AA.

Conclusion. The nutritional quality of fish meat and roe varies seasonally. Otherwise, the umami source aromatic AAs content of fish meat higher than roe.

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Abbreviations

AI: Atherogenicity Index  MUFA: Monounsaturated Fatty Acids
ALA: Alpha Linolenic Acid  n3: Omega 3 Fatty Acids
DHA: Docosahexaenoic Acid  n6: Omega 6 Fatty Acids
EA: Essential Amino Acids  PUFA: Polyunsaturated Fatty Acids
EPA: Eicosapentanoic Acid  SFA: Saturated Fatty Acids
FLQ: Flesh Lipid Quality Index  TI: Thrombogenicity Index

Introduction

Along with the awareness of the world's population and the increasing demand for healthy nutrition, the importance of seafood has also increased. People prefer seafood due to high essential amino acids and fatty acids, mineral substances and dietary fiber content. One of the favorite sea foods that can be caught almost all seasons in the territorial waters of our country is the whiting fish. Whiting (Merlangius merlangus euxinus Nordman 1840) is a demersal fish species which is preferred by consumers and which can reach to 50cm in length and hunting in the Black Sea coasts throughout the year [1, 2]. Whiting which is spawning irregularly throughout and it usually begins in October and end of July to August [3, 4]. This means that the whiting roes can be consumed during the fishing season. These roes, called caviar by the public, are considered as a distinct flavor. In 2016, 11540 tones whiting were caught in Turkey land waters. This amount corresponds to about 4.3% of all fish caught in our seas. 11354 tons of the 11540 tons of whiting were landed and freshly presented for human consumption [5].

Some studies have been carried out on the whiting, some of which are related with changes in nutritional composition [6–10] and others related with meat yield and spawning grounds [11–13], processing technologies [14, 15].

In this study, it was monthly investigated the proximate composition, fatty acids and amino acid contents of the whiting meats and their roes caught in the Middle Black Sea Region (Sinop).

Materials and methods

Materials

The study was carried out between December 2016 and May 2017 with the whiting (Merlangius merlangus euxinus Nordman, 1840) caught from the Sinop region of the Middle Black Sea Region. Sampling were carried out twice a month. For sampling, three kilos fresh fish were obtained from the fisheries co-operative. The fish were transported to the laboratory under cold storage conditions, the length and weight measurements were made. Then the roes were separated from the fish and filleted.
Proximate and amino acids analysis of samples

Crude protein, crude ash and moisture analyses were performed according to AOAC [16] (Ref. no: 925.52, 923.03, 925.10), crude fat analysis was performed according to the Soxhalelt method [17] and energy value was determined according to Falch et al. [18].

Atwater Method

\[
C (g/100g) = 100 - (W + F + P + A),
\]
\[
\text{Energy (Kcal)} = (F \cdot 9) + (P \cdot 4) + (C \cdot 4)
\]

where C: Carbohydrate content of sample (g/100g);
W: Water content of sample (g/100g);
F: Crude fat content of sample (g/100g);
P: Crude protein content of sample (g/100g);
A: Crude ash content of sample (g/100g).

Amino acid analyzes and fatty acids composition were performed after digestion derivatization method according to HPLC pre-column [19] and IID-19 method [20], respectively.

Lipid quality indexes of sample lipids

Lipid quality indexes of lipid [22-24], following formulas were used;

\[
\text{AI} = \frac{[C_{12}:0 + (4 \cdot C_{14}:0) + (C_{16}:0)]}{[\Sigma n6 + \Sigma n3 + \Sigma MUFA]}
\]
\[
\text{TI} = \frac{[(C_{14}:0 + C_{16}:0 + C_{18}:0)]}{[(0.5 \cdot \Sigma MUFA) + (0.5 \cdot \Sigma n6) + (3 \cdot \Sigma n3) / (\Sigma n6)]}
\]
\[
\text{FLQ} = 100 \cdot \frac{[\text{EPA}\% + \text{DHA}\%]}{(\text{Total fatty acids } \%)}
\]
\[
\text{HH} = \frac{(C_{18}:1n-9 + C_{18}:2n-6 + C_{20}:4n-6 + C_{18}:3n-3 + C_{20}:5n-3 + C_{22}:5n-3 + C_{22}:6n-3)}{(C_{14}:0 + C_{16}:0)}
\]

where AI: Atherogenicity Index;
TI: Thrombogenicity Index;
FLQ: Flesh Lipid Quality Index;
HH: Hypocholesterolaemic/Hypercholesterolaemic Ratio.

Statistical analysis

All analyzes were performed in 2 replicates with 3 parallel. The data obtained at the end of the study were evaluated with one-way ANOVA using Minitab Release 17 package program and Tukey test was used for determination of the significance level of differences in-groups and between groups [25]. Figures and schedules are prepared using MS Office 2010 software.
Results

Length and weight data’s

Figure 1. shows the length and weight data of the whiting fish between December and May. The maximum weight of whiting fish during the study was 29.68±0.74 g in December and the max. length was 16.60±0.14 cm in May. The length of the fish used in the sampling was minimum 14.15±0.08 cm. Although the fish weight varied between months, it did not fall below 22.25±0.37g (Figure 1).

Figure 1. The length and weight of whiting fish

Proximate composition and energy value of whiting meat and roe

Crude fat, crude protein, crude ash, moisture, carbohydrate contents and energy values of the whiting meat and roe used in the study are given in Table 1.

While the crude fat ratio of the whiting meat was determined at the minimum level in April, the crude fat ratio in fish roe reached the maximum value at the same month. The moisture content of fish meat was found the higher in April, compared to other months (p<0.05). Although the highest protein content of fish meat was determined in May (18.61g/100g), fluctuations in protein value were statistically insignificant during 6 months except for April (p>0.05). The carbohydrate content of fish meat varied between 0.09–1.06 g/100g.

The crude fat, crude ash, carbohydrate, water and energy values of fish roe determined every month were not different statistically (p>0.05) but the crude protein contents were different statistically during six months.

In general, the amount of crude ash of fish roes were found quite high when compared to meat except for January (p<0.05). The amount of crude ash did not change with respect to the month of both meat and roe (p>0.05).
The minimum amount of carbohydrate in the whiting roe was 0.63g/100g and the maximum was 1.97g/100g. When the fish meat and roes were compared in terms of energy content, the maximum value was determined as 78.79 kcal in January for fish meat. The minimum amount of energy was obtained in fish roes in the same month but the difference between the groups was statistically insignificant (p>0.05).

Table 1
Proximate composition of Whiting meat and roe (g/100g) and energy value (Kcal)

<table>
<thead>
<tr>
<th></th>
<th>Crude fat</th>
<th>Water</th>
<th>Crude ash</th>
<th>Crude Protein</th>
<th>Carbohydrate</th>
<th>Energy (Kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/100g</td>
<td>±0.02Aa</td>
<td>±0.03Ab</td>
<td>±0.02Ba</td>
<td>±0.07Aa</td>
<td>±0.03Bb</td>
</tr>
<tr>
<td>Dec.</td>
<td>0.38</td>
<td>±0.07</td>
<td>81.50</td>
<td>0.38</td>
<td>17.66</td>
<td>0.09</td>
</tr>
<tr>
<td>Jan.</td>
<td>0.48</td>
<td>±0.01Aa</td>
<td>80.42</td>
<td>0.48</td>
<td>18.29</td>
<td>0.33</td>
</tr>
<tr>
<td>Feb.</td>
<td>0.37</td>
<td>±0.01Ab</td>
<td>81.19</td>
<td>0.37</td>
<td>17.01</td>
<td>1.06</td>
</tr>
<tr>
<td>Mar.</td>
<td>0.26</td>
<td>±0.00Ab</td>
<td>81.52</td>
<td>0.24</td>
<td>17.88</td>
<td>0.11</td>
</tr>
<tr>
<td>Apr.</td>
<td>0.17</td>
<td>±0.00Bc</td>
<td>82.88</td>
<td>0.23</td>
<td>15.92</td>
<td>0.79</td>
</tr>
<tr>
<td>May.</td>
<td>0.32</td>
<td>±0.07Aa</td>
<td>80.36</td>
<td>0.57</td>
<td>18.61</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>g/100g</td>
<td>±0.07Ab</td>
<td>83.66</td>
<td>±0.08Ba</td>
<td>13.96</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>±0.07Ba</td>
<td>±0.14Ba</td>
<td>±0.00Ba</td>
<td>±0.00Ba</td>
<td>±0.09Ba</td>
<td>±0.02Aa</td>
</tr>
</tbody>
</table>

|        |          | ±0.07Ab| ±0.08Bd   | ±0.01Ba       | ±0.14Ba      | ±0.09Ba       | ±0.02Aa       |
| Dec.   | 0.41     | ±0.03Aa| 83.66     | ±0.07Ba       | 13.96        | 0.87          | 63.04         |
| Jan.   | 0.42     | ±0.05Aa| 84.89     | ±0.01Ba       | 11.77        | 1.97          | 58.69         |
| Feb.   | 0.41     | ±0.03Aa| 84.33     | ±0.05Aa       | 13.03        | 1.12          | 60.25         |
| Mar.   | 0.41     | ±0.03Aa| 84.73     | ±0.14Ba       | 12.22        | 1.61          | 59.01         |
| Apr.   | 0.46     | ±0.03Bc| 81.50     | ±0.00Ba       | 16.30        | 0.63          | 71.85         |
| May.   | 0.38     | ±0.03Aa| 84.34     | ±0.04Ba       | 12.61        | 1.59          | 60.24         |

↓ (a, b…. ) Means with different lowercase letters in the same column are significantly different (p<0.05) from month to month in same group. n=6±Std.Error, p<0.05.
↓ (A, B... ) Means with different capital letters in the same column are significantly different (p<0.05) between groups in same month. n=6±Std.Error, p<0.05.

Fatty acids composition of whiting meat and roe

The fatty acid composition results of whiting meat (Figure 2) and roe shown in Figure 3.

The amount of SFA (saturated fatty acids), MUFA (monounsaturated fatty acids) and PUFA (polyunsaturated fatty acids) of fish meat was max. 43.42% (in March), max. 38.21% (in March) and max. 37.97% (in April), respectively (Figure 4). A large amount of SFA...
content is composed from palmitic acid (max 18.42%), stearic acid (max 8.74%), butyric acid (max 7.59%) and behenic acid (max 4.42%). While, about 56% of the MUFAs composed of oleic acid. The predominant n3 fatty acids found in fish meat are EPA and DHA. Most of the n6 fatty acids form was linoleic acid. During the study, the maximum n3/n6 proportional value was determined as 14.01 in April.

SFA’s, MUFA’s and PUFA’s of fish roes were determined as max. 33.90% (in December and May), max. 58.45% (in April) and max. 13.13% (in January), respectively (Figure 5). A large amount of SFA content constituted butyric acid (max. 7.59%) and stearic acid (max. 7.77%). While about 53% of the MUFA’s were composed of oleic acid, the total MUFA contains oleic acid, palmitoleic acid, erucic acid, nervonic acid and eicosenoic acid in abundance. The EPA content of fish roes was significantly lower than meat in all months (p<0.05). The predominant n3 fatty acids found in fish roe were DHA and alpha linolenic acid. Most of the n6 fatty acids were linoleic acid. The maximum amount of linoleic acid in fish roes determined in January (4.25%) but this difference between the months was not statistically significant (p>0.05).

The maximum n3/n6 proportional value was found to be 1.45 in the fish roe in March, but this value was statistically different from the value determined in only January (p<0.05). The maximum and minimum n3/n6 values were found to be 14.01 in April and 4.47 in March in the fish meat, respectively.

Amino acids composition of whiting meat and roe

The results of the amino acid compositions of the whiting meat and roe in the study were shown in Figure 6–7. Total nine essential amino acids and seven non-essential amino acids; histidine, threonine, arginine, valine, methionine, phenylalanine, isoleucine, leucine and lysine were identified in the meat and roe of whiting. The maximum amount of aspartic acid in whiting meat was detected in February, but this value was not different from the amounts detected in the other months (p>0.05). The content of glutamic acid in fish meat was found to be high during the study period, but the difference was statistically insignificant (p>0.05).

Fish roes also contained high levels of aspartic acid (max 2393.5mg/kg), glutamic acid (max 2232.0mg/kg) and lysine (max 1894.8 mg/kg), which were similar with meat. The ratio of EA / non-EA of fish roe was maximum 0.9. This rate determined in January and February, was statistically similar with other months (p<0.05). EA/non-EA ratio of fish roes was higher than fish meat in January and February (p>0.05).

The highest amount of essential amino acids was detected for lysine in both groups. The amount of lysine was higher in fish meat than in roe. The ratio of essential amino acids to non-essential amino acids (EA/non-EA) in fish meat was found to be 0.9 in March (p>0.05). The fish roe’s EA/nonEA ratio were found between 07-09 in fishing season.
Figure 2. Fatty acid composition of whiting meat (%)
Figure 3. Fatty acid composition of whiting roe (%)
Figure 4. The total fatty acid composition of whiting meat (%)

Figure 5. Total fatty acid composition of whiting roe (%)

Figure 6. Amino acid composition of whiting meat (mg/kg)
Figure 7. Amino acid composition of whiting roe (mg/kg)
**Discussion**

**Lengths and weights of whiting and proximate composition of whiting meat and roes**

During the six months, the length and weight of whiting used in the study varied between 14.15–16.60 cm and 24.49–29.68 g, respectively. Minimum length and weight were determined in March. Similarly, Kaba et al. [10], the minimum length and weight found in male individuals in March.

The proximate composition of fish meat varies according to the annual nutrition and ovulation cycle [26]. In our study, the proximate composition of both fish meat and roe varied during the caught season. The moisture content of fish meat in April was found to be maximum (p<0.05) compared to the other month, inversely proportional to the fat ratio, which is an indication of an inverse proportion between fat and water. So if the fat rate is low, the amount of water is high. The length and weight of fish in March was the minimum value. Although the highest protein content of fish meat was determined in May, during 6 months, fluctuations in protein value were insignificant except for April (p> 0.05). April is the month which the amount of water, crude fat and crude protein in fish meat was most affected. The highest fat and protein values in fish roes were determined in April. In general, the fat content of fish meat decreased from January to April, and increased again in May. Similarly, Tufan and Köse [27] also reported that the fat content of whiting decreased from December to April and increased after that period. The maximum crude protein content of the fish was determined to be 18.61 g/100 g in our study. Mol et al. [28] reported 20.35% of whiting meat protein in their study from larger whiting (average height: 22.29 cm, average weight: 104.6 g). Kaba et al. [10] reported that crude protein content of female whiting meat and roe varied between 12.50–16.02 g/100g and between 12.34–15.46 g/100g from November to March. The amount of protein in fish used in our study was higher than those found in the previous studies except for April.

The carbohydrate content of fish meat varied between 0.092-1.058 g/100g. The minimum content of carbohydrate in the whiting roe was 0.633g/100g, maximum 1.970g/100g. When the fish and roes were compared in terms of energy value, the maximum value was determined as 78.79 Kcal in January. The minimum energy value was obtained in fish roes in the same month (p<0.05).

In our study, crude protein, crude fat, crude ash and carbohydrate content of fish roe were as follows; maximum 16.29, 0.460, 1.115 and 1.970 g/100g, respectively. Kocatepe et al. [9] determined the crude protein, crude fat, crude ash and carbohydrate content of the roes of the whiting roe caught from the Black Sea for a period of 7 months, maximum 14.44, 9.71, 1.49 and 2.77 g/100g. Kaba et al. [10] reported that the protein content of female whiting roe varied between months and reached maximum of 15.46 mg/100g in January. In our study, when the maximum crude protein content in the roe was detected in April, the maximum value was reached in December in this literature [10]. April is the month which the fish rises again after reaching the minimum length and weight in March. The difference in crude fat ratios may be due to the difference in the length and weight of the fish. In addition, such as seasonal conditions, nutritional status, temperature factors are effective on fish composition. In general, the amount of crude ash of fish roes was found quite high compared to meat, and the two groups were different from each other except for January (p<0.05).

Bledsoe et al. [29] reported that crude fat contents of trout, berlam and whiting roe were 6.6–9.8%; 5–9% and 9% respectively. The crude fat content of the whiting roe in this study ranged from 0.383 to 0.460 g/100 g. While the crude fat, protein and ash contents of the roe
were at maximum level in April, these values decreased in May. Kocatepe et al. [9] stated that the energy value of the whiting roe was 108.52 kcal/100g on average. In our study, the energy value of the fish roe was determined as maximum of 71.85 kcal/100g in April. The energy of the roe decreased from 71.849 kcal to 60.236 kcal. A similar decrease was found [9] in the whiting in March, and they correlated this with the weakening of the gonads' proximate composition after spawning. Huss [26] noted that migrated fish naturally during migration and spawning periods due to natural causes and that this resulted in a very high energy expenditure, depending on the length of migratory routes during and after spawning.

**Fatty acid composition of whiting meat and roes**

When fatty acids content of fish meat was compared, it was seen that the amount of SFA, MUFA and PUFA were changed between 30–40%, 25–40% and 20–40%, respectively. Tufan ve Köse [27] reported that in their study, the meat of whiting varied between 20-25% of the SFA content, 10-25% of the MUFA content, and 25-50% of the PUFA content. In our present study, the PUFA content decreased after the February and increased again in June. The fatty acids composition of whiting was found as 29.6% SFA, 19.2% MUFA and 39.6% PUFA by Özogul et al [8]. Fish fats contain 20–30% of saturated fatty acids, 70-80% of unsaturated fatty acids. PUFAs are generally in the form of n-3 (omega 3 fatty acids) [30, 31]. The PUFA content of the fish roe was found less than meat in all months (p<0.05) during the experiment. Essential fatty acids cannot be synthesized while many fatty acids are synthesized in the human body. Essential fatty acids for human body are n-3 PUFA α-linolenic acid and n-6 PUFA linoleic acid [32]. In all months, linoleic acid and α-linolenic acid contents of fish roes were higher than fish meat (p<0.05).

The minimum value of PUFA/SFA ratio recommended is 0.45 [33]. PUFA/SFA ratio of fish meats were higher than the limit value in all months except for March (Table 2.). But PUFA/SFA value in fish roe was determined under the 0.45 value, all the months.

<table>
<thead>
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<tbody>
<tr>
<td><strong>PUFA/SFA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Whiting meat</td>
<td>0.97</td>
<td>0.58</td>
<td>0.56</td>
<td>0.41</td>
<td>1.07</td>
<td>1.00</td>
</tr>
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<td>0.50</td>
<td>0.49</td>
<td>0.56</td>
<td>0.33</td>
<td>0.36</td>
</tr>
<tr>
<td>TI</td>
<td>0.19</td>
<td>0.32</td>
<td>0.33</td>
<td>0.45</td>
<td>0.17</td>
<td>0.19</td>
</tr>
<tr>
<td>FLQ</td>
<td>27.12</td>
<td>14.20</td>
<td>14.29</td>
<td>13.89</td>
<td>31.25</td>
<td>29.65</td>
</tr>
<tr>
<td>H/H</td>
<td>3.19</td>
<td>2.26</td>
<td>2.25</td>
<td>1.85</td>
<td>3.38</td>
<td>3.18</td>
</tr>
<tr>
<td>EPA+DHA</td>
<td>27.12</td>
<td>14.14</td>
<td>14.11</td>
<td>13.84</td>
<td>30.93</td>
<td>29.5</td>
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<tr>
<td><strong>PUFA/SFA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Whiting roe</td>
<td>0.34</td>
<td>0.41</td>
<td>0.41</td>
<td>0.35</td>
<td>0.44</td>
<td>0.33</td>
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<tr>
<td>AI</td>
<td>0.27</td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
<td>0.22</td>
<td>0.26</td>
</tr>
<tr>
<td>TI</td>
<td>0.24</td>
<td>0.24</td>
<td>0.09</td>
<td>0.23</td>
<td>0.23</td>
<td>0.25</td>
</tr>
<tr>
<td>FLQ</td>
<td>4.42</td>
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<td>4.00</td>
<td>4.37</td>
<td>4.87</td>
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<tr>
<td>H/H</td>
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<td>10.20</td>
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<td>3.99</td>
<td>4.11</td>
<td>4.79</td>
<td>4.17</td>
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</tbody>
</table>
FLQ indicate the global dietetic quality of lipids and their potential effects on the development coronary disease [34]. AI and TI indexes should be low to prevent cardiovascular diseases related with lipid intake [22] and the high value of H/H ratio represents high quality lipids. Ouraji et al [35] and Stancheva et al. [36] reported that higher values of AI and TI (>1.0) are detrimental to human health. In this study, AI and TI indexes were measured to be lower than 1.0 but high in <h/H in whiting meat and roe. Especially the H/H ratio of roes were higher than meat. It was showed that the lipids of roe had higher quality of the dietary lipid source than whiting meats.

Tufan and Köse [27] investigated the change of fatty acids content in the whiting during a year and found that the amounts of palmitic acid, stearic acid, oleic acid, EPA, DHA were; 14.9–18.0, 4.6–6.2, 8.0–13.1, 4.5–9.0, 25.3–40.6, respectively. In our study, whiting fishes were analyzed for 6 months and the same fatty acids were found between 13.18–18.42, 6.01–8.74, 15.82–22.71, 7.42–10.72, 3.39–22.67 respectively. When two studies were compared, palmitic acid, stearic acid, and EPA contents were similar, while oleic acid and DHA contents were different. The oleic acid content of the whiting meat in our study was detected at maximum level in March. Similarly, Tufan ve Köse [27] stated that oleic acid content was maximum in January and March. In the same study, the DHA content of fish meat was about twice as high as in our study.

The ratio of n3/n 6 fatty acid is commonly used as an index for assessing the nutritional quality of fishery products [34]. The ratio of n3/n6 of whiting meat and roes were the highest in winter. The ratio of fish meat n3/n6 ranges from 5.13 (January) to 14.01 (April). The maximum amount of n3 of fish meat was detected in April. Tufan and Köse [27] also detected fish meat at the highest level of n3 content in spring. Tufan and Köse [27] reported the content of n3/n6 of whiting meat as 14.2 and 12.6 respectively for the same months. The difference in the fatty and fatty acid composition of seafood depends on different factors such as nutritional pattern, geographical conditions, environmental temperature, season, hunting area, fish size, sex and species [31, 37].

Tufan and Köse [27] reported that palmitic and stearic acids from the SFAs; oleic acid and palmitoleic acid as MUFAs and DHA, EPA, eicosatrienoic acid as PUFAs of the whiting gonad. In our study, butyric acid, stearic acid, heptadecanoic acid and myristic acid content were higher than the SFAs of fish roes. The proportion of MUFA was similar to result of Tufan ve Köse [27]. However, the oleic acid content was measured as 16.4% in the study mentioned above, but 31.05% in April. In our study, the n3/n6 ratio of fish roe examined ranged from 1.04 to 1.45, while that of Tufan ve Köse [27] ranged from 7.7 to 14.8.

2% of the energy of a healthy adult fed on a daily diet with 2000 kcal is consumed by linoleic acid (4.44 g/day), 3% from alpha linolenic acid (ALA) (2.22 g/day), 0.3% from DHA + EPA (0.65 g/day) is recommended [38]. With a daily consumption of 200 g whiting meat, a maximum of 70% (in January) and a minimum of 13% (in April) of the amount of linoleic acid are met, while a minimum of 63% (in March) and a maximum of 84% (in April) is met with the same amount of whiting roe consumption. Similarly, ALA coverage rate is maximum (60%) in January, minimum (5%) in April. During the season, the percentage of whiting roe receiving ALA varies between 52% and 76%.

The British Nutrition Foundation [39] has emphasized that people who care for balanced and healthy nutrition should get 0.2 g of EPA + DHA every day. Daily intake of 200 g whiting meat consumption is meet the EPA + DHA requirement of 100% in December, 95% in May; and the minimum value of 35% in March. On the other hand, whiting roe meet the requirement of 22% in April. On average around 18% in the other months.
Amino acid composition of whiting meat and roes

Fish meat is a nutritious food with high protein content. In fish meat containing all essential amino acid as aspartic acid, glutamic acid and lysine [40]; aspartic acid and glutamic acid are important amino acids that play a role in enzyme activation, preservation of the solubility and ionic character of proteins. One of the most important sources (50-85%) of non-protein nitrogen in fish meat is free amino acids. Free amino acids give fish meat a characteristic taste. Most of these are proline, arginine, glycine, alanine, histidine, glutamic acid and taurine [41]. In this research, whiting meat contained glutamic acid (max. 3548.5 mg/kg), alanine (max. 1065.3 mg/kg) and arginine (max.927.0 mg/kg) from free amino acids. In general, when comparing fish meat and roe, it can be said that the content of essential amino acid in meat was higher than that of roe. The difference between the groups was statistically important (p<0.05) except for January and April. In April, the essential amino acid content of fish meat protein reached a maximum level (7986.3 mg/kg).

The World Health Organization’s [42] on protein and amino acid requirements for human nutrition reports an adult daily protein intake of 0.83g/kg, with essential amino acids; leucine 59 mg/g, lysine 45 mg/g, isoleucine 30 mg/g, threonine 23 mg/g, and methionine 16 mg/g. In our study, the leucine, valine and threonine content of the whiting meat and roe was determined about twice, about 1.5 times and more than 3 times of these amino acids daily requirement, respectively. In addition, fish meat meets half of the daily need for lysine.

Glutamate, aspartame and some nucleotides are associated with umami taste, which is called as the 5th taste. Glutamate is the free amino acid form of glutamic acid [43]. The content of glutamic acid in some foods is high and they are called as aromatic foods. For example; sea crab, blue crab, and Japanese fish sauces. The free glutamic acid content of these foods is high. By Yamaguchi and Ninomiya [44]; the free glutamic acid contents of foods were indicated as 140, 843 and 1383 mg/100 g, respectively. In this research glutamic acid content of both meats and roe were found at a maximum level in April. When compared with these foods given above, it can be said that the umami taste of both meat and roe were more dominant than, during study.

Conclusion

In conclusion; whiting fish meat and roe are good sources of n-3 PUFA, EPA and DHA. The n-3/n-6 ratio and EPA+DHA values of fish meat were higher than roe in all fishing months but the h/H ratios of roe were higher than fish meat. The index of AI and TI was no more than 1.0 which according to the data literature is detrimental to human health. The lipids nutritional quality of whiting meat and roe can be beneficial for human health. In addition, it can be said that the whiting is a delicious fish with essential amino acids content and high umami flavor. By the reason of the essential amino acid content and EPA + DHA content of both whiting meat and roes are high in April, it can be said that the nutritious quality of the whiting caught this month is higher.

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References


Effect of packaging type and storage temperature on the quality characteristics of beef longissimus lumborum and triceps brachii muscles aged for extended storage postmortem

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Keywords:
Triceps brachii
Beef
Drybag
Dry aging
Extended aging

Abstract

Introduction. The purpose of the study was to quantify the impact of packaging type, storage temperature, and length of postmortem aging to consistently increase palatability and color stability of Longissimus lumborum (LL) and TB muscles that represent the bulk of today’s supply.

Materials and methods. Paired longissimus lumborum (LL) and triceps brachii (TB) muscles were selected from 27 and 54 A-maturity beef carcasses with marbling scores of Slight 50 to Small 50 at grading. One muscle from each pair was stored at 0 and 4 °C, respectively, for 21, 32, or 42 days for LL, and 21, 28, or 35 days for TB, in one of three packaging options; DryBag®, traditional vacuum-bag, or no bag.

Result and discussion. Saleable yields were similar for DryBag® and traditional dry aged subprimals. Aging temperature and packaging type had little impact on any quality parameters evaluated. Steaks from LL muscles aged for 42 days had lower shear force values and more tender trained sensory panel values than steaks from LL aged for 21 days, although the actual difference was marginal. Tenderness of steaks from TB muscles was similar regardless of aging. Length of aging had more influence on saleable yields than palatability, and storage temperature and packaging had little influence on either.

Conclusion. Traits measured from subprimals aged in a DryBag® were similar to traditional dry aging. Packaging (vacuum vs. non) had a slight influence on palatability. Storage temperature (0 vs. 4 °C) had little impact on any trait evaluated. Length of aging (21 to 42) had more influence on cutting yields than palatability.

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1. Introduction

Tenderness has been consistently ranked as the most important aspect of a satisfactory beef eating experience by consumers (Morgan, Savell, Hale, Miller, Griffin, Cross, and Shackelford, 1991; Miller, Hoover, Cook, Guerra, Huffman, Tinney, and Huffman, 1995; Miller, Carr, Ramsey, Crockett, and Hoover, 2001). Retail cuts from the rib and loin containing the longissmus are marketed at a premium due to their potential innate tenderness; however, those from the chuck and round often are discounted because of real or perceived problems with tenderness (Belew, Brooks, McKenna, and Savell, 2003).

Postmortem aging is well recognized as a consistent method of increasing the tenderness and palatability of fresh beef (Warner and Kastner, 1992; Miller, Kerth, Wise, Lansdell, Stowell, and Ramsey, 1997; Gruber, Tatum, Scanga, Chapman, Smith, and Belk, 2006). There are two generally recognized packaging methods for postmortem aging: wet and dry (Smith, Nicholson, Nicholson, Harris, Miller, Griffin, and Savell, 2008). Dry aging refers to carcasses or subprimal cuts being held at humidity controlled refrigerated temperature without any type of protective packaging. Dry aged flavor attributes of a beefy, brown roasted flavor differ from the bloody, serumy flavors with metallic notes that can be produced with wet aging (Warren and Kastner, 1992; Campbell, Hunt, Levis, and Chambers, 2001). Wet aging is more common and refers to meat that is aged in a vacuum sealed barrier package at refrigerated temperatures. In the USA, the majority of all beef is vacuum packaged at the packer level then shipped to its destination where it can then be further wet aged or removed from its packaging and dry aged. Wet aging is more common because it will produce the desired increase in tenderness and flavor without the loss of yield and the necessary increase in expense associated with dry aging in regards to careful temperature and humidity control. A third method of aging beef has recently been introduced to the industry in an attempt to alleviate the challenges of dry aging. The use of a vacuum bag that is highly permeable to water vapor would in theory produce a product with the flavors associated with dry-aged beef while blocking oxygen to reduce off-flavors and possibly reduce yield loss (Ahnström, Seyfert, Hunt, and Johnson, 2006; DeGeer, Hunt, Bratcher, Crozier-Dodson, Johnson, and Stika, 2009; Dikeman, Orbuz, Gök, Akkaya, and Stroda, 2013; Li, Babol, Wällby, and Lundström, 2013).

Many studies have explored the effect of postmortem aging on the quality and palatability of steaks from the rib and short loin, however, most focused on products with Modest or greater marbling. Approximately 60 percent of all young fed beef slaughtered has between Slight \(^{50}\) and Small \(^{50}\) degrees of marbling (Cargill, 2011). Also, few studies have assessed the palatability of the primary muscle of the US clad or chuck, the Triceps brachii (TB; Shackelford, Wheeler, and Koochmarai, 1995; Rhee, Wheeler, Shackelford, and Koochmarai, 2004; King, Wheeler, Shackelford, and Koochmarai, 2009). Although many studies agree that aging increases tenderness and palatability, they disagree on the magnitude of variation among the between dry and wet aging methods (Parrish, Boles, Rust, and Olson, 1991; Sitz, Calkins, Feuz, Umberger, and Eskridge, 2006; Laster, Smith, Nicholson, Nicholson, Miller, Griffin, and Savell, 2008).

Postmortem aging has also been reported to affect lean color stability and shelf-life of beef (Ledward, 1985; Feldhusen, Warrantz, Erdmann, and Wenzel, 1995; Tang, Faustman, Hoagland, Mancini, Seyfert, and Hunt, 2005, King, Shackelford, Kalchayanand, and Wheeler, 2012). Lean color is the most important characteristic relative to a consumer’s purchasing decision of fresh beef at retail (Faustman, Cassens, Schaefer, Buege, Williams, and Scheller, 1989; Faustman and Cassens, 1990). Consumers associate a youthful, cherry-red, beef lean color with a safe, wholesome, and highly palatable fresh beef product. When
consumers see product displaying a darker lean color or lean discoloration, they associate this with potentially being less than desirable relative to palatability or that the product is not safe to consume (Smith, Tatum, and Morgan, 1993). Consumers rely on color because they have no other means of assessing quality when purchasing meat.

Gruber, Tatum, Scanga, Chapman, Smith, and Belk. (2006). reported that the longissimus, was one of seventeen beef muscles that responded most to postmortem aging and was continuing to show improvements in shear force values up to 28 days postmortem, especially in lower degrees of marbling (Slight). King, Wheeler, Shackelford, and Koohmaraie(2009) reported that slight differences in aging temperature impacted tenderness and that increasing aging time from 28 to 42 d postmortem improved slice shear force of center-cut sirloin steaks. Researchers (Ahnström, Seyfert, Hunt, and Johnson, 2006 and DeGeer, Hunt, Bratcher, Crozier-Dodson, Johnson, and Stika, 2009) have demonstrated the effectiveness of alternative packaging methods when aging beef for extended periods of time postmortem but did not include intermediate levels of marbling nor muscles other than the longissimus in their respective studies. Individually, each of the factors (i.e. temperature, time, and packaging) have been studied to some extent. However, the combination of temperature, aging period, and storage environment have not been thoroughly evaluated, particularly not with muscles other than longissimus of product quality representing the bulk of the U.S. beef supply. The purpose of the study was to quantify the impact of packaging type, storage temperature, and length of postmortem aging to consistently increase palatability and color stability of Longissimus lumborum (LL) and TBmuscles that represent the bulk of today’s supply.

2. Materials and Methods

2.1. Carcass Data

Carcasses classified as A-maturity were evaluated for marbling using the VBG 2000 gradingsystem (E+V Technology, Oranienburg, Germany). Instrument marbling scores for both sides of each carcass were required to be between Slight50 and Small50 degrees of marbling at the 12th/13th rib interface. This approach was consistent with normal application of official USDA quality grades for beef carcasses (USDA, 1997).

Paired beef LL (boneless, beef strip loin, IMPS# 180; n = 54) and paired TB (boneless, beef clod heart, IMPS # 114E; n = 108) were collected at 24h postmortem from 27, or 54 commercially slaughtered A-maturity beef carcasses, respectively (Table 1).

<table>
<thead>
<tr>
<th>Trait</th>
<th>LLa</th>
<th>TBa</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of carcasses</td>
<td>27</td>
<td>54</td>
</tr>
<tr>
<td>Hot carcass wt., kg</td>
<td>298.4 ± 30.7</td>
<td>319.7 ± 45.1</td>
</tr>
<tr>
<td>12th-rib fat thickness, cm</td>
<td>0.91 ± 0.4</td>
<td>0.80 ± 0.3</td>
</tr>
<tr>
<td>LM area, cm2</td>
<td>76.7 ± 7.3</td>
<td>82.6 ± 10.8</td>
</tr>
<tr>
<td>USDA YGb</td>
<td>2.6 ± 0.6</td>
<td>2.4 ± 0.6</td>
</tr>
<tr>
<td>Marblingc</td>
<td>410.5 ± 30.1</td>
<td>406.1 ± 32.0</td>
</tr>
</tbody>
</table>

LA0ngissimus lumborum (LL) (IMPS# 180; n = 54),
Triceps brachii (TB) (IMPS # 114E; n = 108).
bCalculated according to USDA-AMS, 1997.
c300 to 399 = Slight; 400 to 499 = Small; 500 to 599 = Modest.
Samples were vacuum sealed and shipped under refrigeration to the University of Florida Meat Processing Center.

2.2. Temperature Variation

All LL and TB muscles were trimmed to no more than 0.64 cm external fat thickness prior to further fabrication. One LL (n = 26), and one TB (n = 54) from each carcass were held at 0°C in a humidity (72 - 85 %) and temperature controlled environment. The LL and TB muscles from the opposite side of the same carcase was held at 4°C in similar conditions for their respective postmortem aging period.

2.3.1. Longissimus Lumborum

One LL from one side of each carcase (n = 27 per temperature) was separated into three equal portions along the long axis. Within each loin, the three sections were randomly allotted to aging for 21, 32 or 42 days postmortem. Also, within each loin, the three sections were allotted to one of three packaging treatments: DryBag® (B; DryBag®, MacPak, LLC, Wayzata, MN) having a water vapor transmission rate of 2500 g/m²/24 h at 38 °C and 50% relative humidity, Traditional vacuum-bag (V; 8600-14EL, Cryovac-Sealed Air Corporation, Duncan, SC) having a water transmission rate of 0.5–0.6 g/64,516 cm²/24 h at 37.8 °C and 100% relative humidity, and No packaging (D). All LL sections were weighed before and after assigned aging times. The strip loin (LL) from both sides of 3 carcasses were used to complete the random allocation into the 18 different treatment combinations. After the assigned postmortem aging period, LL sections were fabricated into 2.54 cm steaks (n = 3) for sensory, Warner-Bratzler shear force (WBSF) and color stability evaluations, respectively.

2.3.2. Triceps Brachii

One TB from one side of each carcase (n = 54 per temperature) were randomly assigned to one of nine packaging × aging combinations, for each of the two storage temperatures (0 or 4°C). Packaging treatments for TB were the same as described for LL subprimals: B, V, or D and were allotted to postmortem aging periods of 21, 28, or 35 days. The clod heart (TB) from both sides of 9 carcases were used to complete the random allocation into the 18 different treatment combinations. After the assigned postmortem aging period, TB muscles were fabricated into 2.54 cm steaks, the most medial steaks (n = 3) were allocated to sensory, WBSF and color stability evaluations.

2.4. Saleable yield and steak processing

For saleable yield, all LL sections and TB muscles were weighed before and after the assigned aging periods. After aging, all muscles were trimmed to 0.25 cm external fat and dry and discolored portions of D and B muscles were removed. Saleable yield was reported as the weight of the non-discolored steak and lean trim divided by the section or muscles initial pre-aged weight × 100. Steaks for color stability were individually placed on a Styrofoam tray containing a Dri-Loc 40 g white meat pad (Sealed-Air Corporation, Elmwood Park, NJ) and overwrapped with polyvinylchloride film (23,250 mL of O²/m²/24 h °C/90% relative humidity). Sensory and WBSF steaks were vacuum sealed and frozen at -40°C until analysis was completed at a later date.

2.5. Sensory Attributes

At 24 h prior to cooking, steaks were thawed at 4°C±2 °C. Preheated Hamilton Beach Indoor/Outdoor open top grills (Hamilton Beach Brand, Washington, NC) were used to cook steaks according to the American Meat Science Association guidelines (AMSA, 1995). Steaks were cooked to an internal temperature of 71 °C, flipping once at 35 °C.
Thermocouples (Omega Engineering, Inc., Stanford, CT) were placed in the geometric center of each steak to constantly monitor temperature. Temperatures were recorded using 1100 Labtech Notebook for Windows 7 (Computer Boards Inc., Middleboro, MA) (Computer Boards, Inc., Middleboro, MA). The cooked steaks were sliced and served to panelist in warmed, covered containers. During sessions, panelists were randomly seated in individual cubicles in a temperature and light controlled room designed with positive pressure air flow. While being served, the panelists were under red filtered lights as suggested by the American Meat Science Association (AMSA, 1995). Each panelist evaluated 4-6 samples, per session and 2 cubes per sample (1.27 cm$^3$). A panel of 7-11 trained members, in accordance with the AMSA sensory guidelines, assessed each sample for 5 attributes. These evaluated sensory traits included juiciness (1= extremely dry, 2= very dry, 3= moderately dry, 4= slightly dry, 5= slightly juicy, 6= moderately juicy, 7= very juicy, 8= extremely juicy), beef flavor intensity (1= extremely bland, 2= very bland, 3= moderately bland, 4= slightly bland, 5= slightly intense, 6= moderately intense, 7= very intense, 8= extremely intense), overall tenderness (1= extremely tough, 2= very tough, 3= moderately tough, 4= slightly tough, 5= slightly tender, 6= moderately tender, 7= very tender, 8= extremely tender), connective tissue amount (1= abundant, 2= moderately abundant, 3= slightly abundant, 4= moderate amount, 5= slight amount, 6= traces amount, 7= practically, 8= none detected), and off-flavor (1= extreme off-flavor, 2= strong off-flavor, 3= moderate off-flavor, 4= slight off-flavor, 5= threshold; barely detected, 6= none detected).

2.6. Warner-Bratzler Shear Force Analysis

Steaks were cooked to the above specifications and were then chilled at 4°±2°C for 24 h. After cooling, 6 cores, 1.27 cm in diameter, were removed parallel to the orientation of the muscle fibers. Each core was sheared once, perpendicular to the orientation of the muscle fibers using an Instron Universal Testing Machine (Model 1011, Instron Corporation, Canton, MA) with a Warner-Bratzler shear head at a speed of 200 mm/min.

2.7. Color Stability

Steaks were displayed in a Hill (Hill Refrigeration Div., Trenton, NJ) coffin-style retail case at 2±3°C for 5-d. Cases were illuminated with GE T8 Linear Fluorescent lamps (2,800 lm, 4,100 K; General Electric Company, Fairfield, CT) that emit a case average of 1,148 lx with a 12-h on, 12-h off lighting schedule. Steaks were rotated daily to compensate for uneven temperature and light distribution within the case. Each steak was used for daily lean color evaluation. Following collection of visual data, Hunter L*, a*, and b* reflectance data was collected for each steak in duplicate and averaged using a Hunter Miniscan XE Plus (Hunter Laboratory, Reston, VA) with an illuminant setting of D65/10 with a 2.54 cm aperture. Visual and objective color data was collected for a five day period for each cut and steak.

2.8. Statistical Analysis

The LL muscles were analyzed as a split-plot design with the whole-plot a 2 X 3 factorial representing temperature x aging periods, with packaging treatment as the sub-plot. The TB muscles were analyzed as a split-plot design with the whole-plot a 2 X 3 X 3 factorial design, representing temperature x packaging x aging periods and nested within animal with subprimal as the experimental unit.
3. Results and Discussion

3.1. Saleable yield

Vacuum packaged subprimals of both muscles had greater saleable yield percentages \((P \leq 0.05)\) than the other packaging treatments represented (Table 2). These results were expected and are consistent with several previous studies (Parrish, Boles, Rust, and Olson, 1991; Warren and Kastner, 1992; Smith, Nicholson, Nicholson, Harris, Miller, Griffin, and Savell, 2008; Laster, Smith, Nicholson, Nicholson, Miller, Griffin, and Savell, 2008). Subprimals stored in B packages did not differ from D aged subprimals for saleable yield percentage for either muscle \((P \geq 0.2)\). Previous authors were similar reporting no differences in total loss percentages between cuts stored in a highly water permeable bag and those dry aged traditionally (DeGeer, Hunt, Bratcher, Crozier-Dodson, Johnson, and Stika, 2009; Dikeman, Obuz, Gök, Akkaya, and Stroda, 2013), but contrary to findings by Ahnström, Seyfert, Hunt, and Johnson (2006) who reported meat aged in dry ageing bags for 21 d had a lower aging loss and trim loss than traditionally dry aged beef.

Storage temperature did not affect \((P > 0.70)\) the saleable yield percentages of LLsubprimals but, TB steaks aged at 4 °C tended \((P = 0.09)\) to have greater saleable yield than the same muscles stored at 0 °C (Table 2). For each muscle evaluated, the subprimals fabricated after the shortest postmortem aging period had greater saleable yield percentages \((P \leq 0.05)\) than subprimals fabricated after either of the more extended aging periods, which did not differ \((P > 0.10)\). These results are consistent with previous studies stating the least amount of aging, regardless of packaging type, results in the least amount of saleable yield lost (Smith, Nicholson, Nicholson, Harris, Miller, Griffin, and Savell,, 2008; Laster, Smith, Nicholson, Nicholson, Miller, Griffin, and Savell,, 2008), and increasing postmortem aging time decreases yield and increases trim (Parrish, Boles, Rust, and Olson, 1991; Ahnström, Seyfert, Hunt, and Johnson, 2006).

Table 2
Effect of subprimal packaging type, storage temperature, and days of postmortem age on saleable yield % of *longissimus lumborum* and *triceps brachii* muscles

<table>
<thead>
<tr>
<th>Muscle</th>
<th>Packaginga</th>
<th>Temperature</th>
<th>P-value</th>
<th>4 °C</th>
<th>0 °C</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>LL</td>
<td>B</td>
<td>63.8±1.0</td>
<td>V</td>
<td>79.3±1.0</td>
<td>D</td>
<td>62.0±1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TB</td>
<td>60.5±1.5</td>
<td>73.7±1.5</td>
<td>V</td>
<td>60.1±1.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Muscle</th>
<th>Postmortem age</th>
</tr>
</thead>
<tbody>
<tr>
<td>LL</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>72.4±1.4</td>
</tr>
<tr>
<td>TB</td>
<td>68.4±1.6</td>
</tr>
</tbody>
</table>

aB; DryBag®, MacPak, LLC, Wayzata, MN having a water vapor transmission rate of 2500 g/m²/24 h at 38 °C and 50% relative humidity, V; Traditional vacuum-bag (V; 8600-14EL, Cryovac-Sealed Air Corporation, Duncan, SC) having a water transmission rate of 0.5–0.6 g/64,516 cm²/24 h at 37.8 °C and 100% relative humidity; D; No packaging.

bFor variables with three treatments, values lacking a common superscript differ \((P \leq 0.05)\).
3.2 Longissimus Lumborum

3.2.1. Color Stability. The LL steaks aged for 42 d were darker, less red, and less yellow (lower \(L^*\), \(a^*\), and \(b^*\) values; \(P \leq 0.03\)) during the first 3 d of display than steaks aged for 21 and 32 d, respectively (postmortem age \(\times\) retail display day, \(P < 0.001\); Figure 1). As the days of retail display progressed, the steaks aged for 42 d became lighter (greater \(L^*\) values) while those steaks with fewer days of postmortem aging became darker (lower \(L^*\) values) during retail display (postmortem age \(\times\) retail display day, \(P < 0.001\); Figure 1). Interestingly, LL steaks aged for 42 d were subjectively brighter (greater subjective lean color scores; \(P \leq 0.03\)) than steaks aged for 21 and 32 d, respectively (postmortem age \(\times\) retail display day, \(P < 0.001\); Figure 1).

The discrepancy between the greater subjective scores and objective values for the 42 d aged steaks is likely due to their greater percentage of surface discoloration, which due to the contrast between red and brown, potentially increased the subjective scores. Also, panelists were not able to compare steaks among aging periods concurrently, which in combination with contrast in colors, could have also increased scores of 42 d aged steaks. Also, previous reports have reported wet aged beef to have reduced total plate counts (Minks and Stringer, 1972) and greater retail shelf life (Miller, Davis, and Ramsey, 1993) compared to dry aged steaks, however no microbial evaluation was conducted in this study.

It is well established that consumers prefer bright, youthful beef lean color at retail (Faustman, Cassens, Schaefer, Buege, Williams, and Scheller. 1989; Faustman and Cassens, 1990; Carpenter, Cornforth, and Whittier, 2001), however, the differences in lean discoloration, though not reported, suggests that consumers would not have preferred the longer aged steaks at retail.

The LL steaks from subprimals stored in V for 32 or 42 d were more yellow (greater \(b^*\) values; \(P \leq 0.02\)) than steaks given D or B storage for the same aging periods (packaging type \(\times\) postmortem age, \(P = 0.01\); Figure 2). Subprimal packaging type or storage temperature did not affect \((P \geq 0.39)\) the lightness of LL steaks during retail display (Table 3).

### Table 3

<table>
<thead>
<tr>
<th>Objective Color Trait</th>
<th>Packaging</th>
<th>Temperature</th>
<th>4 °C</th>
<th>0 °C</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>L*</td>
<td>B</td>
<td>V</td>
<td>D</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>32.6 ±0.4</td>
<td>33.7 ±0.4</td>
<td>32.7 ±0.4</td>
<td>33.0 ±0.3</td>
<td>33.0 ±0.3</td>
</tr>
<tr>
<td>a*</td>
<td>10.7 ±0.2</td>
<td>11.2 ±0.2</td>
<td>10.2 ±0.2</td>
<td>&lt; 0.001</td>
<td>10.8 ±0.2</td>
</tr>
<tr>
<td>Subjective Color</td>
<td>3.9 ±0.3</td>
<td>4.7 ±0.3</td>
<td>3.8 ±0.3</td>
<td>0.05</td>
<td>4.2 ±0.2</td>
</tr>
</tbody>
</table>

*B: DryBag®, MacPak, LLC, Wayzata, MN having a water vapor transmission rate of 2500 g/m²/24 h at 38 °C and 50% relative humidity; V: Traditional vacuum-bag (V; 8600-14EL, Cryovac-Sealed Air Corporation, Duncan, SC) having a water transmission rate of 0.5–0.6 g/64,516 cm²/24 h at 37.8 °C and 100% relative humidity; D: No packaging.

*L*: measure of darkness to lightness (larger value indicates a lighter color); \(a^*\): a measure of redness (larger value indicates a redder color).

*Subjective color: 1: Extremely dark red, 2: Dark red, 3: Moderately dark red, 4: Slightly dark red, 5: Slightly bright cherry red, 6: Moderately bright cherry red, 7: Bright cherry red, 8: Extremely bright cherry red.

For variables with multiple treatments, values lacking a common superscript differ \((P \leq 0.02)\).
Storage temperature did not affect \((P \geq 0.19)\) redness or subjective color scores during retail display (Table 3). The LL steaks from subprimals aged in V were more red (greater a* value; \(P \leq 0.02\)) and brighter (greater subjective lean color scores; \(P \leq 0.02\)) than steaks from subprimals aged in D, which did not differ from subprimals aged in B (Table 3). The variation in color for steaks subprimals given B or D is likely driven by greater evaporative loss and/or greater oxidation during retail display compared with steaks from V packaged subprimals, resulting in a darker surface (Faustman and Cassens, 1990; Miller, Davis, and Ramsey, 1993).

![Figure 1. Interactive effect of days of postmortem age and day of retail display on lightness (L*) values (\(P < 0.001\)), redness (a*) values (\(P < 0.001\)), yellowness (b*) values (\(P < 0.001\)), and subjective lean color scores (\(P = 0.06\)) of longissimus lumborum steaks. Values within day of retail display lacking common letters differ (\(P \leq 0.03\)).](image-url)

\(1 = \) Extremely dark red, \(2 = \) Dark red, \(3 = \) Moderately dark red, \(4 = \) Slightly dark red, \(5 = \) Slightly bright cherry red, \(6 = \) Moderately bright cherry red, \(7 = \) Bright cherry red, \(8 = \) Extremely bright cherry red.
Figure 2. Interactive effect of subprimal packaging type and days of postmortem age on yellowness ($b^*$) values ($P=0.01$) of longissimus lumborum steaks. Values with different letters differ ($P \leq 0.02$).

$\text{a} = \text{B; DryBag, MacPak, LLC, Wayzata, MN having a water vapor transmission rate of 2500 g/m}^2/24 \text{ h at 38 °C and 50% relative humidity, D = No packaging; V= Traditional vacuum-bag (V; 8600-14EL, Cryovac-Sealed Air Corporation, Duncan, SC) having a water transmission rate of 0.5–0.6 g/64,516 cm}^2/24 \text{ h at 37.8 °C and 100% relative humidity.}$

3.2.2. Warner-Bratzler Shear Force and Trained Sensory Panel. The LL steaks from subprimals aged for 42 d had lower ($P \leq 0.01$) WBSF values than steaks from subprimals aged for 21 or 32 d (Table 4). It is well documented that aging increases beef tenderness (Bate-Smith, 1948; Smith, Culp, and Carpenter, 1978; Calkins and Seideman, 1988), complementing the decrease in WBSF values of steaks aged for 42 vs. 21 d. However, the findings for steaks aged for 32 d to have greater ($P \leq 0.01$) WBSF values than the same steaks aged for 21 d (Table 4), is possibly an artifact of the data, and defies explanation.

Subprimal packaging type or storage temperature did not affect ($P \geq 0.15$) WBSF values, or trained sensory panel values for juiciness or connective tissue of LL steaks (Table 4). Trained sensory panelist found LL steaks from muscles aged for 42 d were more tender ($P \leq 0.01$) than steaks aged for 21 days (Table 4), complementing the results for WBSF. However, the average value from all steaks would be described as “slightly tender”. This is similar to Sitz, Calkins, Feuz, Umberger, and Eskridge (2006) who found no significant difference between dry- and wet-aged strip loins for flavor, juiciness, or overall acceptability.

Steaks from subprimals given D packaging had more off-flavors ($P \leq 0.01$) than steaks that had been aged in V packaging, which did not differ from steaks from B packages (Table 4). However, it should be noted that the mean value of the off-flavor of steaks from all three packaging treatment is described as “threshold, barely detected”. The primary reason for processors to D age beef is to impart a different flavor compared to V packaged beef. Numerous reports have found D aged beef to have a different flavor profile than V packaged beef (Warren and Kastner, 1992; Campbell, Hunt, Levis, and Chambers, 2001). It should be noted that despite training, members of this sensory panel were generally accustomed to the serumy and sour notes of V packaged beef compared to D aged beef, potentially rationalizing the difference in off-flavors.
Table 4
Effect of subprimal packaging type, storage temperature, and days of postmortem age on Warner-Bratzler shear force (WBSF) and trained sensory panel values for *longissimus lumborum* steaks

<table>
<thead>
<tr>
<th>Trait</th>
<th>Packaging&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Temperature</th>
<th>Postmortem age</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>V</td>
<td>D</td>
</tr>
<tr>
<td>WBSF, N</td>
<td>32.7±0.9</td>
<td>32.8±0.9</td>
<td>32.3±0.9</td>
</tr>
<tr>
<td>Juiciness&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.2±0.1</td>
<td>5.1±0.1</td>
<td>5.1±0.1</td>
</tr>
<tr>
<td>Beef flavor&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.6±0.1</td>
<td>5.4±0.1</td>
<td>5.4±0.1</td>
</tr>
<tr>
<td>Tenderness&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.9±0.1</td>
<td>5.8±0.1</td>
<td>5.7±0.1</td>
</tr>
<tr>
<td>Connective tissue&lt;sup&gt;b&lt;/sup&gt;</td>
<td>6.4±0.1</td>
<td>6.3±0.1</td>
<td>6.4±0.1</td>
</tr>
<tr>
<td>Off-flavor&lt;sup&gt;c&lt;/sup&gt;</td>
<td>5.5±0.1</td>
<td>5.6±0.1</td>
<td>5.3±0.1</td>
</tr>
</tbody>
</table>

<sup>a</sup>B; DryBag, MacPak, LLC, Wayzata, MN having a water vapor transmission rate of 2500 g/m²/24 h at 38 °C and 50% relative humidity, V; Traditional vacuum-bag (V; 8600-14EL, Cryovac-Sealed Air Corporation, Duncan, SC) having a water transmission rate of 0.5–0.6 g/64,516 cm²/24 h at 37.8 °C and 100% relative humidity; D; No packaging.

<sup>b</sup>Juiciness: 1 extremely dry, 2 very dry, 3 moderately dry, 4 slightly dry, 5 slightly juicy, 6 moderately juicy, 7 very juicy, 8 extremely juicy; Beef flavor: 1 extremely bland, 2 very bland, 3 moderately bland, 4 slightly bland, 5 slightly intense 6 moderately intense, 7 very intense 8 extremely intense; Tenderness: 1 extremely tough 2 very tough 3 moderately tough 4 slightly tough 5 slightly tender 6 moderately tender 7 very tender 8 extremely tender; Connective tissue: 1 abundant amount, 2 moderately abundant, 3 slightly abundant, 4 moderate amount, 5 slight amount, 6 traces amount, 7 practically none, 8 none detected.

<sup>c</sup>1 extreme off-flavor, 2 strong off-flavor, 3 moderate off-flavor, 4 slight off-flavor, 5 threshold, barely detected, 6 none detected.

<sup>d,e,f</sup>For variables with three treatments, values lacking a common superscript differ (*P* ≤ 0.01).

Steaks of LL stored at 4 °C tended (*P = 0.08*) to have greater sensory panel values for tenderness than those stored at 0 °C (Table 4). Postmortem aging did not affect (*P ≥ 0.11*) trained sensory panel values for juiciness, beef flavor, off-flavor or connective tissue of LL steaks (Table 4). Most researchers have reported length of postmortem aging to affect beef flavor (Spanier, Flores, McMillin, and Bidner, 1997; Gorraiz, Beriaint, Chasco, and Insausti, 2002; Yancey, Dikeman, Hachmeister, and Milliken, 2005).
3.3. Triceps Brachii

3.3.1. Color Stability. Collectively, all TB steaks had similar lightness values at the start of retail display, but steaks from subprimals aged for 35 d trended darker (decreasing L* values) throughout display, compared with steaks from subprimals given 21 or 28 d of aging which trended lighter throughout retail display (postmortem age × storage temperature × retail display day, \( P \leq 0.02 \); Figure 3).

![Figure 3. Interactive effect of days of postmortem age and subprimal storage temperature on lightness (L*) values (\( P = 0.02 \)) of triceps brachii steaks during 5 d of retail display. Values within day of retail display lacking common letters differ (\( P \leq 0.024 \))](image)

Opposite to findings with the LL steaks, TB steaks from subprimals aged for 35 d had lower subjective color scores (\( P \leq 0.03 \)) than steaks from subprimals given shorter postmortem aging periods (postmortem age × retail display day, \( P = 0.02 \); Figure 4), which were similar to results for lightness values and postmortem aging period of TB steaks during retail display. Subprimal packaging type did not affect (\( P \geq 0.28 \)) lightness, redness, or yellowness of TB steaks during display and subprimal storage temperature did not affect (\( P \geq 0.20 \)) redness or yellowness values for TB steaks during retail display (Table 5). The redness and yellowness values of TB steaks were lower (\( P \leq 0.02 \)) as length of retail display increased (Table 5). Some justification of the differences seen between the TB and LL were described by McKenna, Mies, Baird, Pfeiffer, Ellebracht, and Savell (2005) as a “very low” color stability muscle, compared to LL which was classified as a “high” color stability muscle due to differences in myoglobin content, myoglobin reductase activity, and nitric oxide metmyoglobin reduction ability.
3.3.2. Warner-Bratzler Shear Force and Trained Sensory Panel. Subprimal packaging type or storage temperature did not affect \((P \geq 0.23)\) trained sensory panel values for juiciness, tenderness, connective tissue or off-flavor of TB steaks (Table 6). Additionally, subprimal packaging type did not affect \((P = 0.63)\) trained sensory panel values for beef flavor, however, steaks from subprimals stored at 4 °C tended \((P = 0.07)\) to have greater sensory panel values for beef flavor than steaks from subprimals stored at 0 °C (Table 6). Length of postmortem age did not affect \((P \geq 0.25)\) trained sensory panel values for juiciness, beef flavor, tenderness, or connective tissue of TB steaks (Table 6). Trained sensory panelist found TB steaks from muscles aged for 35 d to have more off-flavor \((P< 0.01)\) than steaks aged for 21 or 28 d which did not differ (Table 6). As stated for a previous statistical
difference in off-flavor, all three means were described as “threshold/barely detected.” The authors’ findings for off-flavor differed from those of King, Wheeler, Shackelford, and Koohmaraie, (2009) who reported no difference in flavor or off-flavor as aging of TB steaks increased from 7 to 42 d.

The TB steaks from subprimals aged for 35 d in V packaging had greater ($P \leq 0.02$) WBSF values than steaks from any other packaging type × days of postmortem aging combination (packaging type × postmortem age, $P= 0.01$; Figure 5), suggesting that the subprimals which were allocated to this particular combination were innately tougher than subprimals allocated to the other combinations.

Table 6
Effect of subprimal packaging type, storage temperature, and days of postmortem age on Warner-Bratzler shear force (WBSF) and trained sensory panel values for triceps brachii steaks

<table>
<thead>
<tr>
<th>Trait</th>
<th>Packaging a</th>
<th>Temperature</th>
<th>Postmortem age</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>V</td>
<td>D</td>
</tr>
<tr>
<td>WBSF, N</td>
<td>5.2 ±0.1</td>
<td>5.2 ±0.1</td>
<td>5.2 ±0.1</td>
</tr>
<tr>
<td>Juiciness b</td>
<td>5.6 ±0.1</td>
<td>5.6 ±0.1</td>
<td>5.5 ±0.1</td>
</tr>
<tr>
<td>Beef flavor b</td>
<td>5.5 ±0.1</td>
<td>5.4 ±0.1</td>
<td>5.6 ±0.1</td>
</tr>
<tr>
<td>Tenderness b</td>
<td>6.1 ±0.1</td>
<td>6.0 ±0.1</td>
<td>6.2 ±0.1</td>
</tr>
<tr>
<td>Connective tissue b</td>
<td>5.6 ±0.1</td>
<td>5.5 ±0.1</td>
<td>5.5 ±0.1</td>
</tr>
</tbody>
</table>

a B; DryBag, MacPak, LLC, Wayzata, MN having a water vapor transmission rate of 2500 g/m²/24 h at 38 °C and 50% relative humidity; V; Traditional vacuum-bag (V; 8600-14EL, Cryovac-Sealed Air Corporation, Duncan, SC) having a water transmission rate of 0.5–0.6 g/64,516 cm²/24 h at 37.8 °C and 100% relative humidity; D; No packaging.

b Juiciness: 1 extremely dry, 2 very dry, 3 moderately dry, 4 slightly dry, 5 slightly juicy, 6 moderately juicy, 7 very juicy, 8 extremely juicy; Beef flavor: 1 extremely bland, 2 very bland, 3 moderately bland, 4 slightly bland, 5 slightly intense 6 moderately intense, 7 very intense 8 extremely intense; Tenderness: 1 extremely tough 2 very tough 3 moderately tough 4 slightly tough 5 slightly tender 6 moderately tender 7 very tender 8 extremely tender Connective tissue: 1 abundant amount, 2 moderately abundant, 3 slightly abundant, 4 moderate amount, 5 slight amount, 6 traces amount, 7 practically none, 8 none detected.

c 1 extreme off-flavor, 2 strong off-flavor, 3 moderate off-flavor, 4 slight off-flavor, 5 threshold; barely detected, 6 none detected.

d,e For variables with three treatments, values lacking a common superscript differ ($P< 0.001$).
Figure 5. Interactive effect of subprimal packaging type and days of postmortem age on Warner-Bratzler shear force values ($P=0.01$) of triceps brachii steaks. Values with different letters differ ($P \leq 0.02$)

$^a = $ B; DryBag, MacPak, LLC, Wayzata, MN having a water vapor transmission rate of 2500 g/m²/24 h at 38 °C and 50% relative humidity; $V =$ Traditional vacuum-bag (V; 8600-14EL, Cryovac-Sealed Air Corporation, Duncan, SC) having a water transmission rate of 0.5–0.6 g/64,516 cm²/24 h at 37.8 °C and 100% relative humidity; $D =$ No packaging.

4. Summary and Conclusions

Tenderness did increase in LL steaks as the length of aging progressed, but the actual difference was marginal. Tenderness in TB steaks was similar throughout the aging process, except for the one subgroup which was speculated to simply be innately tougher. The lightness of the longest aged LL steaks and TB steaks trended oppositely during retail display, but redness and yellowness values trended similarly for steaks from both muscles during display. All three aging methods used in our study resulted in similar palatability, but V packaged subprimals had greater saleable yield percentages than B and D packaged subprimals which were similar. Thus, V packaging will likely continue to be the preferred type of postmortem aging utilized in the U.S. beef industry.

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Lignin-cellulosic biomass delignification for methylated alcohol production

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Abstract

Introduction. Sugar’s molecules of lignin-cellulosic biomass make them inaccessible for carrying-out of polysaccharose depolymerization. The aim of investigation is power of physical-chemical parameters on the process of organosolv delignification of lignin-cellulosic biomass.

Materials and methods. Target of research is the way of organosolv lignin dilution. As a raw stuff we used a wheat straw, afterharvesting maize shruffs and halm of sugar broomcorn. Lignin was determined by the hydrolysis of mixed of concentrate hydrochloric acid and 72% sulphuric acid, polysaccharides - in amount of monosaccharide by the Machen and Schoorl method.

Results and discussion. For maximum lignin dilution a solvent composition, fineness degree of row, treatment temperature and a process time were investigated. Depending on concentration change of sulphuric acid (from 1 to 3,9%) in solvent, lignin yield from maize'chaff is increased from 14,4 to 29,2%, content of undissolved remainder is decreased from 66,7 to 55,4%. The lignin yield is changed from 19,3 to 32,4% in stalk of sugar sorghum in the same condition. Treatment temperature rising of chopped wheat straw from 70 to 100 °C contributed to an increase in the degree of conversion of lignin by 3%, and for the stalks of corn - this indicator changed from 6.8% to 17.1%. Maximum lignin dissolution is at the temperature of 100 C°, wherein the highest yield of reducing substances is achieved within 1:00, regardless of the type of plant material. Lignin conversion increases at increase processing time to 6:00, but at the same time there is a destruction of sugar molecules, the content of which is almost halved.

Conclusions. The hydrolysis degree of lignin by an organosolvent solvent can be adjusted by choosing rational modes of grinding of raw materials, temperature and duration of the process.

Keywords:
Alcohol
Cellulose
Biomass
Solvent
Lignin

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Introduction

However the global trend is a significant incline in the production of bioethanol, a decrease in its cost, and an increase in competitiveness basing with the use of non-food raw materials, in particular, lignocellulosic biomass.

Bioconversion of renewable materials to ethanol considered as one of the key branches of biotechnology [1].

Literature review

Lignin-cellulose transformation into ethanol for sugar’s releasing from biomass and their hydrolysis by ferments to distiller's monosugar [2]. Cellulose and hemicellulose contain sugars in polymeric form and can be hydrolyzed by enzymes to fermented monosaccharides for further fermentation into bioethanol. The barrier to cellulose hydrolysis is lignin, which protects it from chemical reagents, microbial and enzyme attacks [3]. Therefore, in order to increase the availability of cellulose and hemicellulose to hydrolysis, the cellular structure of plant biomass must be destroyed by breaking their chemical bonds with lignin.

There is a wide range of methods for the pretreatment of cellulose-containing raw materials, the said methods being divided into four types according to the nature of their impact: physical, mechanical, chemical and biological. Physical methods are the treatment with γ-rays or a stream of electrons, processing with microwave radiation (2400–2500 MHz), heating in air or in an atmosphere of CO2 (100 °C), in water or in a gas, cooling, processing under elevated or reduced pressure, action of ultrasound [4–8]. The structure of cellulose is also destroyed when it is heated beyond the elevated pressure [9]. Processing methods increase the reactivity of cellulosic raw materials by 2-5 times [10].

Mechanical methods of pretreatment of cellulose-containing raw materials (CCRM) consist in their grinding in various types of mills (ball, colloid, and vibration), disintegrators and crushers, dispersing on rollers, etc. CCRM are ground both in dry and in wet form [9]. The use of mechanical methods leads to the destruction of the crystal structure of cellulose, an increase in the surface available for cellulolytic enzymes and, as a result, a significant increase in the reactivity of CCRM (10 or more times) [10, 11, 12].

Chemical pretreatment methods are based on the ability of certain chemical compounds to dissolve lignin or cellulose, or lead to swelling and destruction of its structure. When such solutions are diluted with water, acetone or alcohol, precipitation (regeneration) of cellulose occurs. Regenerated cellulose is practically amorphous, and if regeneration is not carried out in an aqueous medium, this significantly increases the specific surface area of the regenerated cellulose.

Cellulose swelling, dissolution and amorphization are also occurring in solutions of inorganic salts, accompanied by mercerization (swelling and rearrangement of the structure) and amorphization of cellulose [13].

Pretreatment methods with 0.2% H2SO4 at 180 °C for 30 s and 0.1% at 180 °C for 45 minutes are described [14]. The hydrolysis of cellulose under these conditions is insignificant, but the degree of polymerization and the crystallization index decrease, there is also a substantial hydrolysis of hemicellulose. Delignification of cellulosic raw materials with ammonia with hydrogen peroxide, peracetic acid, a mixture of 99.9% acetic anhydride and 30% hydrogen peroxide (1: 1) at 80 °C is also described [15].
Research and development of numerous methods of delignification of lignin-cellulosic biomass testify to the urgency of the problem of its use for the production of cellulose as a raw material in biotechnological and chemical processes.

The above methods of delignification have their advantages and disadvantages, in particular low efficiency, multi-stage technological process and negative impact on environmental safety.

Recently, intensive research and development has been carried out to improve the known methods and to develop new ones for the preliminary preparation of lignocellulose biomass for its hydrolysis. One of the modern trends is the implementation of steam technology by saturating the crushed mass within a few minutes with high-pressure steam at a temperature about 200 °C, followed by an instantaneous decrease in pressure [US Patent No. 4461648 Delignification steam, unauthorized slightly acid and enzymatic hydrolysis, Canada Patent No. 1287705 Continuous process bioethanol production from lignin-cellulosic biomass using continuous steam production technology and auto hydrolysis]. Under such conditions, the lignin-cellulose matrix is destroyed.

There are data [16, 17] on new organosolv cellulose extraction methods based on the ability of organic solvents (acetone, ethanol, methanol, etc.) to dissolve lignin and hemicellulose under certain conditions by depolymerizing molecules and their fragments. After dissolving lignin and hemicellulose, these reagents make cellulose available for the action of catalysts or enzymes. Thus, the pretreatment of plant materials is just the destruction of lignin. A feature of the chemical reactions of this process is that these are heterogeneous reactions of high-molecular compounds, the intensity of which depends on the availability of the reaction centers in the polymer structure. Among organosolv solvents for organic solution methods of delignification of lignin-cellulose biomass, ethyl alcohol, in the form of bioethanol as the final product of biomass processing, is the most acceptable by technological, economic and environmental indicators [18,19].

Ethanol production with previous biomass structure destruction by organosolvent method was implemented by Biogabol (Denmark) at the pilot plant level, by Amerikan Process Inc. (USA) implemented an industrial installation in a pulp and paper mill.

Taking into account the peculiarities of ethanol production, varieties of vegetable raw materials and its processing, the study of the influence of the parameters and composition of the solvent on the course of the hydrolysis process is relevant.

So, the purpose and objectives of the study are to develop scientific and methodological foundations of organosolv delignification of lignin-cellulosic biomass for the production of second-generation bioethanol.

According to the goal, the ratio of the components of an organosolv solvent to the degree of delignification of wheat straw, post-harvest corn waste, and dried sorghum stalk was determined; the influence of temperature and pressure, the degree of grinding of raw materials and treatment duration on the process of delignification was investigated.

Materials and methods

Materials

In research, raw materials for delignification wheat straw, post-harvest corn waste and dried sorghum (Mohawk variety) stalk were used as raw materials. The chemical composition of the raw materials is given in Table 1.
As it can be seen from Table 1, the waste of corn and the stalk of sugar sorghum compared with wheat straw are characterized by lower cellulose content by 4.5% and 9.5%, respectively. In addition, they are distinguished by a high content of hemicellulose (by 8.1% for corn stalk and by 9.6% for sugar sorghum stalks), which is easily hydrolyzed to form reducing sugars.

The content of ballast substances in the stalk of sugar sorghum is almost two times higher compared to wheat straw and post-harvest corn waste. Such substances include pectin-containing gums and other compounds not applicable for the production of ethanol [1].

Since the lignin content in the stalk of sugar sorghum is rather low, it is hypothetically possible to predict a high yield of sugars suitable for fermentation into ethanol [2].

### Preparation of prototypes

To release the plant mass from the lignin, it was ground to a particle size of 1–3 cm, mixed with a solvent in a ratio of 1:4, the composition of which had 50% ethyl alcohol, 47% water and 3% of normal sulfuric acid, carried out delignification in a sealed autoclave at temperature 100–150 °C and excess pressure 0.25–0.3 MPa.

**Procedure for conducting research.**

The prepared reaction mixture with dissolved lignin was separated by filtration. The lignin-free solid phase was used for hydrolysis to the fermented sugars by cellulolytic enzymes, and the solvent was removed from the liquid fraction by the method of distillation. Under these conditions, lignin precipitates and after drying can be used as an end product.

### Research methods

- The moisture content of cellulosic raw materials was determined by drying to constant weight at a temperature of 100-105 °C;
- Lignin content - by direct method by hydrolysis with a mixture of concentrated hydrochloric acid and 72% sulfuric acid [20];
- The amount of polysaccharides, easily and difficultly hydrolyzed, was determined by the number of monosaccharides by reducing ability determined by the Maquenne-Schoorl method [20].
Results and discussion

Effect of solvent composition on the yield of lignin and reducing sugars

In the technology of organosolv delignification of vegetable raw materials, the composition of the solvent is an important factor that affects the intensity, completeness and course of the dissolution of lignin [16, 17]. As a result of experimental studies, it was observed that the ratio of the components of the solvent, in particular, the content of sulfuric acid, has a certain effect on the release of lignin [21]. In experiments with delignification of the fine ground wheat straw (Figure 1) an increase in the concentration of sulfuric acid in the mixture volume in the range of 1.0–3.9% by volume contributed to a higher yield of lignin from 14.4% to 29.2% and the transition of easily hydrolyzed polysaccharides into solution. The amount of reducing substances in the filtrate was 30.2% more compared to the lower acid content. In the case, deeper destruction of the raw material polymers and a decrease in the undissolved residue from 66.7 to 55.4% in terms of absolutely dry matter (ADM) of the analyzed samples occurs.

Figure 1. Effect of solvent components ratio on the yield of lignin and reducing sugars from wheat straw:
1 - Content of residual lignin, % of primary lignin brought with ADM;
2 - Conversion grade of lignin, % of primary lignin brought with ADM;
3 - Conversion of reducing substances, % of brought ADM;
4 - Yield of solid residue, % of brought ADM

The same pattern of influence of the acid content on the conversion of lignin and reducing substances continued in the experiments of delignification of the stalks of sugar sorghum (Figure 2). The increase in the amount of acid in the solvent contributed to a more complete release of lignin (from 19.3 to 32.4%). This is because the increase in the amount of sulfuric acid in the solvent, which is a catalyst for the polysaccharide hydrolysis reaction and in aqueous solutions, dissociates into the hydroxonium (H3O +) ion, which protects the glycosides’ bond. As a result, acetyl oxygen goes into a 4-valent state, the stability of the glycosides’ bond decreases, and it splits with the formation of two parts of macromolecules.
The final reaction product is monosaccharide’s [1]. The grade of lignin conversion of the stalks of sugar sorghum was higher compared to the ground wheat straw, the possible explanation of the fact being a lower crystallinity index of sorghum cellulose [21].

Analyzing the parameters studied, we can conclude that for the delignification of the grinding of wheat straw, sorghum stalks and maize the most effective is the use of a water-alcohol oxidizer, which containing 3% (by volume) of sulfuric acid as a catalyst.

![Figure 2. Effect of the ratio of solvent components on the yield of lignin and reducing sugars from the stalk of sugar sorghum: 1 – Content of residual lignin, % of primary lignin brought with ADM; 2 - Conversion grade of lignin, % of primary lignin brought with ADM; 3 - Conversion of reducing substances, % of brought ADM; 4 - Yield of solid residue, % of brought ADM](image)

**Treatment temperature influence of vegetable raw materials on the lignin yield**

Based on the supramolecular structure of the cellulose and the presence of amorphous and crystalline fractions, it can be assumed that the increase in temperature promotes the penetration of the catalyst into amorphous regions, where it acts on all macromolecule bonds, which accelerates the hydrolysis of lignin-cellulose biomass.

Data characterizing the degree of bioconversion of lignin from the grinding of wheat straw are given in Table 2, and from the stalks of corn in Table 3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Temperature during dwell time, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70</td>
</tr>
<tr>
<td>Lignin content in sample weight, g</td>
<td>4.65</td>
</tr>
<tr>
<td>Yield of solid residue, %</td>
<td>63.7</td>
</tr>
<tr>
<td>Conversion grade of lignin, %</td>
<td>26.0</td>
</tr>
<tr>
<td>Residual lignin content, % of ADM</td>
<td>74.0</td>
</tr>
</tbody>
</table>

---

From Table 2 it can be seen that with an increase in the processing temperature of ground straw, the yield of solid sediment decreases to 60.9%, while the residual lignin content decreases to 70.7%, that is that the temperature can be considered to rise, the hydrolysis of the carbohydrate part of the straw to increase, and selectivity and degree of lignin conversion to incline up to 29.3%.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Temperature during dwell time, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70</td>
</tr>
<tr>
<td>Lignin content in sample weight, g</td>
<td>4.39</td>
</tr>
<tr>
<td>Yield of solid residue, %</td>
<td>68.6</td>
</tr>
<tr>
<td>Conversion grade of lignin, %</td>
<td>1.8</td>
</tr>
<tr>
<td>Residual lignin content, % of ADM</td>
<td>98.2</td>
</tr>
</tbody>
</table>

Other results were obtained when delignifying corn stalks, where the yield of solid residue was significantly lower than that from wheat straw, it was 48.3%, but the lignin conversion grade was also significantly less – 13.7% (Table 3). This can be explained by the fact that the decrease in the yield of solid residue is due to a higher content of easily hydrolytic polysaccharides, in particular hemicelluloses [22]. At the same time, the lignin conversion grade was almost two times less compared to that of wheat straw, being in our opinion due to the degree of grinding [18,19].

Pre-grinding of raw materials increases the specific surface area and reduces the degree of polymerization of the cellulose substrate, while reducing the crystallinity index [19]. The combination of these factors positively affects the reactivity of the cellulose substrate [23].

To confirm or refute this conclusion, a study was conducted on the processing of corn stalks, ground in a laboratory mill (Table 4).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Temperature during dwell time, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70</td>
</tr>
<tr>
<td>Lignin content in sample weight, g</td>
<td>4.39</td>
</tr>
<tr>
<td>Yield of solid residue, %</td>
<td>63.3</td>
</tr>
<tr>
<td>Conversion grade of lignin, %</td>
<td>6.8</td>
</tr>
</tbody>
</table>

The data of Table 4 confirm the conclusion about the impact of the degree of grinding on the delignification of raw materials, the conversion of lignin increases significantly and reaches 17.1% at a temperature of 100 °C.

Influence of treatment duration on lignin-cellulosic biomass delignification

The duration of the delignification process also affects the content of residual lignin, the degree of its conversion and the content of reducing substances, as the data in Table 5 confirm.
Table 5

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Processing time, hours</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Yield of solid residue, %</td>
<td>57.3</td>
</tr>
<tr>
<td>Content of residual lignin, %</td>
<td>82.1</td>
</tr>
<tr>
<td>Lignin conversion grade, %</td>
<td>15.9</td>
</tr>
<tr>
<td>Content of reducing substances, %</td>
<td>24.3</td>
</tr>
</tbody>
</table>

The data adduced show that at a constant temperature and an increase in processing time up to 6 hours, the yield of solid residue decreases to 50% of the initial mass of raw materials, the content of residual lignin in biomass decreases to 68.9%, and the degree of lignin conversion increases to 23.7% of its content in the straw.

At the same time, with an increase in the duration of the process, the destruction of sugar molecules occurs, the number of which constantly decreases and amounts to 10.7% of processing for six hours versus 24.3% in the first hour of hydrolysis. Therefore, the most acceptable is the period of treatment for one hour stipulated with fine grinding [16, 17].

Thus, the promise of using a solvent of lignin based on ethyl alcohol is experimentally proven this making the process of hydrolysis of lignin-cellulosic biomass economically feasible. According to the results of research, an experimental regulation has been developed for the delignification of CCRM, as the first regulatory document for organizing the pilot-industrial production of bioethanol from starch-containing raw materials and CCRM.

**Conclusion**

1. The methodological basis for the delignification of CCRM with organosolv solvents using the example of wheat straw, corn stalks and sugar sorghum stalks is theoretically and experimentally substantiated.
2. Cellulosic biomass delignification is carried out by using a lignin solvent based on ethyl alcohol and sulfuric acid.
3. That according to the total conversion grade of cellulose-containing components of the raw materials into reducing substances, the most rational is the use of a solvent with a concentration of sulfuric acid of 3% (by volume) for wheat straw and corn stalks and 1% (by volume) for stalks of sorghum for the duration of the process within one and three hours.
4. The yield of the solid residue after the treatment of the raw material with an organosolv solvent decreases, and the degree of lignin conversion increases with increasing treatment temperature and the degree of biomass grinding.

**References**

Influence of damaged starch on the quality parameters of wheat dough and bread

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Keywords:
- Starch
- Dough
- Bread
- Rheology
- Gelatinisation

Abstract

Introduction. A certain degree of damage to the starch granules is desirable but excessive level of starch damage can have deteriorating effect on the quality of the bakery products.

Materials and methods. The wheat flour with lower (3.15%) and higher degree of starch damage (6.13%) were produced by repeat grinding (two passes) in a laboratory mill. The rheological measurements of dough samples were conducted using Farinograph and Extensograph, and gelatinisation and pasting properties – differential scanning calorimetry and Micro Visco-Amylo-Graph. Texture profile analysis of bread samples were performed using a texture analyser, and specific volume by laser topography method.

Results and discussion. The dough mixing properties were generally better for the samples with a higher level of starch damage and the most significant improvement has been manifested in the increased water absorption, from 60.7% to 63.8%. Higher water absorption can be associated with the influence of starch damage but also with the effect of flour particle size because smaller particles have larger total surface area. The starch damage had no significant effect on most of the extensographic indicators, although a slight decrease in resistance and extensibility was observed. Samples with a higher degree of starch damage showed decreased gelatinisation power. The gelatinization enthalpy (ΔHg) decreased from 1.41 to 1.31 J/kg, and amylographic peak viscosity from 582.5 to 505.0 BU. This could be explained by the restricted swelling of damaged starch granules due to the loss of organised structure. There were no significant differences in the moisture content and water activity between samples with different damaged starch content. The starch damage had a significant impact on majority of the bread quality parameters but the hardness increase and specific volume were most pronounced. The hardness increased from (from 4.09 N to 5.25 N) and specific volume (from 4.04 cm³/g to 3.53 cm³/g) when flour with a higher degree of damaged starch was used.

Conclusions. The level of starch damage had a significant effect on the dough rheological properties, starch gelatinisation and pasting properties, as well as on the bread quality parameters.

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Introduction

Although the name “damaged starch” may suggest that this is an undesirable phenomenon, a certain degree of damage to the starch granules has a favourable effect on the quality of the bakery products. Damaged starch is formed during milling of wheat due to mechanical shear between the mill rolls [1, 2]. The level of starch damage is affected by several parameters during milling: pressure and gap size between the reduction rolls, roll speed ratio, rolls diameter, milling time, wheat tempering conditions (or moisture of the wheat entering the milling process), and wheat hardness. The milling of soft wheat results in less damaged starch than the milling of hard wheat [3–6]. A higher degree of starch damage in flours can be also achieved by grinding wheat in multiple passages through mill rolls, or with more intensive grinding in a ball or disk mill, which is generally performed during laboratory testing.

Knowledge of the physical state of starch granules, as well as their size and shape, is very important for predicting the technological process conditions and manifestation of starch properties (e.g. water absorption, gelatinization properties, rheological characteristics ...) [7]. Damaged starch differs from intact in several important features: it is much more susceptible to enzymatic hydrolysis, has an increased ability to absorb water, and has modified gelatinisation and pasting properties [8]. Intact starch granules can absorb water up to 40% of their weight, while damaged ones absorb up to 300%. The benefits of increased water absorption are evident due to encashed dough mixing properties, while greater susceptibility to amylolytic enzymes results in increased maltose and dextrin production during fermentation. However, too much starch damage can cause production problems and lead to a decline in bread quality such as reduced volume, poor texture and cell structure, grey crumb and dark crust colour, etc. This deteriorating effect of excessive level of starch damage on the bakery products can be explained in a way that the higher water absorption of the damaged starch prevents the full development of gluten. Furthermore, during fermentation, the starch is degraded too much, which leads to excessive water release, and to decrease in the dough consistency and gas retention capacity [9, 10].

There are different methods for determining damaged starch, but today the enzymatic/spectrophotometric AACC method 76-31.01, and Chopin’s SDmatic device which combined iodometric/amperometric methods (AACC International Method 76-33.01) are the most commonly used. Usually, degree of starch damage for wheat flours is in the range of 4–10%. Hard wheat flour may show higher values, and vice versa, soft wheat flour may have a lower degree of starch damage.

Therefore, the aim of this study was to investigate the effect of damaged starch on the quality parameters of wheat dough and bread using a wide variety of methods to gain insight into the mechanisms of damaged starch influence on the rheological properties of the dough, gelatinization and pasting properties of the starch, and on the qualitative parameters of bread.

Material and methods

Flour Samples

Commercial all-purpose plain white flour (Podravka d.d. Koprivnica, Croatia) was used in this study as a reference flour sample with the lower level of starch damage (DS1). According to the conducted composition analysis (ISO standard methods 712:2001; 20483:2006; 2171:2007), moisture, protein and ash content of this flour was 12.22%,
11.18%, and 0.54%, respectively [11]. Level of starch damage of DS1 sample was 3.15% (Megazyme kit, Ireland; AACC method 76-31.01) [12]. This flour was subjected to repeat grinding (two passes) in a laboratory mill MLU-202 (Bühler, Switzerland) with tightened reduction rolls to obtain more crashing force and pressure to the flour particles in order to get more damaged starch. This sample was marked as DS2, and showed higher degree of starch damage (6.13%).

Particle size analysis

The particle size distribution of the flour samples was tested by sieving on a laboratory vibrating shaker “Analysette 3” (Fritsch, Germany) using sieves with apertures of 0.125 mm, 0.100 mm, 0.075 mm and 0.050 mm. Three rubber balls were placed on each sieve for the purpose of cleaning and facilitating the flow of flour during testing. The sieving time was 10 minutes with an amplitude of 2 mm. The weight of each sieve was recorded before and after the analysis.

Geometric mean particle size (average size) of samples was calculated from the following equations [13, 14]:

\[ d_i = (d_i \times d_{i+1}) \]  
\[ d_{gw} = \log^{-1} \left[ \frac{\sum (W_i \log d_i)}{\sum W_i} \right] \]

where:
- \( d_i \) – sieve openings diameter of the \( i \)th sieve;
- \( d_{i+1} \) – sieve openings diameter of the next larger sieve;
- \( \bar{d}_i \) – mean diameter of the openings of two adjacent sieves;
- \( d_{gw} \) – geometric mean diameter;
- \( W_i \) – weight of particular fraction.

Dough rheological characterisation

Rheological measurements of dough properties prepared from samples with different levels of starch damage (DS1 and DS2) were conducted using Farinograph and Extensograph (Brabender OHG, Duisburg, Germany). Farinographic analyses were made using a 300-g mixing bowl according to an ISO standard method 5530-1 and the results were expressed according to the Hungarian national standard MSZ 6383. Extensographic analyses were conducted according to an ISO standard method 5530-2 [11, 15].

Determination of starch gelatinisation and pasting properties

The differential scanning calorimeter (DSC822e, Mettler-Toledo, Switzerland) was used to determine the gelatinisation properties of dough samples. The measurements were carried out under ultrahigh-purity nitrogen atmosphere, and calibration was performed by measuring the thermal properties of indium. Samples of 10-15 mg of dough were weighed into standard aluminium pan (40 μL) immediately after mixing the dough in the farinograph mixing bowl. The pans were sealed and immediately analysed. Three measurements were performed for each sample. An empty, hermetically sealed pan was used as a reference. The samples were subjected to a heating program of 30-100 °C, with a heating rate of 10 °C/min. Gelatinisation
parameters were extracted from the peak endotherm of thermogram: onset temperature ($T_0$), peak temperature ($T_p$), conclusion temperature ($T_c$), gelatinization temperature range ($T_c-T_0$), and the starch gelatinization enthalpy ($\Delta H_g$) were determined.

The pasting properties of samples with different levels of starch damage were evaluated using Micro Visco-Amylo-Graph (MVA, Brabender, Germany). A suspension containing 15 g (14 % w. b.) of flour sample and 100 ml of distilled water was held under constant shear of 250 min$^{-1}$, heated from 30 to 92 °C at 5 °C/min rate, held at 92 °C for 5 min, cooled down to 50 °C at 5 °C/min rate and held at 50 °C for 1 min. The following data was recorded: pasting temperature (°C), peak viscosity (BU), peak temperature (°C), breakdown viscosity (BU) and setback viscosity (BU).

**Baking tests**

Bread loafs containing flour with different levels of starch damage were produced according to the ICC standard method 131 [16]. The dough was mixed in a laboratory mixer (Diosna, Germany) for 9 minutes (2 min at speed 1, and 7 min at speed 2). After mixing, the dough was divided into 250 g pieces and rested in proofer (30 °C and 85% RH), then moulded by hand and placed into the baking pans and proofed for another 60 min (30 °C and 85% RH). The samples were baked in an oven (Wiesheu Minimat Zibo, Wiesheu GmbH, Germany) for 20 min at 200 °C. Bread samples were prepared in triplicate batches.

**Bread quality evaluation**

Bread quality evaluation was conducted four hours after baking. Analysis of moisture content and water activity was performed separately for bread crumb and crust. Moisture was determined in accordance with the two-stage air oven method (AACC method 44-15.02) [12]. Water activity measurements were conducted using portable water activity meter (HygroPalm AW1, Rotronic, USA).

Texture profile analysis (TPA) of bread samples were performed using a TA.XT2i Texture Analyzer (Stable Microsystmes Ltd., Surrey, England). The bread loafs were precisely sliced to obtain four uniform slices of 25 mm thickness. TPA test included double compression of slices to 40% of their thickness with a 25 mm aluminium cylindrical probe. The force-time curves were recorded at 1.7 mm s$^{-1}$ crosshead speed with a trigger force of 5 g. The following parameters were quantified: hardness (N, the maximum force required to compress the sample), springiness (the ability of the sample to recover its original form after the deforming force was removed), resilience (the ratio of work returned by the sample when compressive strain is removed), cohesiveness (the extent to which the sample could be deformed prior to rupture), and chewiness (N, the force needed to chew a food product calculated as hardness x cohesiveness x springiness).

The specific volume of bread samples was calculated as ratio of bread volume and loaf weight. The volume was measured by laser topography method with the use of Volscan Profiler (Stable Microsystmes Ltd., Surrey, UK).

**Statistical data analysis**

All the tests were performed in at least three replications. Obtained experimental data was analysed by an analysis of variance (ANOVA) and Fisher’s least significant difference (LSD), with significance defined at $p<0.05$. A statistical analysis was carried out with Statistica ver. 12.0 software (Stat Soft Inc. Tulsa, OK, USA).
Results and discussion

The degree of starch damage is defined as the percentage of starch that is subject to enzymatic hydrolysis. The principle of AACC method 76-31.01 is based on the hydration and hydrolysis of damaged starch granules of the sample using fungal α-amylase at 40 °C for 10 minutes. These conditions allow for almost complete hydrolysis of damaged starch granules and minimal degradation of undamaged granules. Hydrolysis products are maltooligosaccharides and α-limit dextrins. Dextrins are converted to glucose by amylglucosidase and, after reaction with oxidase/peroxidase reagent, the resulting colour is determined by spectrophotometer (AACC). In this research, in order to obtain two samples of wheat flour with the same chemical composition but with a different degree of starch damage, all-purpose plain flour was subjected to repeated grinding in a laboratory mill with tightened reduction rolls. As a result, sample flour with lower (3.15%) and higher starch damage (6.13%) was obtained. Furthermore, in addition to the increased starch damage, intensive grinding results in a significant reduction in the flour particle size (Table 1). Average size of flour particles were 88.11 μm and 63.55 μm, for the DS1 and DS2 sample, respectively.

<table>
<thead>
<tr>
<th>Particle size (μm)</th>
<th>Distribution (weight, %)</th>
<th>DS1*</th>
<th>DS2**</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;125</td>
<td>26.09</td>
<td>2.19</td>
<td></td>
</tr>
<tr>
<td>100-125</td>
<td>29.09</td>
<td>17.28</td>
<td></td>
</tr>
<tr>
<td>75-100</td>
<td>22.50</td>
<td>35.09</td>
<td></td>
</tr>
<tr>
<td>50-75</td>
<td>10.48</td>
<td>24.81</td>
<td></td>
</tr>
<tr>
<td>&lt;50</td>
<td>11.84</td>
<td>20.63</td>
<td></td>
</tr>
<tr>
<td>In total</td>
<td>100.00</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>Average size (μm)</td>
<td>88.11</td>
<td>63.55</td>
<td></td>
</tr>
</tbody>
</table>

*DS1 – wheat flour with 3.15% of damaged starch  
**DS2 – wheat flour with 6.13% of damaged starch

The results on the effect of starch damage on the rheological characteristics of dough are presented in Table 2. The dough mixing properties were generally better for the samples with higher level of starch damage (DS2). The most significant improvement (p<0.05) has been manifested in the increased water absorption, 60.7% for DS1 to 63.8% for DS2. Higher water absorption can be associated with the influence of starch damage but also with the effect of flour particle size because smaller particles have larger total surface area. Development time and stability, and consequently quality number, were also improved with the higher degree of starch damage. This is in accordance with the results of other researches [17–19].

The starch damage had no significant effect on most of the extensographic indicators, although a slight decrease in resistance and extensibility could be observed. This resulted in a reduction in energy required for dough sample extension.

A differential scanning calorimetry (DSC) was used to monitor the process of the starch gelatinisation. As the temperature increased, an endotherm appeared in the thermogram of the test sample. The thermogram peak corresponds to the gelatinization process of the amorphous starch phase (starch gelatinization endotherm) [8, 20]. The thermal parameters of starch gelatinization are shown in Table 3.
### Table 2

#### Effect of starch damage on rheological characteristics

<table>
<thead>
<tr>
<th>Farinograph</th>
<th>DS1&lt;sup&gt;*&lt;/sup&gt;</th>
<th>DS2&lt;sup&gt;**&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water absorption (%)</td>
<td>60.7 ± 1.9&lt;sup&gt;b&lt;/sup&gt;</td>
<td>63.8 ± 1.1&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Dough development time (min)</td>
<td>1.7 ± 0.2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.1 ± 0.1&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Stability (min)</td>
<td>1.7 ± 0.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.0 ± 0.2&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Degree of softening (BU)</td>
<td>61.9 ± 3.1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>62.5 ± 4.3&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Quality number</td>
<td>60.2 ± 2.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>66.9 ± 3.5&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Quality group</td>
<td>B1</td>
<td>B1</td>
</tr>
</tbody>
</table>

#### Extensograph

<table>
<thead>
<tr>
<th></th>
<th>DS1&lt;sup&gt;*&lt;/sup&gt;</th>
<th>DS2&lt;sup&gt;**&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (cm&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>101.1 ± 4.1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>92.7 ± 3.9&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Resistance&lt;sub&gt;50 mm&lt;/sub&gt; (BU)</td>
<td>353.2 ± 13.2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>338.1 ± 15.1&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Extensibility (mm)</td>
<td>174.1 ± 6.6&lt;sup&gt;a&lt;/sup&gt;</td>
<td>160.9 ± 6.1&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>R&lt;sub&gt;50 mm/E&lt;/sub&gt; ratio (BU/mm)</td>
<td>2.0 ± 0.1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.1 ± 0.2&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>*</sup>DS1 – wheat flour with 3.15% of damaged starch  
<sup>**</sup>DS2 – wheat flour with 6.13% of damaged starch  
Values are means of three replications ± SD. Values in the same row with different superscripts (a-b) are significantly different (p<0.05).

### Table 3

#### Effect of starch damage on gelatinisation and pasting properties

<table>
<thead>
<tr>
<th></th>
<th>DS1&lt;sup&gt;*&lt;/sup&gt;</th>
<th>DS2&lt;sup&gt;**&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Differential scanning calorimetry (DSC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T&lt;sub&gt;0&lt;/sub&gt; (°C)</td>
<td>59.98 ± 0.06&lt;sup&gt;a&lt;/sup&gt;</td>
<td>60.36 ± 0.31&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>T&lt;sub&gt;p&lt;/sub&gt; (°C)</td>
<td>69.12 ± 0.29&lt;sup&gt;a&lt;/sup&gt;</td>
<td>69.51 ± 0.21&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>T&lt;sub&gt;c&lt;/sub&gt; (°C)</td>
<td>78.18 ± 0.13&lt;sup&gt;a&lt;/sup&gt;</td>
<td>78.80 ± 0.51&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>T&lt;sub&gt;c&lt;/sub&gt; - T&lt;sub&gt;0&lt;/sub&gt; (°C)</td>
<td>18.21 ± 0.19&lt;sup&gt;a&lt;/sup&gt;</td>
<td>18.44 ± 0.82&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>ΔH&lt;sub&gt;g&lt;/sub&gt; (J/g)</td>
<td>1.41 ± 0.04&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.31 ± 0.03&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

#### Micro Visco-Amylo-Graph (MVA)

<table>
<thead>
<tr>
<th></th>
<th>DS1&lt;sup&gt;*&lt;/sup&gt;</th>
<th>DS2&lt;sup&gt;**&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pasting temperature (°C)</td>
<td>63.1 ± 0.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>62.7 ± 0.6&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Peak viscosity (BU)</td>
<td>582.5±8.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>505.0 ± 9.9&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Peak temperature (°C)</td>
<td>89.1 ± 0.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>88.9 ± 0.3&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Breakdown viscosity (BU)</td>
<td>142.5 ± 2.6&lt;sup&gt;a&lt;/sup&gt;</td>
<td>117.5 ± 3.5&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Setback (BU)</td>
<td>503.5 ± 5.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>464.5 ± 7.8&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Resistant starch (%)</td>
<td>1.35 ± 0.06&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.18 ± 0.01&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>*</sup>DS1 – wheat flour with 3.15% of damaged starch  
<sup>**</sup>DS2 – wheat flour with 6.13% of damaged starch  
Values are means of at least three replications ± SD. Values in the same row with different superscripts (a-b) are significantly different (p<0.05).
There were no differences in the gelatinisation temperatures (pasting, peak and conclusion temperature, and gelatinisation range \(T_0, T_p, T_c, T_c - T_0\)) between samples with different levels of starch damage. In contrast, the gelatinization enthalpy \(\Delta H_g\) were significantly influenced \((p<0.05)\) by damaged starch content, 1.41 J/g for DS1 and 1.31 J/g for DS2 sample. Samples with increased level of damaged starch showed lower thermogram peaks, because gelatinisation process is more pronounced when higher amount of native and intact granules are present in the system [21].

Similar results were obtained when the Micro Visco-Amylo-Graph (MVA) was used to monitor pasting properties of flour samples. Pasting and peak temperatures were not affected by the degree of starch damage but peak viscosity was significantly decreased \((p<0.05)\) with a higher degree of starch damage.

Furthermore, breakdown and setback also decreased when degree of damaged starch increased. This could be explained by the restricted swelling of damaged starch granules due to the loss of organised structure and decrease of their gelatinisation power [5]. On the other hand, decreased gelatinisation power could be also explained with a greater susceptibility of damaged starch granules to amylolytic enzymes (as illustrated on Figure 1), which results in an increased maltose and dextrin production during fermentation.

![Figure 1. The effect of damaged starch on water absorption and enzyme susceptibility](image-url)

The effect of the degree of starch damage on bread quality parameters are presented in Tables 4 and 5. There were no significant differences in the moisture content and water activity between samples with different damaged starch content. Despite the increased water absorption during mixing, the bread samples produced from flour with higher level of damaged starch did not have a higher moisture or water activity. This can be also explained by the increased amylolytic activity during fermentation when starch hydrolysis occurs, resulting in excessive release of water that becomes more mobile, and therefore more susceptible to evaporation during baking.
Table 4

Moisture content and water activity of bread samples with different levels of starch damage

<table>
<thead>
<tr>
<th></th>
<th>DS1*</th>
<th>DS2**</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Moisture content (%)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crumb</td>
<td>41.8 ± 0.3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>41.7 ± 0.2&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Crust</td>
<td>24.6 ± 0.2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>24.8 ± 0.2&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>Water activity</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crumb</td>
<td>0.974 ± 0.003&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.960 ± 0.002&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Crust</td>
<td>0.889 ± 0.002&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.891 ± 0.002&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

*DS1 – wheat flour with 3.15% of damaged starch  
**DS2 – wheat flour with 6.13% of damaged starch  
Values are means of three replications ± SD. Values in the same row with different superscripts (a-b) are significantly different (p<0.05).

Table 5

Effect of starch damage on textural properties and specific volume of bread

<table>
<thead>
<tr>
<th></th>
<th>DS1*</th>
<th>DS2**</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Texture profile analysis (TPA)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardness (N)</td>
<td>4.09 ± 0.55&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.25 ± 1.04&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Springiness</td>
<td>0.95 ± 0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.92 ± 0.02&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Resilience</td>
<td>0.28 ± 0.04&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.27 ± 0.01&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cohesiveness</td>
<td>0.73 ± 0.03&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.79 ± 0.02&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Chewiness (N)</td>
<td>2.84 ± 0.23&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.82 ± 0.46&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>Specific volume (cm³/g)</strong></td>
<td>4.04 ± 0.09&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.53 ± 0.11&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

*DS1 – wheat flour with 3.15% of damaged starch  
**DS2 – wheat flour with 6.13% of damaged starch  
Values are means of three replications ± SD. Values in the same row with different superscripts (a-b) are significantly different (p<0.05).

Data on the textural properties of bread samples is presented in Table 5. The starch damage had a significant impact (p<0.05) on majority of the textural parameters, but the hardness increase was most pronounced, from 4.09 N for DS1 to 5.25 N for DS2. One possible explanation for the increase in bread hardness is the starch-gluten interactions and the increased dough strength that prevents normal expansion during fermentation [10, 22], resulting in a more compact cell structure of finished product. Consequently, there is also a decrease in a specific volume of bread samples with a higher damaged starch content (Figure 2). Specific volume decreased from 4.04 cm³/g for DS1 to 3.53 cm³/g for DS2. In addition to increased hardness and decreased specific volume, the cohesiveness and the force needed to chew the bread were also increased. For this reason, some researchers advise that a higher protein content must be ensured when using flour with high degree of starch damage.
Figure 2. Bread samples made from the wheat flour with 3.15% (DS1) and 6.13% starch damage (DS2)

Conclusion

The results of this research has demonstrated that the level of starch damage had a significant effect on the dough rheological properties, starch gelatinisation and pasting properties, as well as on the bread quality parameters. The benefits of increased content of damaged starch are evident due to an improved dough mixing properties, but too much starch damage can cause production problems and lead to a decline in bread quality. Therefore, it can be concluded that the degree of starch damage in flour is an important factor to consider when producing bakery products.

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References

Effectiveness of natural plant extracts in the technology of combined meatcontaining breads

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Keywords:
Meat
Fish
Bread
Extract
Rosemary
Cranberry

Abstract

Introduction. The aim of this study was to analyze the effectiveness of rosemary and cranberry extracts in the technology of combined meatcontaining breads with freshwater fish and a high content of polyunsaturated fatty acids.

Materials and methods. A model for studying the effectiveness of rosemary and cranberry extracts was meatcontaining bread with freshwater fish. The acid value, peroxide value, thiobarbituric acid reactive species were determined during the storage of meatcontaining breads with extracts.

Results and discussion. Rosemary extract has a high antioxidant activity and effectively inhibits the process of lipid oxidation in meatcontaining combined breads with Muscovy duck meat and freshwater fish meat.

Cranberry extract does not inhibit the hydrolysis of fat during storage of meatcontaining combined breads, and has little positive effect on the formation of primary oxidation products and the accumulation of secondary lipid oxidation products.

The addition of rosemary extract in the amount of 0.02–0.06% allows slowing down the hydrolytic oxidation of minced lipids by 36.19–36.36%. The using of rosemary extract in concentrations of 0.02–0.06% by weight of minced meat helps to slow down the lipid peroxidation in meatcontaining breads with fish, reducing the amount of peroxides almost four times.

The rosemary extract at a concentration of 0.06% by weight of raw materials was the most stabilizing effect. PV in this sample at the end of the study period was 0.013±0.001% J₂, whereas in the control this parameter was 0.05±0.001% J₂, which is almost 4 times higher.

The stabilization of lipid peroxidation in meatcontaining breads with Muscovy duck meat and white carp has the effect of inhibiting the formation of secondary oxidation products, which is confirmed by the results obtained. The amount of aldehydes and ketones was the lowest at the end of the shelf life of breads with rosemary extract and was 0.74–0.76 mg MA/kg, which is lower than in the control sample by 17–20%.

The products contain a significant amount of moisture in the active phase, which prevents long-term storage of products without the use of substances that slow down the oxidation process.

Conclusions. The addition of rosemary and cranberry extracts has been shown to inhibit lipid oxidation during storing meatcontaining breads with a combined raw material composition.
**Introduction**

Meat and meat-containing products technology involves such technological operations as grinding, mixing, heat treatment, during which the lipids of the raw material (pork, poultry meat, pork fat, fat emulsions, etc.) undergo various transformations. Changes also occur in the lipid complex of products during storage. All these factors affect their composition, nutritional and biological efficiency, and, as a result, the consumer appeal of the finished products [1, 2].

The oxidative spoilage of fat in meat products could be explained by three different reactions: enzymatic oxidation; non-enzymatic, free-radical (peroxide) oxidation of lipids; and non-enzymatic, non-radical oxidation. The main reason of oxidative spoilage of meat and meat products is lipid peroxidation caused by reactive oxygen [3, 4].

Lipid peroxidation is a chain reaction that provides extended reproduction of free radicals that initiate the further spread of peroxidation [5]. In the process of meat processing a balanced oxidation system is destroyed as a result of technological operations – grinding, salting and heat treatment [6, 7].

A mixing of lipids and oxidation catalysts, which can contact with oxygen occurs when grinding meat there is [8]. The type and duration of heat treatment have a significant influence on the rate of oxidation processes. There are various technological methods that allow suppressing oxidation processes in fresh raw materials until the formation of oxidation products [9–11]. The use of antioxidants is one method of minimizing the oxidative spoilage problem in the meat industry [12].

Scientists suggest the addition of natural antioxidants, the main source of which is plants, in order to suppress the processes of oxidation in boiled and baked products [13].

Rosemary (Rosmarinus officinalis) has a high content of phenolic components, which include hydroxybutyric acids, including rosemary acid, flavonoids, including quercetin and rutin [14]. Rosemary extract and other antioxidant preparations from this plant have been successfully used to inhibit oxidative spoilage in the food industry [15–17].

Blackberries, strawberries, black currants and other berries can also be described as natural preparations of natural antioxidants [18, 19]. The high concentration of anthocyanins allows suggesting that the addition of berry processing products can be effective in preventing oxidative spoilage of foods with high fat content [20]. In particular, cranberry extract with a high content of phenolic components has a positive effect even on the physiological functions of laboratory animals and humans [21–23].

Moreover, preparations made from cranberries and their waste products can be used to inhibit the oxidation of food lipids in the production of semi-finished products [24–25], various types of cheese [26], cooked sausage products [27], etc.

On the other hand, the promising ways of development of meat-containing products with the combined composition is the use of freshwater fish in their formulations. The addition of freshwater fish mince into the formulations as an ingredient allows obtaining products with high nutritional and biological value and consumer qualities [28–32]. However, the high lipid content of the unsaturated group in fish poses a risk of intensification of the oxidation processes in the minced meat during the processing of raw materials and storage of finished products. For this reason it is important to develop and implement technological techniques designed to prevent oxidative spoilage of such products.

Thus, the effect of natural origin antioxidants on the oxidation processes in meat-containing systems of mixed composition, consisting of meat and fish raw materials, remains unexplored.

Therefore, the aim of our work was to evaluate the effectiveness of rosemary and cranberry extracts in the technology of meat-containing combined breads with duck meat and freshwater fish during storing.
Materials and methods

Experimental design

Combined meatcontaining breads of duck meat and freshwater fish were studied, which included Muscovy duck meat, white carp minced meat, pork fat, dry demineralized whey, wheat flour and functional additives.

The rosemary extract (Food Ingredients Mega Trade, USA) and cranberry extract (CE) (Ukraine) were added to the minced meat. The extracts were added to the forcemeat samples according to the following scheme: № 1 – RE 0,02%; № 2 – RE 0,04%; № 3 – RE 0,06%; № 4 - CE 0,02%; № 5 – CE 0,04%; № 6 – CE 0,06% to the raw material mass, the forcemeat sample without antioxidants was the control one.

The technological concentration of antioxidants for use in the technology of meat products ranges from 0.01 to 0.1% [33–35]. In view of this, an appropriate concentration of rosemary and cranberry extracts was selected, taking into account the content of different groups of substances with antioxidant properties.

The finished breads were stored for 6 days at +4 °C. During the storage of meatcontaining combined breads, acid value (AV) and peroxide value (PV), thiobarbituric acid reactive substances (TBARS) were the controlled indicators. These indicators were determined according to the methods [36, 37].

Manufacture of breads

Meatcontaining breads were prepared using the formulation: 30% duck meat, 45% white carp (Hypophthalmichthys molitrix) meat, 10% pork fat, 5% dry demineralized whey, 2% wheat flour and functional additives (Table 1).

Table 1

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Amount, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muscovy duck meat</td>
<td>30</td>
</tr>
<tr>
<td>Minced white carp meat</td>
<td>45</td>
</tr>
<tr>
<td>Pork fat</td>
<td>10</td>
</tr>
<tr>
<td>Dry demineralized whey</td>
<td>5</td>
</tr>
<tr>
<td>wheat flour</td>
<td>2</td>
</tr>
<tr>
<td>Aprored</td>
<td>3</td>
</tr>
<tr>
<td>XB Fiber</td>
<td>2</td>
</tr>
<tr>
<td>Egg melange</td>
<td>3</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
</tr>
<tr>
<td>Salt</td>
<td>1,5</td>
</tr>
<tr>
<td>NaNO₂</td>
<td>0,0075</td>
</tr>
<tr>
<td>Sugar</td>
<td>0,1</td>
</tr>
<tr>
<td>Pepper black</td>
<td>0,1</td>
</tr>
<tr>
<td>Coriander</td>
<td>0,05</td>
</tr>
<tr>
<td>Fresh garlic</td>
<td>0,2</td>
</tr>
</tbody>
</table>

The preparation of the samples was carried out in accordance with the technology for the preparation of minced meat bread with the addition of 20% water to the main raw material [38].

Minced duck meat is ground into a top with the grating orifices diameter 2-3 mm. After that minced meat of silver carp was added. At the same time, supporting materials are being
prepared. Coriander and ground black pepper are sifted to prevent large particles from being minced.

Raw meat is weighed according to the recipe and sent for processing on a cutter. All ingredients are mixed for 8-10 min. Firstly the Muscovy duck meat was added, then white carp meat, after some water and ice, salt, and processed for 3-5 minutes. Then the rest of the water and ice with fat was added, dry demineralized whey, rosemary or cranberry extract, spices and processed for another 5-6 minutes.

The molding of the products occurs in metallic forms. The formed breads are processed in a rotary oven at a temperature of 100-110°C for 2 hours to a temperature in the center of the product 68-72°C. After heat treatment, they are cooled to a temperature in the center of the product not higher than 8°C. The finished breads were stored for 6 days at +4°C.

**Lipid oxidation measurements (acid value, peroxide value, thiobarbituric acid reactive substances)**

The acid value was determined by the batch titration with sodium hydroxide in the concentration in the presence of fenolftalein alcohol solution [36]. 3-5 g of the investigated forcemeat was weighted in the conic retort with the ume of 150-200 cm³ with the error of no more than 0,001 g. The batch was heated on the water bath and after the addition of 50 cm³ of neutralized ether-alcohol mixture shaken. Then 3-5 drops of fenolftalein alcohol solution with the mass share of 1% were added. The received solution while shaking was titrated fast with potassium hydroxide solution with the molar concentration 0,1 mol/dm³ till the distinct rose coloration appeared and kept for 1 min. The acid number was calculated by the formula:

\[
X = \frac{(V \times K \times 5,61)}{m},
\]

where \(V\) – ume of potassium hydroxide solution, with the molar concentration 0,1 mol/dm³, used for titration; \(K\) – correction to alkali solution for recalculation on the distinct (0,1 mol/dm³) one; 5,61 – number of milligrams of potassium hydroxide, contained in 1 cm³ (0,1 mol/dm³) of solution; \(m\) – forcemeat batch mass, g.

The method of PV determination is based on the batch extraction by the mixture of chloroform and icy acetic acid and further titration by the sodium hyposulfite solution with the previously added starch solution [36].

0,8–1 g of a batch, weighted with accuracy of no more than 0,0002 g were placed in the conic retort with the stopper, melt on the water bath and 10 cm³ of chloroform and 10 cm³ of icy acetic acid were gently poured on the retort sides. 0,5 cm³ of saturated, freshly prepared potassium iodine solution was quickly added. The retort was closed with the stopper; the content was mixed by turning movements and put into the dark place for 3 minutes. Then 100 cm³ of distilled water with the previously added 1 cm³ of starch solution with the mass share of 1% was gently poured into the retort. After that it was titrated with sodium hyposulfite solution with the molar concentration of 0,01 mol/dm³ until the blue coloration disappeared.

To verify the clearness of reagents the control determination without a batch was realized. The peroxide number was calculated by the formula:

\[
X = \frac{[(V - V1) \times K \times 0,00127 \times 100]}{m},
\]

where \(V\) – ume of sodium hyposulfite solution with the molar concentration 0,01 mol/dm³, used for titration in the main experiment with the forcemeat batch, cm³; \(V1\) – ume of sodium hyposulfite solution (0,01 mol/dm³), used for titration in the control experiment without a forcemeat batch, cm³; \(K\) – coefficient of correction to sodium hyposulfite for recalculation on the distinct (0,01 mol/dm³) solution; 0,00127 – number of grams of iodine, equivalent to 1 cm³ (0,01 mol/dm³) of sodium hyposulfite; \(m\) – mass of the studied forcemeat batch, g.
TBARS was determined by measuring the coloration intensity of the mixture of the studied sample distillate and thiobarbituric acid solution (1:1) after 35 minutes on the water bath on the spectrophotocolorimeter “Spekol-11” (Germany) at the wave length 535 nm [37].

50 g of forcemeat batch were put into the porcelain mortar, 50 cm$^3$ of distilled water were measured by the glass cylinder, added to the mortar and ground with the pestle into the uniform mixture. The prepared sample was quantitatively transferred into Kjeldahl retort, remains were washed away from the mortar with 47.5 cm$^3$ of distilled water and then 2.5 cm$^3$ of hydrochloric acid were added. The distillation was carried out in Kjeldahl apparatus, collecting 50 cm$^3$ of distillate in the volumetric flask. 5 cm$^3$ of distillate were taken, poured into the retort with the fitted stopper. After the addition of 5 cm$^3$ of thiobaturic acid, the retort was closed with the fitted stopper and heated on the boiling water bath for 35 min.

Simultaneously the control experiment was held, using 5 cm$^3$ of distilled water instead of the distillate. Then the solutions were cooled in the cold running water for 10 min, and the optic density at the wave length of 535±10 nm as to the control solution was measured.

The thiobarbituric acid reactive species, mg of MA (malonic aldehyde) / kg of the product, was calculated by the formula:

\[ X = D \times 7.8, \]

(3)

where D – optic density of the solution; 7.8 – coefficient of proportional dependency of MA density on its concentration in the solution. This coefficient is a permanent value.

**Statistical analysis**

The absolute error of measurements was determined by Student criterion, the reliable interval \(P=0.95\), the number of repetitions in calculations – 3–4, the number of parallel tests of studied samples – 3.

Parallel to the determination of AV and PV in the test samples were determined values of activity of water \(a_w\).

The definition of \(a_w\) was performed with a portable high-speed instrument of model AquaLab 3TE with measurement accuracy up to±0.003 – according to the requirements [39].

**Results and discussion**

**Study of the plant extracts effect on the hydrolytic lipid oxidation of the meatcontaining breads**

The results of studies on the acid value dynamics during the storage of combined meatcontaining breads with the addition of plant extracts are shown in table 2.

Analysis of the table 2 shows that among the test samples the tendency to decrease the concentration of free fatty acids was observed on the first day of storage. At the end of the shelf life after 6 days AV in samples with rosemary extract reached from 1.05±0.04 mg KOH in sample 1 to 0.91±0.01 in the third sample, which is 36.19–36.36% less than the control. However, the samples containing CE had an acid value greater than the control. Thus, on day 6 of storage, the meatcontaining breads with the addition of cranberry extract samples 2 and 3 have an acid value level of 1.46-1.54, which is 2.1–7.7% higher than in the control.
Table 2

Dependence of the acid value on the concentration of the added extracts, mg KOH

<table>
<thead>
<tr>
<th>Sample</th>
<th>Storage, days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td></td>
</tr>
<tr>
<td>1 (Meatcontaining bread + RE 0.02 %)</td>
<td>1.24±0.01</td>
</tr>
<tr>
<td></td>
<td>1.29±0.03</td>
</tr>
<tr>
<td></td>
<td>1.43±0.08</td>
</tr>
<tr>
<td>2 (Meatcontaining bread + RE 0.04 %)</td>
<td>0.85±0.07</td>
</tr>
<tr>
<td></td>
<td>0.96±0.08</td>
</tr>
<tr>
<td></td>
<td>1.05±0.04</td>
</tr>
<tr>
<td>3 (Meatcontaining bread + RE 0.06 %)</td>
<td>0.74±0.07</td>
</tr>
<tr>
<td></td>
<td>0.79±0.01</td>
</tr>
<tr>
<td></td>
<td>0.97±0.07</td>
</tr>
<tr>
<td>4 (Meatcontaining bread + CE 0.02 %)</td>
<td>1.01±0.03</td>
</tr>
<tr>
<td></td>
<td>1.26±0.01</td>
</tr>
<tr>
<td></td>
<td>1.34±0.04</td>
</tr>
<tr>
<td>5 (Meatcontaining bread + CE 0.04 %)</td>
<td>1.02±0.04</td>
</tr>
<tr>
<td></td>
<td>1.40±0.03</td>
</tr>
<tr>
<td></td>
<td>1.46±0.02</td>
</tr>
<tr>
<td>6 (Meatcontaining bread + CE 0.06 %)</td>
<td>1.11±0.01</td>
</tr>
<tr>
<td></td>
<td>1.45±0.07</td>
</tr>
<tr>
<td></td>
<td>1.54±0.07</td>
</tr>
</tbody>
</table>

The obtained results indicate that the added rosemary extract inhibits fat hydrolysis in systems with combined lipid composition due to the high concentration of flavonoids. The most effectively rosemary extract inhibits the hydrolytic decomposition of acylglycerides at a concentration of 0.06%. Cranberry extract, does not have such effect.

Study of the plant extracts effect on the lipid peroxidation of the investigated meatcontaining breads

The results of the peroxide value dynamics in meatcontaining combined breads during the shelf life are shown in the Figure 1.

![Figure 1. Dependence of the peroxide value on the concentration of the added rosemary and cranberry extract, % J₂](image-url)
The addition of rosemary extract helps to slow down the oxidation processes, as evidenced by the Figure.

Among the experimental samples of combined bread PV increased more intensively in the control sample. The addition of rosemary extract at a concentration of 0.06% by weight of raw materials has the most stabilizing effect. PV in this sample at the end of the study period was 0.013±0.001% J₂, whereas in the control this parameter was 0.05±0.001% J₂, which is almost 4 times higher. This confirms the results of studies [40–42], which say that the most active components of rosemary extract are carnosol, carnosic acid, rosemary acid, are the powerful antioxidants.

The using of cranberry extract in the technology of combined bread also had a positive effect on the accumulation of primary oxidation products. Thus, at the beginning of the shelf life PV in the samples with CE was 0.02% J₂, which is almost identical with the control sample, but at the end of the storage period there was a tendency to decrease this indicator in the experimental samples. Thus, PV on the 6th day of storage in samples 4-5 was 0.02-0.025% J₂, which is 2-2.5 times less than the control. It can be argued that the flavonoids of cranberry extract bind to act as oxidant absorbers, preventing the accumulation of primary lipid oxidation products without participating in the inhibition of lipolysis.

Study of the plant extracts effect on the accumulation of secondary lipid oxidation products of the investigated meatcontaining breads

The antioxidant effect of the additives is observed in the accumulation of mono- and dialdehydes that react with 2-thiobarbituric acid [43]. To determine the concentration of secondary oxidation products on the last day of storage of bread samples, the thiobarbituric acid reactive substances was investigated, the results of the TBARS study are presented in Figure 2.

![Figure 2. The influence of bioflavonoids of the rosemary and cranberry extracts on the accumulation of secondary products of oxidizing the lipids of the meatcontaining loaves, mg MA/kg](image-url)
The thiobarbituric acid reactive substances are an indicator used to evaluate the extent of lipid oxidation during storage. Accumulation of TBARS is facilitated by the second stage of autooxidation, in which peroxides are oxidized to aldehydes and ketones. Lipid oxidation in meat systems, which have the main ingredient as pork, depends on time and temperature [44].

Analyzing the data in Figure 2, it can be argued that added rosemary extract inhibited the formation and accumulation of secondary lipid oxidation products during the storage of meat containing breads with duck meat and white carp.

Thus, at the end of the shelf life, TBARS in the samples with the addition of RE was 0.74-0.76 mg MA/kg of product, which is 17-20% lower than in the control sample of bread. The using of RE in the amount of 0.04 and 0.06% had the same effect. Adding of cranberry extract to the combined bread had an effect only in the sample with a concentration of 0.02% and TBARS in this case was 0.81 mg MA/kg, which is 9.88% lower than in the control sample.

In samples with a concentration of CE 0.04-0.06%, the accumulation of aldehydes and ketones as a result of lipid oxidation was at the same level as in the control sample. In the present study, TBARS is less than 1.0 during the entire study period, which is important because in large quantities the level of TBARS is toxic, carcinogenic and mutagenic [45].

Water activity studying of minced meat samples with cranberry extract and rosemary extract revealed that for all types of meat bread this Figure was within 0.966-0.973 units in minced meat and finished meat loaves. That is, these products contain a significant amount of moisture in the active phase, which prevents long-term storage of products without the use of substances that slow down the deterioration process.

Comparative results show that the effectiveness of rosemary extract is higher than of cranberry extract when added to duck and fish combined products. It should also be noted that the efficacy is directly proportional to the amount of extract applied.

Conclusions

1. Studies have confirmed the high antioxidant activity of rosemary extract and the effective inhibition of the lipid oxidation process in meat containing combined breads with Muscovy duck meat and white carp (Hypophthalmichthys molitrix).
2. Cranberry extract does not inhibit the hydrolysis of fat during storage of meat containing combined breads, and has little positive effect on the formation of primary oxidation products and the accumulation of secondary lipid oxidation products.
3. Adding of RE in the amount of 0.02–0.06% allows to slow down the hydrolytic oxidation of lipids by 36.19–36.36%.
4. The using of rosemary extract in concentrations of 0.02–0.06% by weight of minced meat helps to slow down the lipid peroxidation in meat containing breads, reducing the amount of peroxides almost four times.
5. The stabilization of lipid peroxidation in meat containing breads with Muscovy duck meat and minced meat of white carp has the effect of inhibiting the formation of secondary oxidation products at high values of aw. This fact is confirmed by the obtained results. The amount of aldehydes and ketones was the lowest at the end of the shelf life of bread with RE and was 0.74–0.76 mg MA/kg, which is 17–20% lower than in the control sample.
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Effect of hydrocolloids on properties of dough and quality of gluten-free bread enriched with whey protein concentrate

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Hydrocolloids
Corn
Rice
Flour

Abstract

Introduction. The effect of hydrocolloids (xanthan gum and guar gum) on dough properties and the quality of gluten-free bread from rice and corn flour enriched with whey protein concentrate was studied.

Materials and methods. For the preparation of the whey protein concentrate it was used a laboratory system with a removable flat membrane module, equipped with a 25 kDa polyacrylonitrile ultrafiltration membrane. Dough consistency was measured by degree of immersion, using automatic penetrometer.

Results and discussion. Based on the preliminary experiments (with 5, 10 and 15 %) it was found that the optimal quantity of whey protein concentrate was 10 %. That is why for the further experimental tests 10 % whey protein concentrate was added to control sample bread. Addition of higher quantities of xanthan gum resulted in weak dough consistency. Concerning the dough consistency it can be concluded that the addition of xanthan gum results in release of the dough, regardless of the quantity used. The best result was obtained when 1.5 % guar gum was added. Maximum increase in bread volume was obtained with 1.5 % guar gum. The specific volume of bread significantly improved with hydrocolloids addition. It was found that the control sample had a lower specific volume. The samples containing hydrocolloids had larger volume than the control. The addition of 1 % xanthan gum resulted in an increase in H/D index by 50 %, compared to the control sample. When 1.5 % guar gum was added, the highest results were obtained – the increase compared to the control sample was 100 %. Guar gum had greater influence on sensory properties of gluten-free bread from rice and corn flour than xanthan gum. Addition of 1.5 % guar gum led to the best results for almost all sensory properties (without the porosity and aftertaste). The results concerning porosity and aftertaste did not differ those obtained with the addition of 1 % guar gum. Addition of 1.5 % guar gum in formulation of gluten-free bread from rice and corn flour led to the highest volume, uniform crust and crumb color, with no rust and atypical shades. The flavor was pleasant and very well pronounced, evaluated by the panelists with 8 points, while the flavor of samples with xanthan gum had 3 points. The flavor was weaker when 1 % guar gum was used (5 points). The bread samples with guar gum were appreciated as more crisp, with a very pleasant taste and aftertaste.

Conclusions. For the production of gluten-free bread of rice and corn flour enriched with whey protein concentrate, the addition of 1.5 % guar gum is most appropriate.
Introduction

Worldwide, consumer interest for gluten-free products is increasing. According to Hill et al. [1], celiac disease is one of the most common lifelong disorders on a worldwide basis. It is an immune-mediated enteropathy triggered by the ingestion of gluten in genetically susceptible individuals and is characterized by a strong immune response to certain amino acid sequences found in the prolamin fractions of wheat, barley and rye [1, 2]. The removal of traditional food products – bread and bakery products prepared from gluten-containing crops (wheat, rye, barley, oats and triticale) from the menu of celiac disease requires them to be replaced by the other appropriate ones [3].

The demand of gluten-free products, especially bread is increasing as a result of the increase of celiac disease diagnosis at the recent stage [4]. This has encouraged extensive research for the development of gluten-free breads [5]. Production of high quality gluten-free bread is a big challenge due to the absence of gluten, which confers unique viscoelastic properties to dough. That’s why bread development without gluten has involved the use of diverse ingredients and additives with the purpose of imitating the viscoelastic properties of the gluten [6, 7, 8]. The addition of hydrocolloids or gums to gluten-free bread formulations is a promising alternative.

Lazaridou et al. [9] investigated the effect of hydrocolloids on dough rheology and quality of gluten-free bread with rice flour, corn starch and sodium caseinate. Hydrocolloids added in a quantity of 1 and 2 % were pectin, carboxymethylcellulose, agarose, xanthan, and oat β-glucan. The rheological dough properties with hydrocolloids carried out by farinograph and rheometer indicated that xanthan has the strongest effect on viscoelastic properties, leading to dough strengthening. Bread volume is increased by the addition of hydrocolloids, with the exception of xanthan gum.

Xanthan is the only microbial heteropolysaccharide that has hitherto achieved large-scale industrial production (xanthan gum or gum). The extracts of exopolysaccharide from different strains grown in depth in sugars (glucose, fructose, galactose, rhamnose, xylose, maltose, sucrose, lactose), organic acids, amino acids, polyols, industrial raw materials (molasses, hydrolyzed corn starch, acids, hydrolysates) are very different – from 2.8 to 35.0 g/ dm³ [3, 10, 11, 12]. According to some authors one of the advantages of the xanthan gum is that the quality of this bacterial product can be adjusted using different Xanthomonas strains and fermentation conditions [13]. Therefore, parameters such as temperature, pH, air flow rate, different Xanthomonas species and other sources can be used to improve xanthan gum yield and rheological properties.

Xanthan is an acidic polymer with a molecular weight of 2 – 50.106 D, containing O-glucose, O-mannose, D-glucuronic acid, acetyl groups and pyruvate in a different quantity [14, 15]. The specific structure determines his unique physical and rheological properties [10, 14, 15]: water solubility, very high viscosity at low concentrations, high pseudo plasticity, excellent heat resistance and pH stability, solubility in acids and bases, compatibility with ethanol, methanol, isopropanol and acetone (up to 50–60%), sodium alginate, starch and most salts, stability against microorganisms and enzymes (cellulases, amylases, pectinases). Xanthan has a very wide application in industry, agriculture and medicine [10, 16].

Guar gum is a substance with thickened and stabilized properties, used in various industries, mainly in the food industry. Guar gum is an exo-polysaccharide composed of manganese and mannose. Guar gum has the ability to withstand temperatures of 80 °C for 5 minutes. It is a better emulsifier because of the higher galactose content. It forms a non-ionic hydrocolloid with water. Guar gum is used as a thickening agent in food industry. It is also used as a substitute for replacing wheat flour in bakery products, because it does not
contain gluten. It reduces serum cholesterol and lower blood sugar levels. Guar gum is characterized by good biological activity and is capable of acting as an anticoagulant and it also has anticancer and antiviral properties, helping to remove heavy metals from the body [17].

Numerous other fabric forming substances useful in bread-making are known in the literature. No complete data on effect of xanthan and guar gum on the dough properties and gluten-free bread quality were found.

Therefore, the aim of the present study is to investigate the effect of hydrocolloids (xanthan and guar gum) on some dough properties and the quality of gluten-free bread from rice and corn flour enriched with whey protein concentrate.

Materials and methods

Materials

Raw materials: a standard commercial rice flour with physico-chemical properties: moisture – 13.3 %, titrable acidity – 0.4 °H; a standard commercial corn flour with physico-chemical properties: moisture – 12.2 %, titrable acidity – 3.0 °H;


Methods

Method for ultrafiltration

For the preparation of the whey protein concentrate, a laboratory system with a removable flat membrane module, equipped with a 25 kDa polyacrylonitrile ultrafiltration membrane, shown in Figure 1 [18], was used.

Figure 1. Scheme of a laboratory system with plate and frame membrane module:
1 – valve; 2 – manometer (0–5 MPa); 3 – valve; 4 – manometer (0–0.6 MPa);
5 – replaceable plate and frame membrane module; 6 – tank; 7 – pipeline;
8 – manometer (0–0.8 MPa); 9 – valve; 10 – manometer (0–15 MPa); 11 – pipeline;
12 – pump; 13 – valve; 14 – pipeline; 15 – pipeline; 16 – tank.
This system was equipped with: a 2500 cm$^2$ plate and frame membrane module, a high-pressure triple pump (up to 15 MPa) with a feed flow rate of 330 dm$^3$/h, a pipeline system with two manometers (0-15 MPa) for the inlet and outlet pressure, a special pressure regulating valve.

The ultrafiltration process was carried out with defatted whey from white brined cheese under the following operating conditions: working pressure – 0.4 MPa, working temperature – 20 °C, volume reduction factor – 6, feed flow rate of 330 dm$^3$/h. The whey protein concentrate obtained was used to enrich gluten-free bread.

**Dough and bread formulation**

The bread formulation composition [19] is presented in table 1.

**Table 1**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Control sample (CS)</th>
<th>Sample with 1 % xanthan gum</th>
<th>Sample with 1.5 % xanthan gum</th>
<th>Sample with 1 % guar gum</th>
<th>Sample with 1.5 % guar gum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice flour, g</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>Corn flour, g</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Yeast, g</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Salt, g</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>Water, cm$^3$</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>Margarine, g</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Sugar, g</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Whey concentrate, g</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Xanthan gum, g</td>
<td>–</td>
<td>5.0</td>
<td>7.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Guar gum, g</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>5.0</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Dough preparation is made with two phases with an initial temperature of 29 – 30 °C in kneading machine (Labomix 1000, Hungary), obtained from rice flour, water, yeast and sugar, rising time – 90 minutes. Preliminary infusion of corn flour was applied, then it was cooled and the main dough was prepared. It included 10 % whey protein concentrate, corn flour, margarine, other yeast, salt and hydrocolloids. Mix the dough to obtain a homogeneous mass. The dough rests for 40 minutes, divided and forms on a floor and form bread and final fermentation — 60 minutes at 35 °C (Tecnopast CRN 45–12, Novacel ROVIMPEX Novaledo, Italy). After the final fermentation, the pieces of dough were put into an electric oven (Salva 25, Spain) pre-heated to 200 – 220 °C. The baking time was 24 min for form bread and 16 min. After baking, the bread was allowed to cool down for 3 h at room temperature [19].

**Methods for assessment of dough properties and bread quality**

**Dough consistency by degree of immersion (K$\sigma$), P.U.** It determines the degree of immersion of a calibrated body placed in a bushing of an automatic penetrometer AP-4/2
(Germany). 40 g of dough was prepared and then divided into pieces of 13 g. Each piece of dough was placed in a bush and placed in a laboratory thermostat at 35 °C for 60 min. Then, on a penetrometer, the immersion of the body, which lasts 5 seconds, was determined automatically [19].

**Loaf volume and H/D index (ratio of height to diameter) of bread.** The loaf volume of bread samples was measured 180 min after the loaves were removed from the oven by the seed displacement method using bread volumeter (Sadkiewicz Instruments, Bydgoszcz, Poland) [19].

The height and diameter of the bread samples were measured in 10 replicates (at different positions of the bread samples) each by using digital caliper S301 (Hedue GmbH, Mönchengladbach, Germany), and the average values were determined. On the basis of the results the H/ D index (the ratio of height to diameter) of bread was calculated [19].

**Sensory evaluation.** Sensory evaluation of bread was performed according to ISO 13299:2016 “Sensory analysis. Methodology. General guidance for establishing a sensory profile” [20]. The terms and definitions given in ISO 5492:2008 [21] were applied. Sensory properties of bread were evaluated by a trained sensory panel consisted of 10 panelists (22 – 43 years old), who evaluated the bread’s quality. Sensory analysis of bread was performed 3 h after the loaves were removed from the oven. Panelists were asked to evaluate the following indicators: volume, crust color, crumb color, odor, mastication, porosity, taste and aftertaste. The following conditions were provided: controlled preparation and presentation of the samples, comfortable conditions for consuming the products and for questioning the panelists, and absence of communication (verbal and non-verbal) between them, guaranteeing independent responses. The samples were sliced (slices about 1.5 cm thick) and served in white plates with codes. Plain water was used for mouth rinsing before and after each sample testing. The experimental data were statistically processed using the SPSS statistical package version 17.

**Results and discussion**

Based on the preliminary experiments (with 5, 10 and 15 %) it was found that the optimal quantity of whey protein concentrate was 10 %. That is why for the further experimental tests 10 % whey protein concentrate was added to control sample bread.

When wheat flour is used, the gluten structure makes it possible to attach all the components to the dough, retaining a portion of CO₂ that ensures stability of the system. With gluten-free products, instability of the system and impossibility of gas retention is observed. Gluten-free types of flour cannot participate in a baking process alone, due to the fact that a loose, unrelated and insufficiently developed structure of crumb is produced. For this purpose, hydrocolloids (xanthan and guar gum) should be used. According to Ferrero et al. [17] hydrocolloids can positively or negatively modify dough rheology, which depends on their structure, concentration and the interactions with other components.

**Effect of hydrocolloids (xanthan gum and guar gum) on dough consistency**

The effect of hydrocolloid addition on dough consistence is summarized in Figure 2. When the difference between the experimentally determined results before and after resting increased, the consistency of the dough was weaker.
The initial dough consistency of the control sample is 15 P.U. and after resting (1 hour) it changed insignificantly, reaching 19 P.U. Li & Nie [22] point out that those hydrocolloids were used in gluten-free breads to improve dough handling properties and to enhance the quality of bread. They were capable of controlling the rheology and texture of aqueous systems throughout the stabilization of emulsions, foams and suspensions. The initial immersion of dough with the addition of 1.0 and 1.5% xanthan gum (xanthan gum) did not differ significantly compared to the control sample – results 11 P.U. and 12 P.U. After resting (1 hour), the immersion rate of the samples with xanthan gum changed, more significantly by addition of 1.5% (9 P.U.). It was found that the addition of higher quantities of xanthan gum resulted in weak dough consistency. This is probably due to poorly formed bonds on the part of the added hydrocolloid, which results in insufficient bonding of the dough structure.

The initial consistency of dough was significantly higher than the control sample by addition of guar gum (1.0 %). Upon addition of 1.5 % guar gum, the slightest change in the immersion rate (2.8 P.U.) was achieved. This reveals better structural properties and dough consistency. Capriles & Areas [23] point out, that some hydrocolloids (including guar gum) improved dough development and gas retention through an increase in viscosity, producing gluten-free breads with higher baking and quality properties. Demirkesen et al. [6] also reported that the inclusion of guar gum into rice bread formulation led to increased viscoelastic moduli of dough.

It can be concluded that the incorporation of xanthan gum results in release of the dough, regardless of the quantity used. The best dough consistency was obtained with the addition of 1.5% guar gum.

**Effect of hydrocolloids (xanthan gum and guar gum) on bread volume and H/D index**

The effect of hydrocolloids on bread volume is shown in Figure 3.
Figure 3. Effect of hydrocolloids on the volume of gluten-free bread made of rice and corn flour enriched with whey protein concentrate

The specific volume of bread significantly improved with hydrocolloids addition. It was found (fig. 3) that the control sample had a lower specific volume. The samples containing hydrocolloids had larger volume than the control. The control sample volume was 180 cm$^3$. Addition of 1% xanthan gum resulted in an increased volume by 29.7% compared to the control sample. Increasing of the quantity hydrocolloid, bread volume decreased. Experimental results for samples containing 1.5% xanthan gum and 1.0% guar gum were almost identical. Most significant increase in bread volume was obtained with 1.5% guar gum – by 75% compared to the control sample. These results are supported by those obtained by other authors. Ferrero et al. [17] also reported an improving of bread volume and crumb porosity due to the use of hydrocolloids in bread formulation. Hejrani et al. [24] investigated the specific volume of bread samples prepared with the addition of 0.4% and 0.8% of guar gum and xanthan gum respectively. It was found, that the samples containing hydrocolloids had greater volume. Gambus et al. reported that all loaves with xanthan gum displayed better volume in comparison to standard sample [25].

The results obtained for H/D index of gluten-free bread enriched with whey protein concentrate and hydrocolloids are presented in Figure 4.

From the results obtained for H/D index of gluten-free bread enriched with whey protein concentrate with hydrocolloids, the data presented above were confirmed. The addition of hydrocolloids changes the viscoelastic properties of dough and gives additional strength to the gas cells which leads to increased gas retention. The addition of 1% xanthan gum resulted in an increase in H/D index by 50%, compared to the control sample. When 1.5% guar gum was added, the highest result was obtained – the increase compared to the control sample was 100%.

Effect of hydrocolloids (xanthan gum and guar gum) on sensory properties of gluten-free bread

Sensory evaluation of gluten-free bread samples made of rice and corn flour enriched with whey protein concentrate containing different quantities of guar gum and xanthan gum was performed by 10 trained panelists (Figure 5).
Figure 4. Effect of hydrocolloids on H/D index of gluten-free bread made of rice and corn flour enriched with whey protein concentrate.

Figure 5. Effect of hydrocolloids on the sensory profile of gluten-free bread made of rice and corn flour enriched with whey protein concentrate.
There was a positive effect of hydrocolloids on all sensory indicators. Guar gum had greater influence on sensory properties of gluten-free bread from rice and corn flour than xanthan gum. The addition of xanthan gum and guar gum increased bread volume, compared to the control sample. The most significant effect was obtained with the addition of 1.5% guar gum. Addition of 1.5% xanthan gum led to the most unsatisfactory results. For most of the indicators, points judged by the panelists were lower than those for the control sample and the samples with guar gum. Addition of 1.5% guar gum in formulation of gluten-free bread from rice and corn flour led to the highest volume, uniform crust and crumb color, with no rust and atypical shades. According to Sabanis et Tzia sensory evaluation by a trained panel revealed a preference for bread containing 1.5% hydroxypropylmethylcellulose because of its loaf volume, appearance and firmness characteristics [26]. The flavor was pleasant and very well pronounced, evaluated by the panelists with 8 points, while the flavor of samples with xanthan gum had 3 points. The flavor was weaker when 1% guar gum was used (5 points). The bread samples with guar gum were appreciated as more crisp, with a very pleasant taste and aftertaste. It was concluded, that the use of guar gum increased sensory score of the samples, as the improvement in properties being more pronounced when 1.5% hydrocolloid was used. Gambus et al. also reported that the use of guar gum and pectin mixture in 1:1 ratio reduce gumminess and chewiness of guar bread and too high crispiness and low resilience of pectin bread [27]. Only two indicators make an exception – the results concerning porosity and aftertaste did not differ those obtained with the addition of 1% guar gum.

Gambus et al. reported that irrespective of the share of xanthan gum, its addition to the dough led to better cohesiveness of bread on the day of baking. For these authors’ higher quantities of xanthan gum in mixture of hydrocolloids decreased bread hardness on the day of baking and after 72 hours of storage [25].

**Conclusion**

Results obtained from this study reveal that the use of hydrocolloids in gluten-free bread formulation is appropriate. The addition of xanthan gum resulted in the dough being released, regardless of the quantity used. When 1.5% guar gum was added, an optimal dough consistency is achieved. When using 1.5% guar gum, the highest results for bread volume and H/D index were obtained. With regard to the sensory evaluation, samples prepared with GG in quantities of 1.0 and 1.5% were considered by the panelists as more crisp and obtained higher grades for taste and aftertaste. Most unsatisfactory were the results for sensory quality of bread prepared with 1.5% xanthan gum – uneven crust color, less pronounced aroma and taste, poor mastication, under-developed porosity. As a result of the research carried out, it was found that for the production of gluten-free bread of rice and corn flour enriched with whey protein concentrate, the addition of 1.5% guar gum is most appropriate.

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Chemical aspects of the composition of industrial hemp seed products

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Abstract

Introduction. The purpose of the paper is to study theoretical and experimental aspects of the chemical composition and quality of hemp seed products, including oxidation processes in oils, seeds and processing products.

Materials and methods. Research materials are industrial hemp seeds of «Hlesia» variety, pressed oil and oil compositions, hemp seeds kernel. The quality of the investigated materials was evaluated according to standard and industry methods and to Codex Alimentarius.

Results and discussion. The obtained hemp oils by the content of fatty acids, phospholipids, vitamins A and E have high biological value, and by the content of tocopherols significantly outweigh sunflower, sesame and amaranth oils. The sample of MM60 pressed oil is preferred for antioxidant resistance. The ratio of essential fatty acids is close to ideal: Omega-6 and Omega-3 as 3.0:1 – 3.7:1, while in linseed oil – 1:3.6. Hemp oil also contains biologically valuable gamma-linolenic acid. Spectrophotometric method confirmed the presence of carotenoids and chlorophylls in pressed hemp oil. Vitamin A content in oil is 78 mg/kg, vitamin E (total) – 562.8 mg/kg. Hemp oil is better stored at 8±2 °C without light access by chemical indicators. The obtained hemp oil and oil compositions are of good quality. The composition with a peroxide and acid value of less than 1 and a higher oil output is preferred. The quality of hemp seeds (without the shell) improves compared to the output seeds. The content of oil and protein increased 1.5 times, macro and microelements: phosphorus 1.5 times, ferro 1.25 times, zinc and cobalt 2 times. Hemp seeds without the shell have a high content of essential amino acids and a high content of lysine, which is usually deficient.

Conclusions. It is recommended the hemp oil and hemp seeds kernel in the production of functional food.
Introduction

The qualitative and quantitative composition of lipids and related compounds of oil-protein or protein-oil raw materials varies on a long way from the field, during transportation and storage of seeds and its complex processing, taking into account various chemical and technological influences. The chemical composition of lipids of pressed oils and oilcake determines their quality, ecological and economic efficiency, functional-technological and special properties and biological value for consumers [1–4].

The range of the use of hemp products in global economy is steadily expanding, and industrial technologies for the ingredients production are being developed for use in innovative industries. Cannabis acquires the status of strategic culture, the cultivation, and processing of which is a priority for economic policies of governments in many developed countries and private business [5]. Cannabis sativa seed oil has both medicinal and industrial uses [6].

In the oil and industrial hemp seeds, the ratio of unsaturated fatty acids Omega-3 and Omega-6 is balanced for human health and in line with the recommendations of the World Health Organization (WHO). The world's hemp seed producers position it as a unique source of protein [7]. Further improvements of oilseeds complex processing technology, including the identification of chemical aspects of the composition and hemp seeds quality, oils, composite oils, and products on their base, will ensure the production of competitive functional products in the systemic health concept [8–11].

The purpose of the research is to study the theoretical and experimental aspects of the chemical composition and quality of hemp seed products.

Literature analysis

Chemical and biochemical aspects of the oxidation and scorching of acylglycerols in oilseeds and in vegetable oils. Acylglycerols in vegetable oils are unstable during storage. They are the most labile components of fat and raw materials (seeds, intermediates) and finished products. The instability of oils and fats is a consequence of the peculiarities of their chemical structure. The conversion of triacylglycerols can be divided into reactions occurring with the participation of ester groups and reactions occurring with the participation of hydrocarbon radicals. Oxidation of lipids and oils is based on their interaction with the oxygen of air; the rate of their oxidation is individual and depends on many factors. The substrates of this reaction are generally unsaturated fatty acids. The lipids of tissues of oil raw materials, especially at the beginning of storage are subject to biochemical changes [1, 2, 12, 13].

Triacylglycerols of unsaturated fatty acids are oxidized more quickly than saturated fatty acids. Free fatty acids are oxidized faster than in the composition of triacylglycerols. Fatty acid oxidation is a complex multi-stage process. The ability to oxidize increases with unsaturation and decreases as carbon atoms in fatty acid molecules increase.

Saturated fatty acids are oxidized only at temperatures above 60 °C, while polyunsaturated fatty acids are oxidized even in the frozen state. Similar oxidation reactions are possible in other unsaturated substrates: phospholipids, hydrocarbons, squalene, vitamin A and carotenoids, vitamin E. It should be emphasized that vitamin E as a natural antioxidant delays lipid oxidation and the formation of volatile compounds.

Oxygen absorption is divided into three periods: induction, monomolecular (at the end of this period, a taste of rancidity appears), finally, bimolecular when the intensity of oxygen absorption increases sharply. The spontaneous self-oxidation of lipids (oils) always occurs,
even when stored in a cooled state, protected from light, in non-metallic containers. This is because there are always molecules with energy higher than the average in the system. The rate of oxidation depends on the content of the antioxidant system. Very often, a decrease in the rate of initiation reactions is a limiting factor in lipid oxidation. [1].

According to [14], the oxidative stability of flax and hemp oils, as well as their compositions devoid of minor components, was evaluated in the dark at 60 °C and under fluorescent light at 27 °C. Several analytical methods have been used to evaluate the oxidative stability of oils. Oil extracts for the absorption of 1,1-diphenyl-2-picrylhydrazyl (DPPH) and their total phenolic content were also investigated. The results showed that the bioactive components of these edible oils play an important role in their oxidative stability. However, the composition of phenolic antioxidants and the total content of tocopherols in oil, as well as the type of pigments present, contribute to their stability. Flaxseed oil and hemp oil compositions that were not treated were more stable. In addition, hemp oil had higher oxidative stability than untreated linseed, as evidenced by the purification of the DPPH radical and the total phenol content.

In paper [15], 10 different polar solvent systems were investigated for 40 samples of kernels and cases of two varieties of hemp (Bama and Yunma No. 1). The capacity of the extracts for radical extraction was evaluated using 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 2,2′-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) assays. The total content of phenols was determined using the phenolic reagent Folin-Siocalteu. Correlation analysis showed that the antioxidants in hemp belong to the phenolic DPPH analysis and are suitable for evaluating the activity of radical extraction. Two compounds having predominant antiradical activity were isolated from hemp extract using macroporous resin, LH-20 gel permeation chromatography, and high performance liquid chromatography. The compounds were identified as N-trans-caffeoyltyramine and cannabisin B (resolution of mass spectra, nuclear magnetic resonance spectra, and ultraviolet data). The two compounds exhibited significant high DPPH purification activity and a protective effect against in vitro oxidation of low-density human lipoprotein compared to flaxseed, grape and soy extracts. This suggests that hemp extract is a potential source of natural antioxidants.

In work [16], the organoleptic characteristics of hemp oil samples were investigated, and the comparative analysis of the physicochemical parameters and the fatty acid composition of the oil from organic and conversion hemp seeds were performed.

The quality of 14 oils sold in Europe was evaluated by the author’s team research [17] (2018). Deep chemical profiling of cannabinoids, terpenes, and oxidation products was performed using gas chromatography with mass spectrometry and high performance liquid chromatography-Q-Exactive-Orbitrap-MS to improve knowledge about the characteristics of cannabinoids oils. Nine of the 14 samples tested had concentrations that differed markedly from the claimed amount, and the remaining five had optimal cannabinoids. The results indicate the broad variability of the cannabinoid profile, which justifies the need for strict and standardized rules. In addition, the terpenes can serve as an indicator of the quality of hemp varieties, while the profile of lipid oxidation products can help to evaluate the stability of the oil used as a medium for cannabinoid-rich extracts. This is fundamental to consumer safety since cannabinoid preparations in oil are also used for therapeutic purposes, regardless of whether they are registered as food supplements.

Thus, the problem of lipid oxidation (including peroxides) is associated with the formation of volatile compounds that can limit the storage time of raw materials, affect the process, storage period, quality and safety of oil-containing products.
Chemical and technological aspects of preparation and processing of industrial hemp seeds. New Ukrainian varieties of hemp Viktoriia, Hliana and Nika do not contain tetrahydrocannabinol and have been listed in the State Register since 2011 [18]. This contributes to the development of production and processing of industrial hemp seeds.

According to paper [19], the quality of processing of domestic industrial hemp seeds must be ensured at the stages of harvesting, cleaning, drying, and storage.

In Canada, an approved seed composition of ten industrial hemp varieties is used [20]. Canada is the largest producer of hemp seeds and has been exporting its consignments to EU and US countries for a long time. The area of hemp seed production in Canada is much larger than in France and ten times larger than in Chile, the Netherlands or South Korea. Hemp is also grown in Italy, Serbia, Montenegro, Poland, Hungary, Belarus, India, Iran, Turkey, and other countries [21].

Since 2019, twelve varieties of hemp have been listed in the «State Register of Plant Varieties Suitable for Distribution in Ukraine» [22]. Hemp seeds grown in Ukraine contain on average, 30–35% of lipids, 17–25% of proteins, 14–27 % of fiber, 2.5–7 % of crude ash, non-nitrogenous extractives 14–27 % [23].

The main products of industrial hemp seed processing in Ukraine are oil, flour, bran, and protein. Also halva, salt, and manna are made from hemp seeds. In the world, hemp and their components are used for the manufacture of products, preparations and consumer goods [24]. The health effect of the use of cannabis seeds in food is a scientifically sound fact [25].

Hemp oil contains a unique amount of unsaturated fatty acids compared to known vegetable oils. In the oil of hemp seeds the ratio of essential fatty acids is close to the ideal of the WHO recommendations: Omega-3 and Omega-6 as 1:3, while in linseed oil – 4:1, in rapeseed – 1:2, in soybean – 1:7 [26].

The fatty acid composition and oxidizing ability of oils from different varieties of hemp seeds depend on different localization and region [27]. Therapeutic, preventive, cosmetic effects of using hemp oil are scientifically proven facts. The inclusion of hemp oil in the daily diet can eliminate the broad spectrum of diseases or prevent their development [28].

Oil and seeds, in addition to their nutritional value, have shown a positive effect on the normalization of cholesterol, triacylglycerols, blood pressure, treatment of dermatitis. In addition, hemp oil can be used as an integrator for the preparation of traditional medicines [29].

New Zealand oils obtained by cold-pressed hemp, flax, and rapeseed material were analyzed for the compositions of fatty acids, tocopherols, β-carotene, chlorophyll, total phenols, flavonoids, color, quality, melting and crystallization characteristics. The dominant fatty acid of canola, hemp and linseed oil was oleic (57.0±0.0 %), linoleic (55.7±0.3 %) and linolenic acid (58.7±1.2 %), respectively (p < 0.05). Hemp seed oil had the highest content of tocopherol, flavonoid, and phenolic acid. A significant difference in the color of the oils (p < 0.05) was found due to the chlorophyll content of the oil. All oils had low moisture content and volatile matter, non-volatile substances and free fatty acids. The values of peroxide, p-anisidine, conjugated dienoic acid, iodine, and specific extraction of cold-pressed oil at 232 and 270 nm were within the limits allowed by the general rules [30].

To increase the shelf life and maintain the optimum balance of the most essential unsaturated fatty acids, 2:1:3 and 3:1:4 flax, mustard and hemp oils are recommended [31].

In paper [32], secondary metabolites of hemp seeds were studied to identify bioactive compounds that could contribute to their health benefits. Four new lignanamides have been isolated. Their structures were first identified on the basis of nuclear magnetic resonance, gas chromatography with mass spectrometry, ultraviolet and infrared radiation, as well as in
comparison with the literature. Lignanamides 2, 7 and 9 – 14 showed good antioxidant activity, among which 7, 10 and 13 also inhibited acetylcholine esterase in vitro. Newly identified compounds are added to the diversity of the composition of hemp seeds, and bioassays suggest that hemp seeds, with lignanamides as nutrients, can be a good source of bioactive and protective compounds.

In recent years, the use of by-products in the production of hemp oil, such as antioxidants, proteins, essential amino acids, and dietary fiber has been increasingly emphasized in the food industry [33–35].

In the process of industrial hemp seeds processing when extracting oil (lipids) simultaneously the oilcake is received. Depending on extraction method, the oilcake contains protein, oil, polyunsaturated fatty acids, phospholipids, carotene, phytosterols, micro and macronutrients, cellulose, etc. [10, 16], which are important and contribute to the prevention and recovery of the organism, in particular in the systemic health concept (KTIOL® system) [11].

Based on the analytical review of scientific and technical information, it is found that the discovery of new theoretical, scientific, innovative and practical knowledge regarding the complex processing of industrial hemp seeds, including Ukrainian breeding, into functional foods, supplements, and preparations in the systemic health concept is fundamental, environmental, economic, social and gerontological problem.

**Materials and methods**

**Materials**

The object of study is the chemical aspects of the technology of industrial hemp seeds complex processing.

Research materials are industrial hemp seeds of Ukrainian breeding, in particular, the «Hlesiia» variety, press oil and oil compositions, collapsed hemp seeds. The distinctive feature of this variety is the lack of tetrahydrocannabinol.

Samples of hemp oil and oil compositions were obtained using the press method: P250 oil on a screw press of PS 250 [16]; MM60 oil on MMS-60 auger press [16]; KTIOL-LK oil and oil compositions on the LPS 5 auger press [1]. Quality indicators, in particular chemical, physical and organoleptic of the investigated materials were evaluated according to standard and industry methods and to Codex Alimentarius [1, 16].

**Determination of the fatty acid composition of press oil**

**Preparation of prototypes.** Samples were prepared as follows [1]: a sample of oil (2 drops) was dissolved in 2 ml of hexane in a test tube. 100 μl of sodium methylate solution in methanol at a concentration of 2 mol/dm³ was added by pipette and stirred for 2 min. Then 1 ml of dimethyl carbonate was added, shaken for 2 min, the mixture was brought to the mark with distilled water. The top layer containing fatty acid methyl esters was further separated. The top layer was collected by micropipette and filtered through anhydrous sodium sulfate.

**The procedure for conducting research.** The volume of the injected samples is 1-2 μl. «Supelco» fatty acid of methyl esters was used as external standards. The identification of fatty acids was performed by comparing their retention time with known samples.
Description of methods and installations. The fatty acid composition of hemp oil was determined by gas chromatography [1]. Detection of fatty acid methyl esters was performed on an Agilent 7890 gas chromatograph (USA). The length of the chromatographic column is 50 mm; the inner diameter is 0.22 mm. The temperatures of the evaporator, the detector, and the thermostat were respectively 250, 250 and 150 °C.

Processing of research results. The fatty acid content was calculated as a percentage of their total. Chromatogram registration and processing were performed using HP ChemStation software.

Determination of the presence of hemp oil pigments

Preparation of prototypes. Hemp oil solution in hexane concentration of 10 mg/ml was prepared in the ultraviolet domain, and in the visible domain of 40 mg/ml to determine the absorption spectra of hemp oil solutions [1].

The procedure for conducting research. To determine the absorption spectra of hemp oil solutions in the ultraviolet domain, studies were performed in quartz cuvettes 2 mm thick and 10 mm in the visible domain [1].

Description of methods and installations. The presence of hemp oil pigments was determined on a SPECORD M40 spectrometer (Germany), which is a controlled micro-computer, a two-beam instrument for measuring transmission and absorption in the ultraviolet and visible domains of the spectrum. The instrument allows determining the transmittance, extinction or sample concentration as a function of wave number or wavelength.

The SPECORD M40 spectrophotometer contains two radiation sources: the DZE/I deuterium lamp for the ultraviolet domain (185 – 360 nm) and the halogen lamp 6V, 20W for the visible spectrum (320 – 900 nm). Control of all functions of the device is carried out through a micro-computer.

Processing of research results. The SPECORD M40 is coupled to a managed recorder computing device for spectrum imaging.

Determination of the amino acid composition of the original and collapsed industrial hemp seeds

Preparation of prototypes. Fine-grained cation exchanger (resin) is used for the separation of amino acids, which is a copolymer of styrene and divinylbenzene of spherical form with the functional group -SO\textsubscript{3}-. The hydrolysis method with hydrochloric acid was used to prepare the samples.

Procedure for conducting research. To ensure separation of amino acids mixture on the column, the cation exchanger was pre-equilibrated with a lithium citrate buffer solution. When applied to a column of amino acids mixture at pH 2.2 molecules of amino acids were attracted by ionic forces to the sulfo group of the resin with its positively charged amino group and squeezed ions – Li\textsuperscript{+}, distributed along the column depending on the size of the positive charge. The basic amino acids lysine, arginine, and histidine have the highest positive charge, so they immediately and firmly bind to the resin. Acid amino acids glutamic and asparagine have the least positive charge, so they passed through the entire column and connected with the resin last. Next, the elution (extraction) of amino acids took place under certain conditions: at high speed, at high pressure and temperature, and using five stages of eluent change. The sequence of the release of individual amino acids from the chromatographic column was determined not only by the properties of the cation exchanger.
but by the composition and temperature of the eluent. For the registration of amino acids in eluent, the detection method of ninhydrin was used.

**Description of methods and installations.** The quantitative amino acid composition of the original and collapsed industrial hemp seeds was determined by ion-exchange liquid-column chromatography on an automatic T 339 amino acid analyzer (Czech Republic).

**Processing of research results.** To calculate the number of amino acids in the test sample, a standard mixture of amino acids with a known concentration of each amino acid was applied to the amino acid analyzer column previously. The peak area of each amino acid was calculated on the chromatogram. The number of micromoles of each amino acid \((X_1)\) in the solution under study was calculated by the formula:

\[
X_1 = \frac{S_1}{S_0},
\]

where \(S_1\) is the peak area (or height) of the amino acid in the sample;

\(S_0\) is the peak area (or height) of the same amino acid in a solution of amino acids standard mixture, corresponding to 1 micromole of the number of each amino acid.

**Results and discussion**

**Quality indicators of hemp pressed oil**

In order to preserve the biological value of hemp oil in technology, the method of seed pressing is used [1, 16]. The technology of hemp oil differs from other oil crops in that they do not use pre-wet-heat treatment of the material. This is due to the type of press, the technological parameters (conditions) of the press, the output and the antioxidant resistance of hemp oil. Seeds of industrial hemp by moisture content and purity must comply with the regulations in force as for seeds to be stored [19].

Quality indicators of pressed filtered hemp oil are presented in Table 1.

<table>
<thead>
<tr>
<th>№</th>
<th>Indicators</th>
<th>Sample of oil P 250</th>
<th>Sample of oil MM60</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Peroxide number, ½ O mmol/kg</td>
<td>14.3±0.5</td>
<td>8.6±0.3</td>
</tr>
<tr>
<td>2</td>
<td>Acid number, mg KOH/g</td>
<td>2.6±0.09</td>
<td>1.6±0.08</td>
</tr>
<tr>
<td>3</td>
<td>Moisture and volatile matter content,%</td>
<td>0.1±0.003</td>
<td>0.2±0.005</td>
</tr>
<tr>
<td>4</td>
<td>Content of low-fat impurities,%</td>
<td>0.1±0.003</td>
<td>0.1±0.003</td>
</tr>
<tr>
<td>5</td>
<td>The content of phospholipids, mg/kg, in terms of stearooleoelcitin,%</td>
<td>88.5±2.6</td>
<td>69.3±2.1</td>
</tr>
<tr>
<td>6</td>
<td>Total ash content,%</td>
<td>0.1±0.05</td>
<td>0.1±0.05</td>
</tr>
<tr>
<td>7</td>
<td>Iodine number, g J/100g</td>
<td>158.5±1.6</td>
<td>152.0±1.5</td>
</tr>
<tr>
<td>8</td>
<td>Vitamin content, mg/kg:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>78.0</td>
<td>82.0</td>
</tr>
<tr>
<td></td>
<td>E,</td>
<td>562.8</td>
<td>582.2</td>
</tr>
<tr>
<td></td>
<td>including:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\alpha)-tocopherol</td>
<td>234.0</td>
<td>246.2</td>
</tr>
<tr>
<td></td>
<td>(\beta)-Tocopherol + (\gamma)-Tocopherol</td>
<td>316.0</td>
<td>322.0</td>
</tr>
<tr>
<td></td>
<td>(\delta)-tocopherol</td>
<td>12.8</td>
<td>14.0</td>
</tr>
</tbody>
</table>
From Table 1 data analysis it follows that the content of fatty acids, phospholipids, vitamins A and E (tocopherols), the degree of their unsaturation the obtained pressed oils have a high biological value. For antioxidant resistance, a sample of MM60 pressed oil is preferred. In further studies of organic seeds of industrial hemp new varieties, it is necessary to clarify the influence of technological equipment and technological conditions of conducting the pressing process on the composition and quality of hemp oil.

**Fatty acid analysis of pressed oil**

To confirm data on hemp oil biological value from the seeds of the Ukrainian breeding of «Hlesiia» variety in comparison with linseed oil, their fatty acid composition was analyzed. The research results of fatty acids content, the content of which is ≥ 0.5%, are given in Table 2.

**Table 2**

<table>
<thead>
<tr>
<th>№</th>
<th>Fatty acid</th>
<th>Acid content, %</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sample of oil P 250</td>
<td>Sample of oil MM60</td>
<td>Flaxseed oil</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>C 16: 0 palmitic</td>
<td>5.7</td>
<td>6.3</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>C 18: 0 stearic</td>
<td>3.0</td>
<td>3.2</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>C 18: 1 Oleic (Omega-9)</td>
<td>13.6</td>
<td>13.3</td>
<td>17.9</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>C 18: 2 linoleum (Omega-6)</td>
<td>54.8</td>
<td>56.9</td>
<td>15.5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>C 18: 3 alpha-linolenic (Omega-3)</td>
<td>18.5</td>
<td>16.0</td>
<td>55.3</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>C 18: 2 Gamma Linolenic (Omega-6)</td>
<td>1.3</td>
<td>2.8</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>C 20: 0 peanuts</td>
<td>2.4</td>
<td>0.8</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>

It is found that the ratio of essential fatty acids in hemp oil is close to perfect: Omega-6 and Omega-3 as 3.0:1 – 3.7:1, while in linseed oil is 1:3.6. Hemp oil also contains biologically valuable gamma-linolenic acid, which is quite rare in vegetable raw materials. Nowadays, it is widely recognized [1, 9] the exceptional importance of Omega-3 polyunsaturated fatty acids for maintaining physical and mental health and preventing a number of diseases.

**Presence of hemp oil pigments**

The absorption of monochromatic radiation by hexane solution of hemp oil in the ultraviolet domain of the spectrum is presented in Figure 1.

The spectrum analysis (Figure 1) revealed a band of 200-350 nm, namely, a wide band in the area of 200-250 nm with a maximum at 240 nm with an optical density of D = 1.79. This band is associated with the absorption of saturated and unsaturated fatty acids. The spectra of polyunsaturated fatty acids with isolated double bonds are no different from those of monounsaturated fatty acids since the determining chromophore in the spectra is isolated ethylene bonds. A symmetrical wide band from 260 nm to 310 nm with a maximum at 280 nm with an optical density of D = 4.0 characterizes the absorption of main triacylglycerols.

The absorption of monochromatic radiation by hexane solution of pressed hemp oil in the visible domain of the spectrum is presented in Figure 2.
In spectrum analysis (Figure 2), a band of 360–750 nm was detected, namely, one broad band in 400-480 nm range with a maximum at 420 nm with an optical density $D = 1.50$ is associated with carotenoid absorption. The peak in the area of 500–750 nm at 670 nm with an optical density of $D = 0.37$ refers to chlorophyll a. That is, the hemp oil obtained from the seeds of Ukrainian breeding contains carotenoids and chlorophyll as a part of natural biologically active substances.

Spectrophotometry confirmed the presence of carotenoids and chlorophylls in pressed hemp oil. Vitamin A content in oil is 78 mg/kg, vitamin E (total) is 562,8 mg/kg.
Tocopherols content in vegetable oils

Comparison of tocopherols content and their isomers in hemp press crude oil and in vegetable oils (according to Codex Alimentarius) is presented in Table 3.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Total content, mg%</th>
<th>Isomers, % of the total content</th>
<th>Content interval, mg% a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sunflower high-oleic refined</td>
<td>96±0.85</td>
<td>91.5±0.8 8.5±0.05 -</td>
<td>40.3–102.1</td>
</tr>
<tr>
<td>Sesame is not refined</td>
<td>84±0.7</td>
<td>51.4±0.55 43.0±0.4 5.6±0.05</td>
<td>50.4–114.0</td>
</tr>
<tr>
<td>Amaranth is refined</td>
<td>215±1.5</td>
<td>49.1±0.35 42.4±0.5 8.5±0.1</td>
<td>31.4–347.2</td>
</tr>
<tr>
<td>Hemp press is unrefined</td>
<td>562.8</td>
<td>41.6 48.6 9.8 -</td>
<td>-</td>
</tr>
</tbody>
</table>

Note a – for Codex Alimentarius.

According to the content of tocopherols (Table 3), hemp pressed oil significantly outweighs sunflower, sesame and amaranth oil, which confirms its high biological value.

Indicators of hemp oil quality during storage

Samples obtained from industrial seeds of the 2018 yield were investigated to determine the storage conditions of hemp oil. The oil was obtained from the PS-250 auger press (Institute of bark crops) and had initial data: acid number – 0.4 mg KOH/g, peroxide number – 6.0 ½ O mmol/kg. Samples of hemp oil in sachet packages were stored under the conditions: 1 and 2 at a temperature of 18–25 °C, 1 – with light access, 2 – without light access, 3 – in a refrigerator at 8±2 °C.

The results of determining the chemical properties of the hemp oil samples after a five-month shelf life are presented in Table 4.

<table>
<thead>
<tr>
<th>№</th>
<th>Indicator</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Peroxide number, ½ O mmol/kg</td>
<td>50.2</td>
<td>22.6</td>
<td>8.9</td>
</tr>
<tr>
<td>2</td>
<td>Acid number, mg KOH/g</td>
<td>3.6</td>
<td>3.6</td>
<td>3.4</td>
</tr>
<tr>
<td>3</td>
<td>Anisidine number, mind. units</td>
<td>3.7</td>
<td>3.0</td>
<td>1.3</td>
</tr>
<tr>
<td>4</td>
<td>Totox indicator</td>
<td>105.1</td>
<td>48.2</td>
<td>19.1</td>
</tr>
</tbody>
</table>

From the data table, 4 follows that hemp oil is better stored at 8±2 °C without light access by chemical terms and at a lower integral value (totox).
Quality indicators of oil compositions

One way to increase the resistance of oils to oxidation and sagging is to scientifically prove the creation of oil or oil-fat compositions [1].

In order to improve the antioxidant resistance and functional and technological properties of hemp oil in the systemic concept of health [8, 11] and to expand the range of oil-fat compositions, products and preparations, chemical quality indicators, output of oil and oilcake during the first pressing of the hemp seed and mixtures of flax seeds and hemp KTIOL-LK were investigated. Source moisture of seeds: hemp – 9.3±0.2 %, flax – 5.5±0.1 %; press – screw PLC-5, matrix diameter 10 mm, pressing temperature – 105±2 °C. KTIOL-LK oil compositions are obtained by pressing mixtures of flax and hemp seeds in the ratio: KTIOL-LK11 – 1:1; KTIOL-LK31 – 3:1; KTIOL-LK91 – 9:1. The results of the study are presented in Table 5.

Table 5
Chemical quality indicators and oil output when pressing hemp seeds and the mixture of flax and KTIOL-LK hemp seeds

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Oil/oil composition</th>
<th>Output of pressed oil, %</th>
<th>Output of oilcake, %</th>
<th>Acid number of the oil, mg KOH/g</th>
<th>Peroxide oil number, mmol O/kg</th>
<th>Oilcake moisture content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hemp oil of first pressing</td>
<td>23.8</td>
<td>75.3</td>
<td>1.4</td>
<td>1.4</td>
<td>9.8</td>
</tr>
<tr>
<td>2</td>
<td>KTIOL-LK11 oil</td>
<td>26.1</td>
<td>73.3</td>
<td>0.8</td>
<td>0.7</td>
<td>8.1</td>
</tr>
<tr>
<td>3</td>
<td>KTIOL-LK31 oil</td>
<td>20.9</td>
<td>77.1</td>
<td>0.9</td>
<td>1.1</td>
<td>6.9</td>
</tr>
<tr>
<td>4</td>
<td>KTIOL-LK91 oil</td>
<td>20.9</td>
<td>78.0</td>
<td>0.9</td>
<td>1.1</td>
<td>6.3</td>
</tr>
</tbody>
</table>

It was found (Table 5) that the chemical parameters, in particular, peroxide and acid numbers of pressed hemp oil and KTIOL-LK oil compositions (from hemp seeds and mixtures of flax seeds and hemp seeds) are of good quality. The KTIOL-LK11 oil composition (peroxide and acid numbers less than 1) with a higher oil output was preferred. The data obtained are consistent with theoretical, experimental and innovative data on modern vegetable oil technologies [1].

Indicators of the quality of hemp seeds kernel

One of the actual health problems of the population is providing different age groups with quality, safe lipid, and protein-lipid products [1, 8, 11], in particular on the basis of ecological and economic complex processing of industrial hemp seeds of Ukrainian breeding.

Physicochemical indicators of the hemp seed quality that has been knocked out are presented in Table 6.
Physicochemical indicators of the quality of the collapsed hemp seeds

<table>
<thead>
<tr>
<th>№</th>
<th>Indicator</th>
<th>Indicator value</th>
<th>According to «Hemp-Flax»b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>According to a study of hemp seeds</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Collapsed</td>
<td>Output</td>
</tr>
<tr>
<td>1</td>
<td>Moisture content, %</td>
<td>7.0±0.02</td>
<td>8.4±0.02</td>
</tr>
<tr>
<td>2</td>
<td>Mass fraction of trash, %</td>
<td>0.4±0.02</td>
<td>3.3±0.15</td>
</tr>
<tr>
<td>3</td>
<td>Acid number, mg KOH/g</td>
<td>3.1±0.1</td>
<td>3.3±0.1</td>
</tr>
<tr>
<td>4</td>
<td>Mass fraction of oil a, %</td>
<td>54.0±1</td>
<td>33.3±0.5</td>
</tr>
<tr>
<td>5</td>
<td>Mass fraction of protein a, %</td>
<td>32.8±0.2</td>
<td>22.5±0.15</td>
</tr>
<tr>
<td>6</td>
<td>Mass fraction of fiber a, %</td>
<td>5.5±0.03</td>
<td>32.3±0.2</td>
</tr>
<tr>
<td>7</td>
<td>Mass fraction of ash a, %</td>
<td>6.5±0.03</td>
<td>5.91±0.03</td>
</tr>
<tr>
<td>8</td>
<td>Mass fraction of minerals a:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phosphorus, g/kg</td>
<td>13.5</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td>Calcium g/kg</td>
<td>0.5</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>Magnesium, g/kg</td>
<td>2.7</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>Ferum, mg/kg</td>
<td>94.1</td>
<td>74.7</td>
</tr>
<tr>
<td></td>
<td>Zinc, mg/kg</td>
<td>111.8</td>
<td>56.1</td>
</tr>
<tr>
<td></td>
<td>Cobalt, mg/kg</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Manganese, mg/kg</td>
<td>38.3</td>
<td>59.4</td>
</tr>
<tr>
<td></td>
<td>Kuprum, mg/kg</td>
<td>12.6</td>
<td>not determined</td>
</tr>
</tbody>
</table>

Note: a – in terms of solids.
                        b – hemp and flax processing company in the Netherlands and Romania.

From the data Table 6, it can be seen that the quality of collapsed hemp seed indicators is improved compared to the output seed. The oil and protein content increased 1.5 times, the macro- and trace elements (except calcium and manganese) increased: phosphorus – 1.5 times, ferum – 1.25 times, zinc and cobalt – 2 times.

The ingredients of collapsed hemp seeds are biologically valuable and contribute to the prevention and healing of the organism, in particular in the systemic health concept (the KTIOL® system) [8, 11].

Since the production of hemp seed does not use the process of wet-heat treatment, it was important to determine the resistance of the product to the effects of microorganisms. Bacteria of Escherichia coli group, molds, yeasts and pathogens of the genus Salmonella were not detected in the test samples of the collapsed hemp seeds. It is important to observe the storage conditions of the hemp seed that has fallen off to prevent the development of pathogenic microflora, which may develop in the protein components of the unprotected core, with increasing humidity and temperature [1, 11]. Due to the protein, oil and mineral content, the biological value of the product is increased for consumers.

Organoleptic characteristics of the collapsed hemp seed quality are followed: the color is light beige with shades of green; odor is inherent in healthy hemp seeds, odorless; taste is characteristic of hemp seeds, without bitterness, acid, and other foreign flavors.

The study of the composition of irreplaceable «i» and replaceable «r» amino acids in the collapsed hemp seeds is presented in Table 7.
Table 7

Amino acid composition of collapsed hemp seeds

<table>
<thead>
<tr>
<th>№</th>
<th>Indicator</th>
<th>№ or  №</th>
<th>Value</th>
<th>According to «HempFlax»</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>«i»</td>
<td>Collapsed hemp seeds</td>
<td>Hemp seed output</td>
</tr>
<tr>
<td>1</td>
<td>Alanine</td>
<td>«i»</td>
<td>1624 5.4</td>
<td>642 5.5</td>
</tr>
<tr>
<td>2</td>
<td>Arginine</td>
<td>«i»</td>
<td>4149 13.7</td>
<td>1409 12.1</td>
</tr>
<tr>
<td>3</td>
<td>Aspartic acid</td>
<td>«i»</td>
<td>2616 8.6</td>
<td>1100 9.4</td>
</tr>
<tr>
<td>4</td>
<td>Valine</td>
<td>«r»</td>
<td>946 3.1</td>
<td>351 3.0</td>
</tr>
<tr>
<td>5</td>
<td>Histidine</td>
<td>«i»</td>
<td>936 3.1</td>
<td>326 2.8</td>
</tr>
<tr>
<td>6</td>
<td>Glycine</td>
<td>«i»</td>
<td>1546 5.1</td>
<td>644 5.5</td>
</tr>
<tr>
<td>7</td>
<td>Glutamic acid</td>
<td>«i»</td>
<td>5546 18.4</td>
<td>2370 20.4</td>
</tr>
<tr>
<td>8</td>
<td>Isoleucine</td>
<td>«r»</td>
<td>833 2.8</td>
<td>323 2.8</td>
</tr>
<tr>
<td>9</td>
<td>Leucine</td>
<td>«r»</td>
<td>2023 6.7</td>
<td>791 6.8</td>
</tr>
<tr>
<td>10</td>
<td>Lysine</td>
<td>«r»</td>
<td>1538 5.1</td>
<td>661 5.7</td>
</tr>
<tr>
<td>11</td>
<td>Methionine</td>
<td>«r»</td>
<td>877 2.9</td>
<td>263 2.3</td>
</tr>
<tr>
<td>12</td>
<td>Proline</td>
<td>«i»</td>
<td>1410 4.7</td>
<td>593 5.1</td>
</tr>
<tr>
<td>13</td>
<td>Serine</td>
<td>«i»</td>
<td>1888 6.2</td>
<td>656 5.6</td>
</tr>
<tr>
<td>14</td>
<td>Tyrosine</td>
<td>«i»</td>
<td>1200 4.0</td>
<td>383 3.3</td>
</tr>
<tr>
<td>15</td>
<td>Threonine</td>
<td>«r»</td>
<td>1091 3.6</td>
<td>438 3.8</td>
</tr>
<tr>
<td>16</td>
<td>Tryptophan</td>
<td>«r»</td>
<td>Not determined</td>
<td>210 0.7</td>
</tr>
<tr>
<td>17</td>
<td>Phenylalanine</td>
<td>«r»</td>
<td>1396 4.6</td>
<td>525 4.5</td>
</tr>
<tr>
<td>18</td>
<td>Cysteine</td>
<td>«i»</td>
<td>604 2.0</td>
<td>163 1.4</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td>30223 100</td>
<td>11638 100</td>
</tr>
</tbody>
</table>

From the data Table 7, it can be seen that hemp seed of Ukrainian breeding has a high content of essential amino acids. The content of isoleucine, leucine, lysine, methionine, threonine, phenylalanine significantly exceeds their content in the hemp seed output. High lysine content is found which is usually deficient. Data on increasing the biological value of products can be significantly improved by further processing of hemp seeds to produce flour or protein. In particular, due to the use of post-processing processes, the protein content in terms of solids in hemp flour can reach 44.0%, and in hemp protein – 52.1%.

Conclusions

1. On the basis of a systematic approach and analysis of chemical and technological lipid-containing systems, in particular on the oxidation and scorching of unsaturated and saturated acylglycerols in oils, seeds, and products, the purpose and methodology of studies are considered, taking into account the provisions of the systemic health concept.

2. The content of fatty acids, phospholipids, vitamins A and E, their degree of unsaturation the obtained pressed hemp oil has a high biological value. In terms of tocopherols content, hemp pressed oil significantly outweighs sunflower, sesame and amaranth oils. It is found that the ratio of essential fatty acids in hemp oil is close to perfect: Omega-
6 and Omega-3 as 3.0:1 – 3.7:1, while in linseed oil – 1:3.6. Hemp oil also contains biologically valuable gamma-linolenic acid.

3. In chemical terms and less integral value (totox), hemp oil is better stored at 8±2 °C without light access.

4. Chemical indicators, in particular, peroxide and acid numbers, of hemp oil and KTIOL-LK oil compositions (from mixtures of flax seeds and hemp) were found to be of good quality. KTIOL-LK11 oil composition (peroxide and acid numbers less than 1) with a higher oil output is preferred.

5. The physicochemical indicators of the hemp seeds kernel quality are improving compared to the output seeds. The oil and protein content increased 1.5 times, the macro- and trace elements (except calcium and manganese) increased: phosphorus – 1.5 times, ferric – 1.25 times, zinc and cobalt – 2 times. Hemp seeds kernel has a high content of essential amino acids, which significantly exceeds its content in the output seed. High lysine content is found which is usually deficient.

Further research will focus on identifying new technological innovative solutions for the integrated processing of organic hemp industrial seeds, the identification, creation, and use of biologically active, functional products, supplements and preparations in the systemic health concept.

Acknowledgements. The authors are grateful to Senior Researcher D. Petrachenko for assistance in obtaining pressed oil and hemp seeds kernel; Associate Professors V. Yefimov and D. Masyuk for assistance in conducting research to determine the quality indices of industrial hemp seeds and their processing products; Lead Dr. V. Shevchyk for his assistance in testing product samples in the KTIOL® system.

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Physicochemical and textural properties of reduced sugar jellies from *Physalis peruviana* L. fruit

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2 – Plovdiv University “Paisii Hilendarski”, Plovdiv, Bulgaria
3 – University of Russe, Branch Razgrad, Bulgaria

**Abstract**

**Introduction.** *Physalis peruviana* L. fruit contain various functional compounds with health promoting effects. The aim of this study was to investigate the possibility of obtaining reduced sugar jellies from physalis juice with different sugars and sugar substitutes.

**Materials and methods.** Jellies containing physalis juice and sucrose (sample S), fructose (sample F) or maltitol and maltitol syrup (sample M), respectively, were prepared and studied.

**Results and discussion.** There were no significant differences between the samples in terms of dry matter content, titratable acidity and pH. The highest total sugar content was found in sample S (72.68%), and the lowest – in sample M (7.12%). Sample M had about 90% lower total sugar content than sample S and about 83% lower than sample F. Therefore, according to EU Regulation No 1924/2006, the jelly with maltitol/maltitol syrup can be classified with a nutrition claim “Food with no added sugars”. Due to its composition, the same nutrition claim can be ascribed to sample F. Sample F had the biggest sorption capacity, in which an absorption process was observed, and the moisture content of the jelly increased from 28.23% to 32.65% after 120 h. Samples S and M revealed a desorption process (decrease by about 2-3%, 120 h), thus being more stable in terms of storage. The texture profile of sample M was more favorable with regard to jelly’s further use, as it had the highest hardness and adhesiveness values (10.12 N and 0.42 N.mm, respectively), compared to samples S and F. Additionally, sample M had about 40% lower energy value than sample S (680 kJ/100 g vs. 1142 kJ/100 g), thus allowing for the nutrition claim “Energy-reduced food” under the terms of Regulation No 1924/2006. The calculated glycemic indicator values were 39.2 (sample S), 23.5 (sample M) and 14.6 (sample F), respectively. These results suggest that physalis juice can be successfully processed into functional sweet jellies.

**Conclusions.** The jellies with physalis juice and maltitol/maltitol syrup can be classified with the nutrition claims “Energy-reduced food” and “Food with no added sugars”. 

**Keywords:** *Physalis peruviana* L. Maltitol Fructose Jelly Functional
Introduction

Foods with sweet taste, respectively confectionery, are suitable for the technological realization of certain functional concepts and as carriers of ingredients with functional properties, because they are easily portable, convenient for consumption and are preferred by all age groups [1]. According to the same authors, these types of food can be obtained by adding functional ingredients to the composition of traditional sweet foods or by substituting certain ingredients in their existing composition. An individual segment of the confectionery group of foods is represented by jellies, which are distinguished by their taste, shape and elasticity [2]. The main ingredients used in the production of jellies are water, sugar, glucose syrup and a gelling agent that forms the characteristic consistency of the product [3].

Variants of jelly formulations with sweeteners or various sugars are proposed in order to limit the consumption of sugar (sucrose), which is a major cause of noncommunicable diseases such as obesity, diabetes, etc. [4, 5]. There is an opportunity to replace the water, as well, in the formulation of the jelly, with fruit puree or fruit juice. Usually, those obtained from oranges, apples, grapes, strawberries and some other fruits are used for this purpose [6].

Like other berries, Physalis peruviana L. fruit (also known as Cape gooseberry, Inca berry, Peruvian groundcherry, goldenberry, physalis) contain a variety of highly functional phytochemical and nutritive compounds with health promoting effects (vitamins, minerals, fibers, protein, polyphenols, phytosterols, carotenoids, etc.), and physalis popularity worldwide is constantly growing during the last two decades [7-10]. Fresh physalis fruit are excellent for direct consumption, but considering their limited shelf-life (about one month, without removing the protective calyx), it is a much better option if they are processed into commercially stable products. The latter include various categories of fruit derivatives and functional foods, preferred by the consumers, such as juices, yogurts, ice-creams, jellies, raisins, etc. [11-15]. According to Sheikha et al. [16], physalis juice contained (on a wet weight basis) 89.34% water, 0.13% lipids, 1.02% protein, 6.95% total sugars, and 0.14% pectin. The basic chemical indices of physalis fruit in the study by Yıldız et al. [17] were: dry matter 18.68%, water soluble dry matter 14.17%, ash 2.98%, protein 1.66%, oil 0.18%, carbohydrates 13.86%, total sugar 63.9 g/kg, and reducing sugar 31.99 g/kg. Similar data were reported by Sharoba and Ramadan [18], dry matter 21.00%, water soluble dry matter 16.40%, ash 1.08%, protein 0.84%, and oil 0.32%. Besides, the attractive bright yellow-to-orange color, the tender juicy texture and the exotic flavor (sweet and sour, with a hint of strawberry, citrus and vanilla) of physalis fruit make an excellent contribution to the organoleptic properties of various foods. Physalis fruit and fruit juice are associated with pronounced hypercholesterolemic and anti-diabetic effects [8, 12, 15, 19, 20], thus being a suitable means for reducing the glycemic load of modern human diet.

Undoubtedly the use of non-traditional plant-derived ingredients has been gaining popularity in food technology, which in turn stimulates the development of various and novel arrangements for their incorporation in many food systems. In that way, the bioactive and functional assets of P. peruviana fruit, as well as the possibility for their extended cultivation in many countries of the tropical, sub-tropical and the temperate zones [8, 9], create prerequisites for exploring the options of physalis use in a wide range of foods.

For these reasons, the aim of this study was to investigate the possibility of obtaining reduced sugar jellies from physalis juice (Physalis peruviana L.) with different sugars and sugar substitutes, and to determine the influence of these ingredients on the basic physicochemical and structural properties of the jellies.
Materials and methods

Ingredients and jelly processing

To carry out the study physalis juice obtained under laboratory conditions was used. Physalis fruit were purchased from a local supermarket, with Colombia being the producer (Frutas Comerciales S.A., Bogotá) and were kept in a refrigerator (5-8 °C) until processing. The berries were separated from the husk (calyx) and then were subjected to mechanical grinding in a high-speed vacuum blender HR3752/00 for 4 min. Extracted fruit mass was filtered through a sieve with a mesh size below 215 μm to remove seeds and peels. The moisture content of the berries, determined by drying to constant weight at 105 °C, was 83.07±0.27%.

To determine the effect of physalis juice and the ingredients with sweetening properties on the values of the basic physicochemical parameters and properties of the jelly, three samples were developed and further analyzed (Table 1). The final formulation of the jellies presented in Table 1 was obtained as a result of a series of preliminary tests (data not shown), based on modification of jelly composition with regard to gelling agents, sugars and sugar substitutes and physalis juice participation (i.e. ingredient choice and percentage).

Table 1

<table>
<thead>
<tr>
<th>Ingredients, % (w/w)</th>
<th>Sample*</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S</td>
<td>F</td>
<td>M</td>
<td></td>
</tr>
<tr>
<td>Sucrose</td>
<td>47</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Fructose</td>
<td>-</td>
<td>47</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Maltitol</td>
<td>-</td>
<td>-</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>Maltitol syrup</td>
<td>-</td>
<td>-</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Physalis juice</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Pectin</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Carrageenan</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Citric acid</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

* S – with sugar; F – with fructose; M – with maltitol and maltitol syrup

For convenience the samples in the study were labeled as follows: sample S – containing sucrose; sample F – containing fructose, and sample M – containing maltitol and maltitol syrup. The formulation of sample M (Table 1) was calculated on a dry matter content basis, in order to comply with the other two samples. Crystalline maltitol (food additive code E 965i) with trade name „Maltisorb P90“ (Roquette Freres, France) and maltitol syrup (E 965ii) with trade name „C*Maltidex L 16306“ (Cargill Inc., Minneapolis, MN, USA) were used.

The jellies were obtained under laboratory conditions to a boiling point of around 108 °C, and were further formed by pouring in silicone molds and cooling at 20±2 °C for 24 h.

The described stages of jelly processing in the study are illustrated on Figure 1.
**Figure 1. Stages of obtaining jellies from physalis juice:**
a – physalis berries; b – juice after filtration; c – jelly after cooling (sample M)

**Jelly analysis**

The values of the basic physicochemical parameters of the jellies, such as dry matter content, total sugar content, reducing substances, pH and titratable acidity, were analyzed according to Lurie et al. [21]. The color of the jellies was determined spectrophotometrically on 10% sample solutions at $\lambda = 450$nm.

The sorption properties of the samples were analyzed by the equilibrium moisture determination method described in [21], at a relative air humidity of 75%, maintained over a saturated solution of NaCl.

The texture parameters of the samples were analyzed after 24 h of their formation with a texture meter LS1 (Lloyd Instruments Ltd., UK). The analysis was performed with a cone-shaped probe with a tip angle of 90°, speed 0.2 mm/s and immersion depth of 10 mm. The values of texture parameters like hardness and adhesiveness were reported directly and cohesiveness was calculated according to Seyed et al. [22].

The energy value of the samples was calculated according to the content of macronutrients in their composition and using the conversion factors defined in Regulation (EU) No 1169/2011 [23].

The glycemic indicator was defined and calculated according to the methodology developed by Dorohovich et al. [24].

**Statistical analysis**

All data were expressed as mean ± standard deviation (n=3). ANOVA and Tukey’s multiple comparison test (p<0.05) were applied for the determination of significant differences.
Results and discussion

Physicochemical characteristics of the jellies

The values of the main physicochemical parameters of the analyzed samples are shown in Table 2. Data revealed that, in terms of parameters dry matter content, titratable acidity and pH, no significant differences were observed between the values of the three samples. Significant differences were observed in the total sugar and reducing substances contents between the samples.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Sample¹</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry matter, %</td>
<td>70.23±0.29⁵,a</td>
<td>71.77±0.23a</td>
<td>69.43±0.41a</td>
</tr>
<tr>
<td>Total sugar content (as invert sugar), % dry matter</td>
<td>72.68±0.10a</td>
<td>67.32±0.10b</td>
<td>7.12±0.10c</td>
</tr>
<tr>
<td>Reducing substances (as invert sugar), % dry matter</td>
<td>10.72±0.10a</td>
<td>58.94±0.10b</td>
<td>4.27±0.10c</td>
</tr>
<tr>
<td>Titratable acidity (as citric acid), %</td>
<td>1.81±0.01a</td>
<td>1.86±0.01a</td>
<td>1.82±0.01a</td>
</tr>
<tr>
<td>pH (10% solution)</td>
<td>3.52±0.01a</td>
<td>3.41±0.02a</td>
<td>3.43±0.02a</td>
</tr>
<tr>
<td>Color, E (10% solution; λ=450 nm)</td>
<td>0.28±0.01a</td>
<td>0.48±0.01b</td>
<td>0.29±0.01a</td>
</tr>
</tbody>
</table>

¹S – with sugar; F – with fructose; M – with maltitol and maltitol syrup;
² data expressed as mean ± standard deviation (n = 3);
³ means with different superscripts in a row differed significantly (p < 0.05).

It can be seen (Table 2) that the highest total sugar content was found in sample S, followed by sample F. The lowest value of this parameter was associated with sample M, obtained with sweeteners. The relative content of total sugar for samples F and M, compared to sample S (accepted as 100%) is shown in Figure 2.

From the graphically related dependence (Figure 2) it can be seen that sample M has a total sugar content of about 90% lower than sample S and about 83% lower than sample F. Therefore, according to the terms and provisions of Regulation (EC) No 1924/2006 [25], the jelly from physalis juice with maltitol and maltitol syrup as sweeteners (sample M) can be classified with a nutrition claim “Foods with no added sugars”. Although the total sugar content of sample F was relatively close to that of sample S, the jelly with fructose can also be classified with the same nutrition claim, due to its composition.

In regard to reducing substances, the highest content was found in sample F. This finding can be explained by the participation of fructose in the composition of the sample, which refers to reducing monosaccharides. Respectively, the lowest content of reducing substances is observed in sample M.

The color of the obtained jellies was defined by both the color of the added physalis juice (Figure 1), which has high content of carotenoids [16, 26] and by processes occurring under the influence of temperature during sample boiling. The results obtained (Table 2) show that sample F was the most colored, compared to samples S and M.
Sorption characteristics of the jellies

The sorption properties of the jellies were analyzed during 5 consecutive days, at room temperature and at a constant relative humidity of 75%. The obtained results are shown in Figure 3.
It is evident from the graphically expressed dependencies that sample F possessed the most pronounced sorption properties, in which an absorption process was observed. For example, after 120 h (5 days) the moisture content of this sample increased by about 4% compared to its original one (from 28.23% to 32.65%). The other two samples (S and M) revealed a desorption process, and their moisture decreased with time (by about 2-3%). These results suggested that samples S and M would be more stable for a longer period of storage, with regard to the occurrence of microbiological, oxidative and other transformations, which could deteriorate the quality of the final products.

**Texture profiles of the jellies**

The texture profiles of the jellies are shown in Figure 4, and the values of the determined texture parameters – in Table 3.

**Values of the basic texture parameters of jellies from physalis juice**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hardness, N</td>
<td>Adhesiveness, N.mm</td>
</tr>
<tr>
<td>S</td>
<td>10.12±0.09a</td>
<td>0.08±0.00a</td>
</tr>
<tr>
<td>F</td>
<td>8.70±0.06b</td>
<td>0.15±0.00a</td>
</tr>
<tr>
<td>M</td>
<td>11.81±0.10c</td>
<td>0.42±0.01b</td>
</tr>
</tbody>
</table>

1 S – with sugar; F – with fructose; M – with maltitol and maltitol syrup;
2 data expressed as mean ± standard deviation (n = 3);
3 Exponents with different superscripts in a column differed significantly (p < 0.05).

From the data in Table 3 it can be seen that sample M had the highest hardness, as well as the highest adhesiveness values compared to sample S and sample F. These results suggest that maltitol and maltitol syrup make a good combination with physalis juice, in terms of jelly texture profile. In that way, the jelly obtained after the formulation of sample M would be more suitable for both individual use (for example as jelly candies) and as a part of different confectionery and other sweet foods (such as fruit jelly desserts, candy or pastry filling and others), compared to the rest of the samples. Respectively, the lowest value in terms of adhesiveness was observed in sample S, and it was significantly lower (about five times) than that of sample M. With regard to cohesiveness, samples F and M were both with lower values than sample S, with no significant difference between them. The observed differences in the values of jelly texture indicators were obviously related to the variation in their composition in terms of the used components with sweetening properties, i.e. sugars (sucrose and fructose) and sweeteners (maltitol and maltitol syrup).

To the best of our knowledge, there are no previous studies on jellies from physalis juice and sugar substitutes (maltitol in particular), so it is difficult to make comparisons to literature data. Our results for sample S differed numerically from the texture characteristics of physalis jellies, made from 59.25% physalis juice, 40% sucrose and 0.75% high methoxyl pectin, reported by Curi et al. [11] – hardness 0.22 N, adhesiveness 0.47 N/s, and cohesiveness 0.39, explicable by the different jelly matrix composition and analysis conditions. Obviously, the weaker hardness of sample F was associated to the bigger hygroscopic potential due to the presence of fructose (absorption of moisture after storing for 24 h), thus being in accordance with the results for the sorption properties of the jellies described above.
Figure 4. Texture profile of jellies from physalis juice:
a – with sugar (S); b – with fructose (F); c – with maltitol/maltitol syrup (M)

Energy value and glycemic indicator of the jellies

Based on the composition of the jellies, their energy value was calculated in accordance with Regulation No 1169/2001 of the EU [23], by applying the respective conversion factors listed in the Regulation. The results are shown in Table 4.
From the calculated energy values of the jellies (Table 4), it can be seen that sample M has about 40% lower energy value than sample S. This allows the jelly from physalis juice with maltitol and maltitol syrup to be classified with a nutritional claim “Energy-reduced food” under the terms of Regulation (EC) No 1924/2006 [25], compared to the respective sugar-containing jelly.

Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>Energy value, kJ/100 g</th>
<th>Glycemic indicator</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>1142</td>
<td>39.2</td>
</tr>
<tr>
<td>F</td>
<td>1128</td>
<td>14.6</td>
</tr>
<tr>
<td>M</td>
<td>680</td>
<td>23.5</td>
</tr>
</tbody>
</table>

*S – with sugar; F – with fructose; M – with maltitol and maltitol syrup

From the data presented in Table 4 it can be seen that sample F has the lowest value of the glycemic indicator (about 63% lower than sample S). This is due to the fact that its formulation contained fructose, which has a lower glycemic index (GI) than both sugar and maltitol [27]. The glycemic indicator value of sample M was also significantly lower (by about 40 %) than that of the sugar-containing jelly, which can be considered a promising result in terms of jelly use and promotion.

Conclusion

From the comparative analysis and the obtained results, it can be concluded that physalis juice is an appropriate ingredient for the preparation of jellies with sugar, fructose and maltitol/maltitol syrup. All jellies revealed physicochemical and textural properties, which make them promising material for use in different foods with sweet taste and provide grounds for future research.

The results from the study suggested that maltitol/maltitol syrup sweetener could be selected as the most functional sugar substitute in the composition of jellies from physalis juice. The fruit jelly with maltitol and maltitol syrup had a total sugar content that was 90% lower than that of the jelly made with sucrose and 83% of that with fructose. Additionally, the jelly obtained with maltitol and maltitol syrup had the lowest energy value compared to the jellies obtained with sugar and fructose. With the lowest glycemic indicator was the jelly obtained from a formulation with the participation of physalis juice and fructose. The jelly with maltitol and maltitol syrup had the highest hardness and adhesiveness, which – together with the lower sorption capacity – facilitates the use of the jelly in a wider range of sweet foods.

The jellies with physalis juice and maltitol/maltitol syrup can be classified with the nutrition claims “Energy-reduced food” and “Food with no added sugars” under the terms of the respective European regulations, and can be promoted as such if commercialized in the future.
References


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Biological value in milk-protein concentrates with malt ingredients

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Abstract

Introduction. It is actual to study of biological value of milk-protein concentrates with malt ingredients. Biological value characterizes the quality of the protein composition with the ability to evaluate it according to physiological norms.

Materials and methods. Milk protein concentrates without and with malt ingredients used for research. The biological value and amino acid composition of the samples was determined by ion exchange chromatography on LC 3000 automatic analyzer. Protein digestibility in vitro was determined by hydrolysis of samples using a solution of 6N hydrochloric acid at a temperature of (120 ± 2) °C for 24 hours.

Results and discussion. The total amino acid content in milk protein concentrates with malt ingredients increased compared to control due to the addition of germinated cereals (wheat, barley, oats, corn).

The amino acid score for the studied samples has been calculated. When preparing the mixture: milk-protein concentrate + malt ingredients, the content of limiting amino acids increases – methionine + cystine and threonine. Biological value of the experimental samples is increased.

Conclusion. Milk protein concentrates with malt ingredients have an increased biological value of 1.11–2.98%.
Abbreviation
AAS – amino acid score
EAA – essential amino acids
MPC – milk-protein concentrate
NAA – nonessential amino acids

Introduction

The modern term “biological value” refers to the level of efficient use of protein by the body, which is spent on maintaining nitrogen balance in the body [1]. It depends on the amino acid composition, the balance of amino acids and structural features. Given these premises, this indicator characterizes the quality of the protein composition in the food product with the ability to evaluate it according to physiological norms [2].

It is important not only when assessing biological value the presence of all the essential amino acids (EAA) in the product, their high content, but also the quantitative balance in accordance with the FAO/WHO standards [3]. EAA discrepancy in quantitative characteristics of the amino acid scale of an ideal protein indicates an imbalance in the product - a decrease in its biological value [4].

According to the FAO/WHO scale, an ideal protein contains nonessential amino acids (NAA) (mg%/100 g protein): isoleucine – 4, leucine – 7, lysine – 5.5, methionine + cystine – 3.5, phenylalanine + tyrosine – 6, tryptophan – 1, threonine – 4, valine – 5 [5, 6].

Replaceable amino acids such as cystine and cysteine are synthesized if there is a sufficient amount of methionine, an essential amino acid, the amount of which depends entirely on food intake [7].

Milk protein concentrates with malt ingredients differ in their chemical composition from traditional ones by enrichment with functional and technological components. In this regard, when determining the biological value of such products as a criterion for the quality of a protein, it is necessary to take into account the characteristics of the amino acid composition of animals and plant proteins and the degree of their digestibility after digestion [8, 20]. Animal proteins are complete, while vegetable proteins, because of the relatively low content of lysine, tryptophan, threonine in them, are not. Such features must be taken into account when combining proteins of different origins in dairy products in order to balance the amino acid composition [9, 10]. For example, an insufficient amount of sulfur-containing amino acids in casein is compensated by their content in malt proteins [11].

The aim of research is determination of biological value of milk-protein concentrates in compared with milk-protein concentrate obtained by traditional technology.

Materials and methods

Materials

Object of research – milk-protein concentrates without and with malt ingredients. Milk-protein concentrate (base) was obtained by the acid-rennet method from pasteurized skim milk at a temperature of (78±2) °C with an duration of 20 ... 30 s. Further, milk ripening was at a temperature of (30±1) °C by pure cultures of hetero-and homoenzymatic microorganisms Lactococcuslactis subsp. lactis, Lactococcuslactis subsp. cremoris, Lactococcuslactis subsp. Acetoinicus. In addition to the starter culture, a 40% solution of calcium chloride and a milk-
clotting enzyme preparation were added. Fermentation was carried out until a clot was obtained with an acidity of (75±5) °T. The separation of whey from the clot was carried out to a moisture content (78±2)%. Milk-protein concentrate (MPC) was cooled to a temperature of (4±2) °C.

Malt is pre-soaked, sprouted in artificial conditions and enriched with active enzymes grains of various types of crops [12, 13]. Malt production was carried out in the following sequence: water was collected in a malt-growing box to half its volume, and grains were poured into the water. After mixing, water was added to the full volume of the apparatus and the alloy was removed through a drain box. The washed grains were soaked in an air-water way until the desired moisture content for oats was reached 42–43%; for wheat – 44–46%; for corn – 44–46%; for barley – 43–45%. Germination of soaked grains was carried out at a temperature of 16–18 °C for 3–7 days, depending on the cereal, wheat – 3–4 days, oats – 5–6 days, corn – 7–8 days, barley – 6–7 days. The grain was mixed and blown with air using a fan to aerate and maintain the desired temperature during germination. Grain was dried in warmed up air heated in a heater with a gradual increase in temperature from 30 to 75 °C. Ready sprouted grains were unloaded at the plant and sent for grinding [14–19]. Sprouted grains contain a sufficient set of ingredients necessary for a balanced diet – proteins, carbohydrates which are easily digested, dietary fiber, minerals, vitamins and others. During the development of the embryo, various enzymes are activated, which turn insoluble compounds (starch, protein) into soluble (saccharides, amino acids, etc.). In addition, cereal malt contains coloring and polyphenolic compounds, as well as plant enzymes and hormones [13].

Milk-protein concentrates with malt ingredients were obtained by introducing 5.0% of various malt into the base – wheat, barley, oat, and corn. The quantity was based on observing the principle of preserving the corresponding organoleptic characteristics, which characteristic for traditional MPC with fillers.

**Methods**

**Order of the research.** To study the biological value of milk-protein concentrates with malt ingredients, their amino acid composition has determined by ion-exchange chromatography. Researches have performed on an automatic analyzer LC 3000 of the company «Eppendorf-Biotronic» (Germany). Control sample – MPC with a moisture content (78±2)%, made by classical technology without the addition of malt. Hydrolysis of the sample has realized with a solution of 6N hydrochloric acid, at a temperature (120 ± 2) °C for 24 hours. This method allows to determine with accuracy to ± (5–10)% the presence of up to 18 amino acids with a minimum level of their content in solution (0,500 ± 0,006) μmol/ml [20].

The amino acid content in milk-protein concentrates with malt ingredients (wheat, barley, oat, corn) was compared with their amount in the control sample – milk protein concentrate obtained by the acid-rennet method that was described above.

The biological value of milk protein concentrates without and with malt ingredients has been determined by calculating the following indicators.

**Amino acid score** (AAS, %), which is defined as the ratio of the mass fraction of each essential amino acid in the product (EAA_{pr}, g/100 g protein) to the corresponding essential ideal acid amino acid (EAA_{id}, g/100g protein) on the amino acid scale recommended by FAO/WHO [21–23].
Amino acid score has been calculated by the formula:

\[ C_j = \frac{A_j}{A_{ij}} \cdot 100 \]  

(1)

where \( A_j \) – mass fraction of the j-th acid EAA in the sample, g/100 g of protein; \( A_{ij} \) – the mass fraction of the j-th acid of EAA, in standard, the proportion of the physiologically necessary standard for a certain consumer group, g/100 g of protein.

**Utilitarian coefficient of the amino acid composition of the product** (\( U \)) – numerically characterizes the balance of all EAA proteins with respect to the standard, or physiological norm, and is used to compare the protein composition of various food products based on their amino acid composition and inadequacy of their use in the body.

Utilitarian coefficient has been calculated by the formula:

\[ U = C_{\min} \sum_{j=1}^{8} \frac{A_{ij}}{A_j} \]

\[ U = C_{\min} \sum_{j=1}^{8} \frac{A_{ij}}{A_j} \]  

(2)

where \( A_{ij} \) – mass fraction of the j-th acid EAA in the standard, mg/g of protein; \( A_j \) – mass fraction of the j-th acid EAA in the product protein, mg/g of protein; \( C_{\min} \) – score of the first limited acid EAA, units;

Redundancy coefficient (\( \sigma_{\text{red}} \)) – shows the mass fraction of EAA in 100 g product, which is not fully used by the body.

\[ \sigma_{\text{red}} = \frac{\sum_{j=1}^{8} (A_j - C_{\min} A_{ij})}{C_{\min}} \]  

(3)

**Differential coefficient of amino acid score** (DCAS) and the biological value of protein (BC) – according to the method of M.P. Chernikov. It is based on the postulate that the assimilation of EAA is limited by the content of the limiting amino acid. That is, all of their excess goes to energy needs, but not to protein biosynthesis. The average excess amino acid excess EAA in comparison with the smallest AAS of the limiting amino acid, DCAS has been found by the formula:

\[ DCAS = \frac{\sum \Delta \text{DAS}}{n}, \]  

(4)

where DAS – the difference in amino acid score for each EAA compared to the AS of a limiting amino acid,%; \( n \) – the number of amino acids.

The lower the DCAS value, the more fully EAA is used for the needs of biosynthesis. **Biological value** of the product has been calculated by the formula,%:

\[ BV = 100 - DCAS, \]  

(5)

where, BV – Biological value of the protein,%.
During the assessment of biological value, it is very important to assess the level of mutual balance between the EAA and the NAA protein product, which is based on 4 biomedical positions:

1. The assimilation of the EAA protein product is carried out by the body: for the anabolic needs for the body (nitrogen balance restoration, the synthesis of special proteins) synthesis of NAA, for the energy needs of the body.
2. The use of EAA products for anabolic needs is a priority for the body compared to using them as precursors of NAA biosynthesis and to compensate for energy costs.
3. Due to imbalance, insufficiency or excess of EAA through degradation, they can be spent on the biosynthesis of interchangeable amino acids and energy purposes.
4. From the amount of EAA of the product for anabolic needs can be used a part that is proportional to the level of the first limited EAA, the score of which is calculated according to a reasonable norm, taking into account the physiological specificity of a consumers specific group. This fraction of EAA is the rationality coefficient of the amino acid composition of \( R_{rat} \) protein products and is calculated by the formula:

\[
R_{rat} = \sum_{j=1}^{k} EAA^{anab}_j = \sum_{j=1}^{k} A_j \cdot U_j \, ,
\]

where \( A_j \) – mass fraction of the j-th acid EAA in the product protein, mg/g of protein; \( U_j \) – utilitarian coefficient of the j-th EAA of protein, share units.

The other EAA will be used by the body either as precursors of the biosynthesis of NAA, or as energy material. Their distribution depends on the ratio between the amounts of EAA and NAA in the product, and the level of EAA in the regulatory protein.

In symbolic form, the provisions set forth can be written in a certain way:

\[
\{ R_{rat} \rightarrow \max \sum \text{biosynthesis of NAA} \, EAA \rightarrow \min; \sum \text{energy consumption} \, EAA \rightarrow \min \} 
\]

To assess the level of mutual balance between EAA and NAA in the product protein, 5 mutually exclusive options can be distinguished.

The following designations are introduced: \( \Sigma EAA \) – the total mass fraction of EAA in the evaluated protein; \( \Sigma E \) – is the total mass fraction of EAA in the reference protein; \( U \cdot \Sigma EAA \) – mass fraction of EAA mutual balance.

1. \( U = 1; \Sigma EAA > \Sigma E; C_{min} > 1 \); \( \Sigma EAA \to min; \Sigma E \to max \)
2. \( U = 1; \Sigma EAA \leq \Sigma E; C_{min} < 1 \); \( \Sigma EAA \to min; \Sigma E \to max \)
3. \( U < 1; \Sigma EAA > \Sigma E; C_{min} \geq 1; \Sigma EAA \cdot U \geq \Sigma E \); \( \Sigma EAA \to min; \Sigma E \to max \)
4. \( U < 1; \Sigma EAA \geq \Sigma E; C_{min} < 1; \Sigma EAA \cdot U < \Sigma E \); \( \Sigma EAA \to min; \Sigma E \to max \)
5. \( U < 1; \Sigma EAA < \Sigma E; C_{min} < 1 \)
the action of a protease system: pepsin and trypsin. The hydrolyzed product was diverted through a semipermeable membrane. The amount of protein in the resulting mixture have been determined by the Kjeldahl method. The obtained values are the digestibility of the protein of the studied product, expressed in mg of tyrosine per 1 g of protein. Recalculation of the indicator in percent is carried out according to the formula:

\[ D_{pr} = \frac{10 \cdot D}{T}, \]

where \( D_{pr} \) – the digestibility of the protein in the test product, % of the initial mass fraction of tyrosine in the product; \( D \) – the digestibility of the protein in the test sample, expressed in mg of tyrosine/1 g of protein; \( T \) – mass fraction of tyrosine in the protein of the test object, g/100 g of protein; 10 – proportionality coefficient.

Biological value research of milk-protein concentrates with malt ingredients will justify the feasibility of their implementation in a production environment.

Results and discussion

Determination of amino acid composition and biological value in milk-protein concentrates

Researches have shown that the total amino acid content in milk protein concentrates with malt ingredients increased compared to control due to the addition of germinated cereals (wheat, barley, oats, corn) (Tables 1 and 2). The combination of these plant components with milk protein concentrate is likely to increase the biological value of such compositions.

Table 1

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Control sample</th>
<th>With malt ingredients</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/100 g</td>
<td></td>
<td>Wheat</td>
<td>Barley</td>
<td>Oat</td>
<td>Corn</td>
</tr>
<tr>
<td>% to total amounts</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Valine</td>
<td>870.30</td>
<td>918.27</td>
<td>914.05</td>
<td>906.39</td>
<td>885.63</td>
<td>5.97</td>
</tr>
<tr>
<td>Isoleucine</td>
<td>793.80</td>
<td>829.75</td>
<td>824.09</td>
<td>821.20</td>
<td>814.32</td>
<td>5.26</td>
</tr>
<tr>
<td>Leucine</td>
<td>1491.61</td>
<td>1579.47</td>
<td>1562.71</td>
<td>1559.83</td>
<td>1569.26</td>
<td>10.26</td>
</tr>
<tr>
<td>Lysin</td>
<td>1159.37</td>
<td>1199.06</td>
<td>1202.50</td>
<td>1212.94</td>
<td>1184.41</td>
<td>7.68</td>
</tr>
<tr>
<td>Methionine</td>
<td>419.48</td>
<td>450.49</td>
<td>455.75</td>
<td>444.87</td>
<td>446.28</td>
<td>2.78</td>
</tr>
<tr>
<td>Threonine</td>
<td>599.35</td>
<td>641.70</td>
<td>636.04</td>
<td>643.66</td>
<td>631.83</td>
<td>3.97</td>
</tr>
<tr>
<td>Tryptophan</td>
<td>261.12</td>
<td>260.86</td>
<td>260.86</td>
<td>260.86</td>
<td>260.86</td>
<td>1.73</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>822.22</td>
<td>884.45</td>
<td>871.79</td>
<td>874.35</td>
<td>856.47</td>
<td>5.45</td>
</tr>
<tr>
<td>Amount</td>
<td>6417.25</td>
<td>6764.05</td>
<td>6727.80</td>
<td>6724.09</td>
<td>6649.06</td>
<td>42.51</td>
</tr>
</tbody>
</table>
Table 2
Nonessential amino acids of milk-protein concentrates with malt ingredients

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Control sample</th>
<th>With malt ingredients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wheat</td>
<td>Barley</td>
</tr>
<tr>
<td>Alanine</td>
<td>400.74</td>
<td>402.37</td>
</tr>
<tr>
<td></td>
<td>2.65</td>
<td>2.61</td>
</tr>
<tr>
<td>Arginine</td>
<td>668.31</td>
<td>655.68</td>
</tr>
<tr>
<td></td>
<td>4.43</td>
<td>4.26</td>
</tr>
<tr>
<td>Asparlic acid</td>
<td>897.48</td>
<td>874.54</td>
</tr>
<tr>
<td></td>
<td>5.95</td>
<td>5.68</td>
</tr>
<tr>
<td>Histidin</td>
<td>477.24</td>
<td>455.51</td>
</tr>
<tr>
<td></td>
<td>3.16</td>
<td>2.96</td>
</tr>
<tr>
<td>Glycine</td>
<td>239.16</td>
<td>264.44</td>
</tr>
<tr>
<td></td>
<td>1.58</td>
<td>1.72</td>
</tr>
<tr>
<td>Glutamic acid</td>
<td>2718.72</td>
<td>2788.95</td>
</tr>
<tr>
<td></td>
<td>18.01</td>
<td>18.12</td>
</tr>
<tr>
<td>Proline</td>
<td>1596.21</td>
<td>1567.39</td>
</tr>
<tr>
<td></td>
<td>10.57</td>
<td>10.18</td>
</tr>
<tr>
<td>Serine</td>
<td>744.19</td>
<td>730.57</td>
</tr>
<tr>
<td></td>
<td>4.93</td>
<td>4.75</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>837.89</td>
<td>783.40</td>
</tr>
<tr>
<td></td>
<td>5.55</td>
<td>5.09</td>
</tr>
<tr>
<td>Cystine</td>
<td>98.15</td>
<td>106.04</td>
</tr>
<tr>
<td></td>
<td>0.65</td>
<td>0.69</td>
</tr>
<tr>
<td>Amount</td>
<td>8678.09</td>
<td>8628.88</td>
</tr>
<tr>
<td></td>
<td>57.49</td>
<td>56.06</td>
</tr>
</tbody>
</table>

The compliance degree of the EAA content in the product with the FAO/WHO amino acid scale is calculated by the amino acid score (Cj,%) which shows by which EAA (one, two or more) studied protein is limited [3, 5, 6]. The amino acid score for the studied samples has been calculated. The obtained data indicate that the first limiting amino acids of the control and milk-protein concentrates with malt ingredients are methionine and cystine [7]. Moreover, the amino acid score of MPC obtained by traditional technology is 97.97%. This means that, in general, the norms of EAA MPC by the human body can fully use the following amount of amino acids [5], which is calculated by the formula:

\[ \sum EAA = 0.9897 \cdot \sum_{j=1}^{k} A_{oj}, \]

(14)

where \( \sum EAA \) – the full-fledged portion of the EAA in the product protein, g/100 g; \( A_{oj} \) – the amount of the j-th EAA in the ideal protein, g/100 g.
According to the calculations, when preparing the mixture: milk-protein concentrate + malt ingredients, the content of limiting amino acids increases – methionine + cystine and threonine. Liquidation of their deficit leads to an increase in the degree of use other EAA in milk protein concentrate to restore nitrogen balance and the synthesis of special proteins [1]. The amino acid score of the first limiting amino acids in milk-protein concentrates with malt ingredients is presented in Figure 1.

![Figure 1. Amino acid score of the first limiting amino acids in: milk-protein concentrate (control sample) (1) and milk-protein concentrates with malt ingredients – wheat (2), barley (3), oat (4), corn (5).](image)

The score of each amino acid gives a general idea about biological value of the product [3]. The body's use of protein for anabolic needs is limited by the content of the limiting amino acid, and all excess of other essential substances is used to compensate for the energy consumption and biosynthesis of NAA [4]. To assess the degree of protein utilization, the differential coefficient of amino acid score (DCAS) has been determined – the average excess amino acid scores of essential amino acids compared to score of limiting amino acid. The less DCAS, the more fully amino acids are used in the product. According to the theory of P. Chernikov, the indicator DCAS can be used to compare the biological value of food proteins [2].

Analyzing the obtained data of milk-protein concentrates with malt ingredients, we can conclude that the biological value of the experimental samples is increased. So, with wheat malt this indicator is 65.82%, barley – 65.57%, oat – 64.11%, corn – 63.95%, while for control purposes the value is fixed at 62.84%.

Balance assessment of the amino acid composition of proteins in milk-protein concentrates with malt ingredients is presented in Figure 2.
Figure 2. Balance assessment of the amino acid composition of proteins in (a, b): milk-protein concentrate (control sample) (1) and milk-protein concentrates with malt ingredients – wheat (2), barley (3), oat (4), corn (5).
According to the data (Figure 2), utilitarian coefficient compared with the control sample (0.72) increases and lies in the range 0.76–0.78 for milk-protein concentrates with malt ingredients, and the redundancy coefficient decreases from 13.72 (control sample) to 11.98. For model samples with barley malt, a high utilitarian coefficient (0.78) and a low redundancy coefficient (11.98) have been found, which indicates about better balance of EAA and their effective utilization.

According to five mutually exclusive options (formulas 8–12), the rationality coefficient of the amino acid composition has been calculated – $R_{rat} = \Sigma EAA_{bios} - \Sigma EAA_{energ}$. MPC (control sample) can be estimated by the fourth option ($R_{rat} = U$), and sample with malt ingredients – by the third option ($R_{rat} = U/C_{min}$) [23–25]. Consequently, the rationality coefficient of amino acid composition is 0.74±0.12, which is 3% higher than MPC obtained by traditional technology without malt.

It has found that the introduction of malt ingredients in MPC in the indicated amounts allows replacing part of the protein of animal origin with vegetable, without affecting the quality of the base. In addition, the developed milk protein concentrates with malt ingredients have an increased biological value compared to traditional ones, have dietary and preventive properties due to dietary fiber, macro- and microelements. In general, the research contributes to the rationale for malt using in the production of multicomponent milk-protein products of functional purpose.

**In vitro digestibility of proteins**

Correlation dependence between the biological value of proteins and their amino acid composition is possible only if the digestion rate of proteins is sufficient for digestive tract enzymes [27]. In this regard, for determining the nutritional value of milk protein concentrates with malt ingredients, an in vitro attacked protein complex of proteolytic enzymes, pepsin and trypsin, has been studied. The obtained results on the example of milk protein concentrate (control samples) without and with wheat malt are presented in Figure 3.
According to experimental data, the in vitro digestibility of proteins under the action of enzymes (pepsin + trypsin) with the introduction of malt ingredients in milk protein concentrates is accelerated. This is due to previous hydrolysis and destruction of protein substances during malting of cereals.

The represented data indicate that all samples are easily hydrolyzed. The resulting graphical dependencies have a similar tendency: the process in pepsin and trypsin stages most rapidly occurs in the first hour. The hydrolysis of MPC proteins after preliminary digestion with pepsin is accompanied by the release of the largest number of amino acids. Immediately after the trypsin is added to the system, the concentration of amino acids sharply increases and continues to increase continuously and intensively during the second stage of the experiment.

Conclusions

Amino acid composition and biological value, the balance of the amino acid composition of proteins in milk-protein concentrates with malt ingredients has determined by high-chromatography method.

The biological value of milk protein concentrates is increased for research samples with wheat malt by 2.98%, barley – 2.73%, oat – 1.27%, corn – 1.11% compared with the classic milk protein concentrate.

The rationality coefficient of amino acid composition for all research samples is 0.74±0.12, which is 3% higher than MPC obtained by traditional technology.

According to the classification of A. Pokrovsky all samples of milk-protein concentrates can be attributed to the first group of food products with a high degree of protein in vitro digestibility under the action of enzymes (pepsin + trypsin).

The introduction of malt ingredients in the amount of 5% by weight of MPK allows replacing part of the protein of animal origin with vegetable, without affecting the quality of the base.

The developed milk protein concentrates with malt ingredients have dietary and preventive properties due to dietary fiber, macro- and microelements.

In general, the research contributes to the rationale for malt using in the production of multicomponent milk-protein products of functional purpose.

References


Effect of calcium chloride on sodium alginate on the restructuring of fish products

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Keywords:
Fish
Carp
Restructured
Sodium alginate
Fillets

Abstract

Introduction. The purpose of this publication is to investigate the mechanism of the restructuring of fishery products using calcium chloride and sodium alginate.

Materials and methods. Minced fish fillet of carp (protein – 16.5±0.2%; fats – 1.2±0.03 %; minerals – 1.3±0.03 %); structure-forming agents are sodium alginate, calcium chloride (CaCl₂). The method of rotational viscometry – rheological characteristics; the method of energy absorption in the mid-wavelength range of the infrared spectrum – energy substances; spectrophotometry method and X-ray fluorescence method – mineral composition; descriptive and profile method – organoleptic indicators.

Results and discussion. Adding to the minced meat to 1.0 % of sodium alginate leads to an increase in the effective viscosity of the system to 3.6·10⁻³ Pa·s (shear rate \( \varepsilon = 1.8 \) s⁻¹). Increasing the concentration of sodium alginate from 2 to 3% leads to a similar increase in the effective viscosity from 6.9·10⁻³ to 12.6·10⁻³ Pa·s. At the same time, it was proved that the addition of sodium alginate with a concentration of 2.0 % ensures the complete formation of the structure of fishery products in the process of its formation.

It has been established that the process of structuring fishery products is intensified due to the duration of holding the fish mince/alginate system in a 5 % solution of CaCl₂ for (6–7)·60 s at the required level of effective viscosity. Increased structuring time (> 7·60 s) and subsequent formation lead to a further deterioration of organoleptic characteristics – the appearance of bitter taste, in the presence of free calcium ions.

On the basis of the study it is proved that in the concentration range of sodium alginate 1–3% there is an increase of water-holding capacity of fish products by 1.27–1.45 times. The maximum value of organoleptic indicators – 5 points received fish products with a concentration of sodium alginate 2.0–2.5 %. Further increase in the concentration of sodium alginate from 2.5 to 3.0% leads to an increase in the effective viscosity and gel-forming ability of the system and characterizes the samples with reduced organoleptic characteristics, which are characterized by the rigidity of the structure.

Conclusions. The obtained experimental data prove the influence of technological parameters and their rational values: the concentration of sodium alginate in the prescription mixture – 2.0–2.5%; concentration of calcium chloride in solution – 5.0%; the processing time of the formed samples in solutions of calcium chloride – (6–7)·60 s on the mechanism of restructuring of fishery products.

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Introduction

The above study relates to the food (Kuzmin et al, 2017) [1] and restaurant industry (Kuzmin et al, 2017) [2], namely, to the fish processing industry (Santeramo et al, 2018; Augustin et al, 2016; Pihlajamäki et al, 2018) [3–5]. An important place in human nutrition is taken by the consumption of fish (Anderson et al, 2018; Clark et al, 2018; Fabinyi et al, 2018; Skopenko, Tikhonova, 2013; Raišienė, Morkūnas, 2018; Solomianiuk et al, 2019) [6–11] and non-fish seafood (Anderson et al, 2018; Clark et al, 2018; Fabinyi et al, 2018) [6–8]. This is primarily due to the high nutritional and biological value of this product group and its high consumer properties (Popa et al, 2019; Ariño et al, 2013; Leonardo et al, 2016; Aberoumand, Ziaei-Nejad, 2015; Krumhout, de Goede, 2014; Raji et al, 2014; Butler et al, 2017; Keskin et al, 2019) [12–19].

Nowadays, the quality and assortment of fish products consumed in depends on the global market trends, most of which are increase prices for traditional fish raw materials (Biloukha, Utermohlen, 2000) [20], decrease in the volume of its catch (Martins et al, 2018) [21], impossibility of importing new types of fish, which is limited by law.

Most of the fish species studied are safe to be consumed. Therefore, this study is proposed to draw the attention of health and environmental authorities in need for appropriate regulatory framework (Jothi et al, 2018) [22].

In consequence of the technology of complex processing of raw fish materials (Samsonov et al, 2013; Huang et al, 2019; Tolosa et al, 2017; Han et al, 2017; Grassi et al, 2018) [23–27] from the country's inland water bodies (carps, silver carps, etc.) becomes important, whereby there is a reduction of depending on the external market, more rational use of the edible part of fish is provided, the range of fish products is expanded, and fuller use of raw materials for food purposes is provided.

Previous works reported the effect of processing methods on different fish types for determination of them nutritive values (Aberoumand, Ziaei-Nejad, 2015) [15].

In recent years, the processing of fish raw materials for mince and protein preparations has become widespread, followed by the formation of structured products based on them, including various analogues with a given composition and organoleptic properties, such as crab sticks (Otero et al, 2017; Campo-Deaño, Tovar, 2009; Hur et al, 2011) [28–30], crustacean meat analogues, and caviar of valuable fish species, etc. However, systematic studies aimed at obtaining a restructured fish product from fish in the country's inland waters have not found in the literature.

So, for today, the processing of carp fish species (Liu et al, 2016; Gao et al, 2019; Xu et al, 2010; An et al, 2018; Zhang et al, 2018; Abdollahi et al, 2017; Liu et al, 2014) [31–37] into structured analogues is hampered by an insufficient level of scientific researches, the lack of scientific bases for processing specific types of raw materials. Considering this, the development of a scientifically-based competitive technology of structured analogs of carp fillets for cooking is extremely important.

The aim of the publication is to develop a method of minced carp producing and determination of the effect of calcium chloride on sodium alginate on the restructuring of fish products.
Materials and methods

Materials

The subject of the study was selected mince, which was prepared from carp fillets (Grassi et al., 2018) [27]. At the first stage of research, the modes of mechanical processing of fish carcasses were justified (Liu, 2016) [31].

During the research, gutted frozen carp carcasses with a weight up to 300 g were used.

Defrosting was carried out in air (Xu et al., 2010) [33]. Fish was washed in running water (An et al., 2018) [34]. Flake removal was not performed. The blood kidney located under the vertebral bone was removed (Zhang et al., 2018) [35]. Cut off the head, cut carcasses and separated the fillets without skin and bones. Received food waste was directed to the production of feed products, it is known (Xu et al., 2010; An et al., 2018; Zhang et al., 2018) [33-35] that the cost of processing them for food purposes exceeds the profit obtained from the increase in production.

Description of methods

Sampling, leaching of mass of dry solids, ash and carried out by conventional methods (Horalachuk et al., 2006) [38].

The rheological parameter investigated is accessible by the method (Horalachuk et al., 2006) [38]. With early use of the cylinder system $S^2$ with a joyful clearance of $1.13 \times 10^{-3}$ m and a radius ratio of 1.06. A sample volume $(30\pm1.5) \times 10^{-3}$ dm$^3$ was placed into the outer steel cylinder, which is a measuring capacity of radius $r$. An inner cylinder of radius $r_b$ and height $l$ rotating at a constant velocity $\omega$ is connected through a measuring shaft to a cylindrical spring, the deviation of which is a measure of the torque $M$. The measurement system with zoom once is thermostatically controlled for 30 min. with the moment of torque activation. Measurement results were processed by the method (Horalachuk et al., 2006) [38].

Determination in macro and microelements allows us to estimate the X-ray fluorescence method on a spectrometer Spectroscan. Protein, fat, ash, and solids content were measured on a Bentley-150 device (Moore et al., 2009) [39].

The minimum composition was determined by the method of spectrophotometry on the atomic absorption spectrophotometer AAS-30 (Almeida, 2016) [40].

Sensory analysis of the samples was performed using descriptive and profile methods using a five-point scale (Kuzmin et al., 2018) [41].

Description of research procedure

As a result of the research, data were obtained on the yield of individual anatomical parts, are shown in Table 1.

<table>
<thead>
<tr>
<th>Title</th>
<th>Carp with a weight up to 300 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meat</td>
<td>49.0%</td>
</tr>
<tr>
<td>Food waste</td>
<td>47.1%</td>
</tr>
<tr>
<td>Losses</td>
<td>3.9%</td>
</tr>
</tbody>
</table>

Table 1
Studies of the literature (Liu et al, 2016; Gao et al, 2019; Xu et al, 2010; An et al, 2018) [31–34] have shown that carp is characterized by a specific "silty" smell, which can be removed by flavoring.

An aromatization mixture was developed, by tasting workings, including mustard (1.2%), garlic (0.65%), vinegar (3.0%).

To substantiate the aromatization regime, the fish fillet was kept in the aromatization mixture for 40·60 s at a temperature not higher than 18 °C. At the same time, the organoleptic properties of the fish were controlled, pre exposing its poaching. The results of the research are given in Table 2.

**Table 2**

<table>
<thead>
<tr>
<th>Aromatization time, s</th>
<th>The presence of &quot;silty&quot; smell</th>
</tr>
</thead>
<tbody>
<tr>
<td>10·60</td>
<td>Expressed</td>
</tr>
<tr>
<td>20·60</td>
<td>Mild</td>
</tr>
<tr>
<td>30·60</td>
<td>Absent</td>
</tr>
<tr>
<td>40·60</td>
<td>Absent</td>
</tr>
</tbody>
</table>

It is established that the exposure of carp fillet in the aroma mixture for 30·60 s allows to completely eliminate the "silty" smell. Thus, finished products palatability increased.

Milling of fish mass was carried out in two stages. First, the mass was passed through a meat grinder with a hole diameter of 3 mm. It was established that the intermuscular bone tissue of carp has a small strength and freely crushed to the specified sizes. Re-grinding was carried out on the cutter.

Processing of carp by this technology allows increasing the biological value of finished culinary products due to the elements of the chemical composition of bone tissue.

At the next stage, the chemical composition of the minced meat was investigated. The results of the study are given in Table 3.

**Table 3**

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Mass fraction to raw weight,%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids, including:</td>
<td>19.0±0.2</td>
</tr>
<tr>
<td>Proteins</td>
<td>16.5±0.2</td>
</tr>
<tr>
<td>Fats</td>
<td>1.2±0.03</td>
</tr>
<tr>
<td>Minerals</td>
<td>1.3±0.03</td>
</tr>
</tbody>
</table>

It is known (Kuzmin et al, 2017) [42] that during the storage of minced meat its structural and mechanical properties change significantly, accompanied by compaction of the structure due to the appearance of chemical bonds between proteins. At the same time minced meat presses moisture (Kuzmin et al, 2017) [42]. Reducing of meat stuffing and moisture loss is possible by reducing the concentration of solids (Kuzmin et al, 2017) [42].
Results and discussions

To study the effect of the solids content on the structural and mechanical properties of minced meat, drinking water was added to it to a solids content of 9.0 %. The results of the study are shown on Figure 1.

![Figure 1. Dependence of the effective viscosity of minced carp (η) from the concentration of dry substances (C)](image)

It has been established that a decrease of solids concentration and a protein component in particular, leads to viscosity of minced meat decrease. So, decrease of dry substances concentration from 19.0 to 9.0 % for minced carp, the viscosity decreases by 29.2 times.

It was found that during storage, pressing of moisture is not observed in minced carp at a humidity of 11.0 %. Therefore, these concentrations of dry substances are rational for restructured minced meat, which will ensure the fluidity of minced meat during formation.

At the same time, due to the protein interaction, the minced meat obtained during cooling and heating is not capable of forming homogeneous stable gels that imitating fish meat (Xu et al, 2010; An et al, 2018; Zhang et al, 2018) [33–35]. Therefore, it is necessary to attract additional gelation factors.

Regulation of the functional and technological properties of minced meat can be achieved by intake into its composition food ingredients that can simultaneously change the structural and mechanical parameters and increase the structuring ability (Xu et al, 2010) [33]. Sodium alginate meets these requirements, which, at certain concentrations, can increase the viscosity and the formative capacity of the prescription mixture, and allows ionotropic gelation to be used along with thermotropic ones (Khairou et al, 2002) [43]. At the same time, this makes it possible to avoid certain restrictions of prescription mixture of the formulation, in particular, the formation of a gel when the concentration of gel-forming protein compounds is lower than the critical one (Pérez-Mateos et al, 2002) [44].

The choice of sodium alginate as a gelling agent simultaneously takes into account the following requirements (Moreno et al, 2010) [45]:

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sodium alginate is compatible with the components of meat and can form gels in the presence of various nutrients, particular, proteins; it is able to form gels with a complex of physico-chemical parameters that will provide the necessary texture of the product, suitability for long-term storage; its using makes it possible to regulate the speed of the gelation process, particular, the course of the liquid system in a gel-like state; the absence of toxic and allergic effects, it is has simultaneously low cost.

It is known (Montero, Pérez-Mateos, 2002) [46] that a sufficient height of gelation of minced masses can be achieved with sodium alginate content up to 3 %.

At the next stage, the dependence of the viscosity of minced fish on the content of sodium alginate was investigated at a shear rate $\varepsilon=1.8$ s$^{-1}$ (Figure 2).

![Figure 2. Dependence of the effective viscosity of the samples on the content of sodium alginate:](image)

1 – minced carp with a moisture content of 11.0% (control); 2, 3, 4 – minced carp with a moisture content of 11.0% with the addition of 1.0%, 2.0%, 3.0% sodium alginate, respectively; 5 – minced carp with a moisture content of 19.0%

From the data shown on Figure 2, it is seen that the addition of sodium alginate leads to an increase in the viscosity of the systems. So, at a sodium alginate concentration of 1.0 %, the viscosity of the systems is $3.60 \cdot 10^{-3}$ Pa·s. The introduction of sodium alginate in concentrations of 2.0–3.0 % increases the viscosity to $(6.9–12.6) \cdot 10^{-3}$ Pa·s and provides a continuous structure of prescription mixture. The best structure is observed when the alginate content is 2 %, and the moisture does not precipitate.

Such minced systems are guaranteed ensure, within a certain time, the retention of a given shape when an extruded mass enters the liquid process medium, where the structure is consolidated (gelation) (Moreno et al, 2010) [45].

The obtained minced systems were subjected to heat treatment, which showed that for all the studied concentrations of sodium alginate, minced systems with a solids content of 11.0 % are not capable of forming thermotropic gels. Therefore, to obtain elastic gels, it is necessary to realize the ability of sodium alginate in ionotropic gelation (Khairou et al, 2002) [43].
Ionotropic gelation is a purely chemical process (Khairou et al, 2002) [43], so it is important to determine the parameters that ensure the progress of this reaction, the dynamics and the completeness of its completion. Whereas ionotropic gelation is associated with mass transfer of interacting components, it is necessary to determine rational concentrations that provide, on the one hand, ion-ion interaction, and on the other, the necessary structure indicators in accordance with the requirements of organoleptic indicators.

Extrusion molding a prescription mixture with sodium alginate content up to 3.0% followed by processing samples in calcium chloride solutions always leaves the conditions of a more significant concentration excess of Ca\(^{2+}\) ions over AlgCOO\(^{-}\) ions, which is guaranteed to ensure gelation. In the case of high concentrations of Ca\(^{2+}\) ions in solutions, short exposure to the solution is used; at low concentrations of Ca\(^{2+}\) ions in solutions, the processing time is increased. As a source of calcium ions, a solution of calcium chloride was chosen, the concentration of which was 5.0 %.

From the point of view of the implementation of technology restructured products is important to ensure the necessary organoleptic characteristics of the final products, therefore indicators such as the concentration of sodium alginate, calcium chloride and sample processing time in solutions of calcium chloride are key parameters of the process. The principle fact is in addition to the reaction, it is necessary to ensure the organoleptic characteristics of the product.

The effect of the duration of exposure of meat in a solution of calcium chloride and the concentration of sodium alginate on the structural and mechanical properties of meat were investigated (Figure 3).

![Figure 3](image_url)

**Figure 3. The dependence of the effective viscosity on the duration of structuring:**
minced meat with the addition of 1, 2, 3% sodium alginate, respectively
It was established that under all treatment conditions in CaCl<sub>2</sub> solutions with an increase in the concentration of sodium alginate in the prescription mixture in the range of 1–3%, the viscosity of the samples occurs. Increasing the processing time of samples in a solution of calcium chloride also contributes to viscosity increase. When the concentration of sodium alginate in the systems is 2 % and 3 %, the viscosity increases respectively 1.08 and 1.3 times. With an increase of processing time from 1·60 s to 7·60 s, the viscosity increases, respectively, 1.78 and 1.83 and 1.77 times for systems with sodium alginate contents of 1, 2, 3 % respectively. With further aging, viscosity growth almost does not occur.

The described patterns can be explained by the fact that over time the number of calcium bridges between the individual chains of sodium alginate molecules increases, which leads to their crosslinking and the formation of the spatial structure of the gel; with a low content of the amendment in the system, the distance between the macromolecules of sodium alginate is significant, so the formation of a solid gel network does not occur (Yong, Mooney, 2012) [47].

Thus, the most rational concentrations of sodium alginate, the required viscosity level of the structured systems is provided, lies in the range of 2.0–3.0 % with a duration of formation (6–7)·60 s.

The increase of structuring time causes the appearance of a bitter taste due to the presence of free calcium ions, which did not react with sodium alginate (Senturk Parreidt et al, 2018) [48].

Along the study of the structural and mechanical characteristics changes, some of its functional and technological properties, particular, its water-retaining capacity, was determined (Figure 4).

![Figure 4. Dependence of the water-retaining capacity (WRC) of gels from the concentration of sodium alginate: (C_{CaCl_2}=5\%, \ \tau=7\cdot60 \ s)](image)

It has been established that sodium alginate in the concentration range of 1.0–3.0 % contributes to increase in the water-retaining capacity of samples by 1.45 times – from 64 % to 93 %. At a concentration of sodium alginate of 2.0 % (compared to 1.0 %), the water-retaining capacity of the systems increases by 1.27 times – from 64 % to 81 %. A further increase the concentration of sodium alginate also leads to water-retaining capacity increase,
the value of which increases 1.15 times. This can be explained by the fact that, all other things being equal, with an increase the concentration of the gelling agent, the residual amount of sodium alginate, that did not take part in the ion exchange reaction, increases, that causes an increase of water-retaining capacity (Tønnesen, Karlsen, 2002) [49].

In parallel with the determination of the water-retaining capacity, an organoleptic assessment of ionotropic gels was carried out. It was established that the maximum number of points (5) correspond to samples with the concentration of sodium alginate 2.0–2.5 %. An increase the concentration of the gelling agent to 3.0 % (with a simultaneous increase of the water-retaining capacity), the samples are characterized as too rigid. That is, exceeding the concentration of sodium alginate with 2.5 % leads to the fact that ionotropic gels become uncharacteristic for fish meat that causes a decrease of organoleptic characteristics.

Thus, the conducted studies and results of organoleptic assessment allowed determining the rational values of the technological parameters of the formation of restructured systems based on minced fish that are listed in Table 4.

### Table 4

<table>
<thead>
<tr>
<th>Parameters’ title</th>
<th>Units of measurement</th>
<th>Limiting values</th>
</tr>
</thead>
<tbody>
<tr>
<td>The concentration of sodium alginate in the prescription mixture</td>
<td>%</td>
<td>2.0…2.5</td>
</tr>
<tr>
<td>The concentration of calcium chloride in the solution</td>
<td>%</td>
<td>5.0</td>
</tr>
<tr>
<td>The processing time of the formed samples in solutions of calcium chloride</td>
<td>60, s</td>
<td>6–7</td>
</tr>
</tbody>
</table>

Conducted researches allowed determining the rational content of the main prescription components and developing a technological scheme for the production of semi-finished products. The technological process is carried out in the following sequence:

− minced fish, solutions of sodium alginate, salt, sugar, egg powder, starch, sunflower oil combine and mix thoroughly, until the components are evenly distributed in the recipe mix;
− prescription mixture formation carrying out by using a pressure press, for which the mass is spread on the forms and press the press to seal the structure;
− formed prescription mixture is fed to the reception bath with a calcium chloride solution of 5.0 % concentration and kept at a temperature 8–20 °C for (6–7)·60 s for structuring;
− structured semi-finished products, that are located in perforated containers, are treated in 0.15 % sodium alginate solution at a temperature 18–20 °C in order to remove excess free \( Ca^{2+} \) ions;
− semi-finished products processed in sodium alginate solutions are sent to a cooled chamber at a temperature 2–6 °C for (0.5–1.0)·60² s for fixing a structure.
Conclusions

Fish product from carp, obtained according to that technological scheme, is a semi-finished product of high degree of readiness, which by its organoleptic properties imitates fish meat. This product is new in the existing assortment of restructured fish products; therefore it is advisable to investigate its main indicators of quality in the future.

Conducted researches allowed us to develop recommendations on the use of fish product from carp in the composition of culinary products and determine the effect of calcium chloride on sodium alginate on the restructuring of fish products. It has been established that fish product from carp can be used in the production of cold dishes and snacks, hot snacks, soups, fish dishes, etc.

Summing up the results of research, it should be noted that the use of fish product from carp in the composition of culinary products allows to expand its range, offer products with new consumer properties, improve the efficiency of the enterprises of restaurant business through the use of products in the form of semi-finished products.

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Features of the formation of taste sensations

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Abstract

Introduction. An important characteristic that reflects the quality and forms the price of any food product is its organoleptic properties, for example, taste sensations arising from the use of the product. Currently, there is not enough data that reliably describes the mechanism of occurrence of taste sensations.

Materials and Methods. The subject of research was carbohydrates, proteins, and sodium chloride. The phase structure was studied by x-ray diffraction. Diffraction curves were recorded on an HZG 4A X-ray diffractometer (Carl Zeiss, Jena) using radiation of copper (CuKα) filtered by nickel. Scanning electron micrographs of native starch granules were obtained using a LEO 1420 scanning (scanning) electron microscope.

Results and discussion. The phase and morphological structure of carbohydrates (monosaccharides, disaccharides and polysaccharides) and sodium chloride were studied, as well as the morphological structure of milk proteins. Among carbohydrates, glucose, fructose, sucrose, maltose, lactose, and rhamnose have been found to have a crystalline structure, native starches have an amorphous-crystalline (transitional or intermediate) structure, and maltodextrins have an amorphous structure. Salt has a crystalline structure.

It is shown that in the formation of taste sensations, the geometry of the taste buds of the tongue and the geometry of the analyzed taste objects, which are created in accordance with the principle of complementarity (for example, a lock), are of great importance. Taste language analyzers and analyzed taste objects are universal in size and have a fractal structure. The smallest indivisible fractal unit is an electron. The fractal structure of the taste analyzers is continuous, and the analyzed taste objects are intermittent and depend on the degree of purity of the object. Many substances (protein molecules, etc.) have a complex hierarchical structure and are able to gradually demonstrate their taste characteristics, that is, at each of the hierarchical levels of organization, these substances have their own taste characteristics. Moreover, it often happens that at the last hierarchical level, the geometry of these substances tends to a spherical (neutral) shape. Smell as well as taste is one of the types of chemoreception, therefore, the features of the formation of sensations of smell are similar to the formation of taste sensations.

Conclusion. A hypothesis has been put forward about chemoreception, in particular about the formation of taste sensations, which made it possible to lay the foundations of a mathematical description of taste.
Introduction

An important characteristic reflecting the quality and forming the price of any food product are organoleptic properties, for example, arising from the use of the product taste. Despite the large number of scientific works [1–13] devoted to the study, until now there is no universally recognized and reliable mechanism for the occurrence of taste sensations. Thus, the features of the formation of a bitter taste are discussed in scientific works [1–4, 6, 7], sour – [8–10], and taste by the minds – [12]. The effect of ethyl alcohol and narcotic substances on the perception of bitter taste is shown in the study [1]. The taste perception of amino acids is described in a scientific paper [13]. It is believed that the perception of taste in a certain way depends on the anatomy of taste analyzers [14, 15]. The aim of this research is to study the distinguishing features of the formation of taste sensations in humans.

Materials and methods

Materials

The object of research were carbohydrates (glucose, fructose, sucrose, maltose, lactose, rhamnose, native starch (potato, corn, rice, pea) and maltodextrins (potato, corn)), and also proteins (dry milk products (whey protein concentrate KSB-UV-80 (JSC Schuchinsky MSZ)), whole milk powder for baby food with a fat content of 25% (Bellact), skimmed milk powder (Bellact) cheese demineralized whey 50% (Institute of Meat and Dairy Industry), whey protein concentrate with microparticles Promilk 630M, whey protein concentrate Simplesse 100E)) and sodium chloride (NaCl).

Radiography method

Analysis. The phase structure was investigated by radiography [16, 17]. Samples for recording X-ray diffractograms were prepared in the form of monolithic flat-cylindrical Tablets with a smooth surface. Press pressure was not less than 100 kg/cm². The duration of exposure to the press – from 15 to 30 minutes, depending on the type of sample. All Tablets were the same size. Diffraction curves were recorded on an X-ray diffractometer HZG 4A (Carl Zeiss, Jena) using copper (CuKα) radiation filtered by nickel. All curves were obtained in absolutely identical conditions, in step mode of discrete scanning.

Crystallinity calculation. Radiographs of the samples were described in the «reflection» mode. The degree of crystallinity was calculated as the ratio of intensities of $I_k/I_o$, where $I_k$ is the intensity of X-ray diffraction on crystal regions; $I_o$ is the total intensity of X-ray diffraction.

Scanning Electron Microscopy (SEM)

Sample preparation. Metallization of native starch preparations was carried out with gold in the EMITECH K 550X vacuum unit.

Analysis. Scanning electron micrographs of native starch granules were obtained using a LEO 1420 scanning (raster) electron microscope (Germany) [18, 19].
Results and discussion

Classical atomic and physiological ideas about the formation of taste sensations

Taste is one of the types of chemoreception. This is a feeling that arise when exposed to a variety of substances on the taste receptors located on the taste buds of the tongue, as well as the back wall of the pharynx, soft palate, tonsils, epiglottis. The scheme of the location of taste receptors on the human tongue is shown in Figure 1 [14, 15, 20, 21]. The sense of taste develops with the direct participation of the branches of the facial and glandular nerves, providing taste sensitivity to the front 2/3 and back 1/3 of the tongue, respectively.

![Figure 1. Scheme of the location of taste buds on the human tongue](image)

Briefly, there are four main flavors: sweet, bitter, sour and salty. However, there are also other types of taste: astringent, pungent, minty, alkaline, metal, etc. and many flavors.

Information from the taste receptors is transmitted by afferent fibers of the facial, lingual and vagal cranial nerves to the nuclei of a single pathway of the medulla oblongata, then switching occurs in the nuclei of the thalamus and then in the postcentral gyrus and islet (lat. insula) of the cerebral cortex, where the taste sensations are formed [14]. According to others, the cortical end of the taste system is parahippocampal or hook gyrus (lat. gyrus parahippocampalis or gyrus uncinatus) and in the hippocampus (lat. hippocampus) [15].

According to modern concepts, all substances consist of atoms, molecules and ions united by means of various types of chemical bonds (covalent, ionic, hydrogen) and other interactions. So, the atom (gr. ἄτομος – indivisible, uncut) – a particle of matter of microscopic size and mass, the smallest part of the chemical element, which is the carrier of its properties. The molecule – the smallest particle of matter that determines its properties and is capable of independent existence, which is a set of two or more atoms. The ion (Greek. ἵον-running) – electrically charged non-elementary particle (atom, molecule, free radical), having a positive or negative charge of electricity, is divisible by the electron charge (positively charged ion – cation, negatively charged ion – anion) [22, 23].

All the variety of chemical (inorganic and organic) molecules has its own unique spatial geometry. Organic compounds are carbon compounds formed primarily by hybrid orbitals. Hybridization of orbitals is a hypothetical process of mixing different (s, p, d, f) orbitals of the central atom of a polyatomic molecule with the appearance of identical orbitals, equivalent in their characteristics [22]. The main expected equilibrium configurations of organic molecules are presented in Table 1.
Expected equilibrium configurations of organic molecules

<table>
<thead>
<tr>
<th>Hybrid orbitals</th>
<th>Equilibrium configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp</td>
<td>Linear</td>
</tr>
<tr>
<td>sd</td>
<td>Angular</td>
</tr>
<tr>
<td>sp²</td>
<td>Flat equilateral triangle</td>
</tr>
<tr>
<td>sp³</td>
<td>Tetrahedron</td>
</tr>
<tr>
<td>sp²d</td>
<td>Square</td>
</tr>
<tr>
<td>sp³d²</td>
<td>Octahedron</td>
</tr>
<tr>
<td>sp³d</td>
<td>Trigonal bipyramide</td>
</tr>
<tr>
<td>sp³d⁴</td>
<td>Dodecahedron</td>
</tr>
</tbody>
</table>

Experimental and theoretical research results

Carbohydrate research

The results of our X-ray structural analysis of organic compounds are shown in Figure 2–4.

Thus, data in Figure 2 shows the radiographs of carbohydrates: glucose, fructose, rhamnose, mannose, lactose and maltose, Figure 3 – radiographs of sucrose, and Figure 4 – radiographs of carbohydrates: native starch (potato, corn, rice, pea) and maltodextrins (potato and corn).

Normal, grown in a pure solution of the crystal (i.e., a substance with a molecular structure which is natural for it a grate) sucrose is a complex multi-faceted (more than 15 faces) form of sphenoidale-semiprismal class (a combination of six crystallographic forms) and belongs to wedge-like rhombic or monoclinically systems with the three crystallographic axes in space: vertical (C), horizontal (B) and the axis (A) inclined at angles 103°30’ to the vertical, and 90° to the horizontal (Figure 2 and Table 2) [24, 25]. The ratio of the lengths of the axes within the crystal $A : B : C = 1,2595 : 1,0 : 0,8782$. 15 types of sucrose crystals are known, double crystals are often observed, the shape of the crystals depends on the conditions of the crystallization process, impurities in the initial solution and the degree of supersaturation of sucrose with this solution (Table 2).

Table 2

Main characteristics of sucrose crystals

<table>
<thead>
<tr>
<th>Indicators</th>
<th>Meas. unit</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of the crystal</td>
<td>mg</td>
<td>0,1</td>
</tr>
<tr>
<td>Length of the crystal</td>
<td>cm</td>
<td>0,057</td>
</tr>
<tr>
<td>Volume of the crystal</td>
<td>cm³</td>
<td>0,000063</td>
</tr>
<tr>
<td>Crystal surface</td>
<td>cm²</td>
<td>0,0099</td>
</tr>
<tr>
<td>Number of crystals in 1 g</td>
<td>ps.</td>
<td>10000</td>
</tr>
<tr>
<td>Surface of all the crystals</td>
<td>sm²</td>
<td>99,1</td>
</tr>
</tbody>
</table>
Figure 2 – Radiographs of carbohydrates
1 – glucose; 2 – fructose; 3 – rhamnose; 4 – mannose; 5 – lactose; 6 – maltose
Features of the amorphous crystal structure of the starch granules are shown in Figure 5. Starch granules consist of alternating between crystalline and amorphous regions [26]. The amorphous part of the granules forms a continuous phase and includes crystalline starch formation such as lamellae. Depending on the structural organization of the crystal areas of starch granules are divided into A- and B-type. A-type refers to the starch of cereals, b-type – starch tubers and bulbs. The crystal structures of A- and B-types belong to the amylosis part of the starch and consist of parallel twisted right double helices packed antiparallel. Each spiral contains six residues of α-D-glucopyranose. Within the spiral formed channel with a diameter of 0,5 nm. The conformations of the double helix of amylose in A- and B-structures are the same, but the A-structure is characterized by an orthorhombic unit cell with parameters a = 1,190 nm, b = 1,770 nm, c = 1,052 nm, while the B structure is characterized by a hexagonal unit cell with parameters a = b = 1,85 nm, c = 1,04 nm. Complexes of amylose with lipids in the natural starch form a structure of V-type. The degree of crystallinity of natural starch depends on its origin and is 15–45%.

Figures 2 and 3 show that there are compounds with a crystalline structure (glucose, fructose, sucrose, maltose, lactose and rhamnose) among carbohydrates, with an amorphous-crystalline (transition or intermediate) structure (native starches) and with an amorphous structure (maltodextrins). It should be noted that carbohydrates with a crystal structure have a pronounced sweetness, and carbohydrates with an amorphous-crystalline and amorphous structure did not have a well-pronounced sweet taste. It should be noted that the geometry of the crystals in each of the studied compounds having a crystal structure is unique.

Substances having an amorphous-crystalline or amorphous (especially amorphous) structure in an ideal state form a supramolecular structure that tends in its form to be spherical (Figure 6). Ball – a geometric body; the set of all points of space, located from the center at a distance, no more than a given. This distance is called the radius of the ball. The ball is formed by rotating a circle or semicircle around its fixed diameter. This diameter is called the axis of the ball, and both ends of the specified diameter – the poles of the ball. The surface of the ball is called a sphere: a closed ball includes this sphere, an open ball excludes. All flat sections of the ball are circles. The largest circle lies in the section passing through the center of the ball (sphere), and is called the big circle. Its radius is equal to the radius of the ball (sphere). Thus, the ball (sphere) – an infinite number of ordered arranged circles.
Figure 4. Radiographs of carbohydrates:
Native starch: 1 – potato; 2 – corn; 3 – rice; 4 – pea.
Maltodextrins: 5 – potato; 6 – corn.
Figure 5. Features of amorphous crystal structure of native starch:

- **a** – possible variants for twisting amylose;
- **b** – crystalline areas of starch (crystallites);
- **c** – the structure of the water molecule;
- **d** – the structure of amylopectin:
  - A – amorphous lamella, K – crystal lamella;
- **e** – the structure of the starch granules:
  - 1 – amylopectin spirals;
  - 2 – hybrid spirals of amylose and amylopectin;
  - 3 – free lipids;
  - 4 – free amylose;
  - 5 – V-structure of amylose
A circle is a special (unique) geometric Figure that combines two opposites: finiteness and infinity. Infinity in the circle can be considered the length of the circle (it has no beginning or end), and the limb – the diameter and chords of the circle (they are always limited to two points lying on the circle).

Thus, the matter striving to get out of the state of infinity (non-manifestation) and become finite (manifested) chose the circle for its primary organization, since it is an intermediate stable state between infinity and finiteness. The circle can be otherwise called finite infinity or infinite finiteness, i.e. it is a figure in which two dialectical opposites converged. In this case, the number PI – π (the ratio of the circumference and its diameter) [27, 28] can be considered as an asymmetry between infinity and finiteness. In addition, the length of an infinitely large circle can be considered as an infinite straight line, because in
these conditions, the curvature is infinitely small, it can be equated to zero. Therefore, the circle, the diameter of which tends to infinity can be taken as a straight line, which closes itself. At the same time, if the diameter of the circle tends to zero, the length of the circle can be considered a straight line equal to the point.

Salt research

Sodium chloride (NaCl, sodium chloride) is a sodium salt of hydrochloric acid, known in everyday life as Table salt [29, 30]. It occurs in sea water in the form of the mineral halite (rock salt). Pure sodium chloride is a colorless crystals, but with various impurities its color can acquire blue, purple, pink, yellow or gray. Sodium chloride has a face-centered cubic crystal structure, with the ions Na\(^+\) and Cl\(^-\) have octahedral coordination geometry (Figure 7).

![Image](image_url)

**Figure 7 – Features of the structure of sodium chloride:**
1 – radiograph; 2 – scanning electron microphotography

Proposed hypothesis of chemoreception on the example of the formation of taste sensations

It is known that the number of regular and semi-regular polyhedra in nature is limited [31, 32]. Thus, Table 3 shows all known regular polyhedra, and Table 4 shows all semi-regular polyhedra.

Natural crystals have only some elements of symmetry, among which are: the center of symmetry, symmetry axes of the second order, the third order, the fourth order, the sixth order, the mirror-rotating axes of the fourth and third order, the plane of symmetry [31]. The axis of symmetry of the fifth order in the crystals does not occur, since the angle of the Pentagon is 108°, and this number is not divided by the angle of 360°. There are 32 combinations of symmetry elements peculiar to crystals. These combinations are called symmetry types or classes of crystals.

Thirty-two types (classes) of symmetry crystals are divided into six systems or crystal symmetry [33]:

1. A cubic system (sometimes called isometric) with third-and fourth-order symmetry axes (fourth-order axes can be of mirror-rotating type).
2. Tetragonal system with one fourth-order axis.
3. Hexagonal or trigonal system (includes rhombohedral crystals) with one axis of the sixth order or one axis of the third order.
4. Rhombic system with two or three planes of symmetry or axes of symmetry of the second order, forming right angles to each other.
5. Monoclinic system with one plane or one axis of the second order, or with both elements of symmetry.
6. Triclinic system with the center of symmetry or without symmetry elements.

### Table 3

<table>
<thead>
<tr>
<th>Name</th>
<th>Appearance</th>
<th>Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tetrahedron</strong></td>
<td><img src="image" alt="Tetrahedron" /></td>
<td>face – triangle, faces – 4, ribs – 6, vertices – 4, faces at the top – 3, symmetry group – tetrahedral (Th).</td>
</tr>
<tr>
<td>(ancient Greek τετρά-εδρον – tetrahedron, from ancient Greek τέσσερες, τέσσερες, τέτταρες, τέττορες – &quot;four&quot; + ancient Greek ἔδρα – «seat, base»)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Octahedron</strong></td>
<td><img src="image" alt="Octahedron" /></td>
<td>face – triangle, faces – 8, ribs – 12, vertices – 6, faces at the top – 4, symmetry group – octahedral (Oh).</td>
</tr>
<tr>
<td>(ancient Greek οκτάεδρον, from ancient Greek οκτώ, eight and ἔδρα – «seat, base»)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Icosahedron</strong></td>
<td><img src="image" alt="Icosahedron" /></td>
<td>face – triangle, faces – 20, ribs – 30, peaks – 12, faces at the top – 5, symmetry group – icosahedral (Ih).</td>
</tr>
<tr>
<td>(from ancient Greek εἴκοσι &quot;twenty&quot;; ἔδρα - &quot;seat&quot;, «base»)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cube</strong></td>
<td><img src="image" alt="Cube" /></td>
<td>face – square, faces – 6, ribs – 12, vertices – 8, faces at the top – 3, symmetry group – octahedral (Oh).</td>
</tr>
<tr>
<td>(ancient Greek κύβος) or the correct hexahedron (&quot;correct hexahedron&quot; from ancient Greek ἕξας – six &quot; and ancient Greek ἔδρα – «seat, base»)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Dodecahedron</strong></td>
<td><img src="image" alt="Dodecahedron" /></td>
<td>face - Pentagon, faces – 12, ribs – 30, vertices – 20, faces at the top – 3, symmetry group – icosahedral (Ih).</td>
</tr>
<tr>
<td>(from Greek δώδεκα – twelve and Greek ἔδρον – «seat, base»)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Table 4**

Main characteristic of semi-regular polyhedra (Archimedean and Catalan solids)

<table>
<thead>
<tr>
<th>Archimedean solids</th>
<th>Characteristic</th>
<th>Catalan solids</th>
<th>Name and appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cuboctahedron</td>
<td>faces – 8 triangles and 6 squares, ribs – 24, vertices – 12, the symmetry group – octahedral (Oh).</td>
<td>Rhombic dodecahedron</td>
<td>(Oh)</td>
</tr>
<tr>
<td>Icosidodecahedron</td>
<td>faces – 20 triangles and 12 pentagons, ribs – 60, vertices – 30, the symmetry group – icosahedral (Ih)</td>
<td>Rhombic triacontahedron</td>
<td>(Ih)</td>
</tr>
<tr>
<td>Truncated tetrahedron</td>
<td>faces – 4 triangles and 4 hexagons, ribs – 18, vertices – 12, the symmetry group – tetrahedral (Th).</td>
<td>Triakistetrahedron</td>
<td>(Th)</td>
</tr>
<tr>
<td>Truncated octahedron</td>
<td>faces – 6 squares and 8 hexagons, ribs – 36, vertices – 24, the symmetry group – octahedral (Oh).</td>
<td>Broken cube (tetrakishexahedron)</td>
<td>(Oh)</td>
</tr>
</tbody>
</table>
Table 4 (Continue)

<table>
<thead>
<tr>
<th>Shape</th>
<th>Faces Description</th>
<th>Edges</th>
<th>Vertices</th>
<th>Symmetry Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Truncated icosahedron</td>
<td>12 pentagons and 20 hexagons, 90 ribs, 60 vertices (Ih)</td>
<td>90</td>
<td>60</td>
<td>Icosahedral (Ih)</td>
</tr>
<tr>
<td>Pentakisdodecahedron</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Truncated cube</td>
<td>8 triangles and 6 octagons, 36 ribs, 24 vertices (Oh)</td>
<td>36</td>
<td>24</td>
<td>Octahedral (Oh)</td>
</tr>
<tr>
<td>Pentakisdodecahedron</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Truncated dodecahedron</td>
<td>20 triangles and 12 decagons, 90 ribs, 60 vertices (Ih)</td>
<td>90</td>
<td>60</td>
<td>Icosahedral (Ih)</td>
</tr>
<tr>
<td>Triakisoctahedron</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rhombicuboctahedron</td>
<td>8 triangles, 18 squares (6 in cubic position, 12 in rhombic), 48 ribs, 24 vertices (Oh)</td>
<td>48</td>
<td>24</td>
<td>Octahedral (Oh)</td>
</tr>
<tr>
<td>Deltoid icositetrahedron</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rhombicosidodecahedron</td>
<td>20 triangles, 30 squares, and 12 pentagons, 120 ribs, 60 vertices (Ih)</td>
<td>120</td>
<td>60</td>
<td>Icosahedral (Ih)</td>
</tr>
<tr>
<td>Deltoidal hexecontahedron</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rhombo truncated cubic octahedron</td>
<td>Hexakis octahedron</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------------------</td>
<td>------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>faces - 12 squares, 8 hexagons, and 6 octagons, ribs – 72, vertices – 48, the symmetry group - octahedral (Oh).</td>
<td>(Oh)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rombo truncated icosidodecahedron</th>
<th>Hexakis octahedron</th>
</tr>
</thead>
<tbody>
<tr>
<td>faces - 30 squares, 20 hexagons, and 12 decagons, ribs – 180, vertices – 120, the symmetry group – icosahedral (Ih).</td>
<td>(Ih)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Snub-nosed cube</th>
<th>Pentagonal icositetrahedron</th>
</tr>
</thead>
<tbody>
<tr>
<td>faces – 32 triangles and 6 squares, ribs – 60, vertices – 24, the symmetry group - octahedral (O).</td>
<td>(O)</td>
</tr>
</tbody>
</table>
Snub-nosed dodecahedron

 faces – 80 triangles and 12 pentagons,
 ribs – 150,
 vertices – 60,
 the symmetry group – icosahedral (I).

Pentagonal hexecontahedron

Table 4 (Continue)

Crystals and their elementary cells can be described by axes of symmetry, which in some cases can be located at right angles to one another, in others at angles of 120° (in the case of hexagonal and trigonal systems), or at other angles. Different systems are characterized by the following types of axes [33]:

- cubic system: three equal mutually perpendicular axes of length a;
- tetragonal system: two equal axes of length a and third axis of length c; all axes are mutually perpendicular;
- hexagonal or trigonal system: two equal axes of length a form an angle of 120°, the third axis of length c is at right angles to the first two;
- rhombic system: three axes of length, respectively, a, b, c, arranged perpendicular to each other;
- monoclinic system: two axes (a and c) form an angle β, and the third axis b is at right angles to the axes a and c;
- triclinic system: three axes a, b and c form angles α, β and γ.

There must be rational relations between the crystal faces and the axes: the segments of the axes cut off by the face refer to the lengths of the axes a, b and c as Prime numbers.

By types of bonds all crystals can be divided into 5 groups [33]: ionic, covalent, metal, molecular and crystals with hydrogen bonds.

Thus, it can be assumed that the formation of taste sensations of great importance belongs to the geometry of the analyzed object. Apparently, the geometry of the taste receptors of the tongue and the analyzed taste objects is created on the principle of complementarity (i.e., by the type of lock-key) (Figure 8).

It is important to note that the analyzed objects of taste have not only a unique geometry and different sizes. Probably, taste analyzers are universal in relation to the size of the analyzed object and have a fractal structure that allows you to accurately determine the taste of any test sample [34].
Figure 8. Possible geometry options on the principle of complementarity of the taste buds of the tongue and objects of taste:
1 – the object of taste; 2 – the taste receptor of the tongue; 3 – the surface of the tongue.

Fractal (lat. fractus – crushed, broken, broken) – a mathematical set that has the property of self-similarity, that is, uniformity in different scales of measurement. In mathematics, fractals are understood as sets of points in Euclidean space that have a fractional metric dimension (in the sense of Minkowski or Hausdorff), or a metric dimension different from the topological, so they should be distinguished from other geometric Figures limited by a finite number of links [34]. The most well-known at present and simple fractals (Koch curve, Levy curve and Hilbert curve) are presented in Figure 9.

Figure 9. Known fractals:
1–6 – step-by-step construction of fractal curves

The fractal structure of the taste analyzers seems to be continuous. The surface geometry of the analyzed taste object has a complementary discontinuous fractal structure. The discontinuity of the fractal in the analyzed object of taste is probably due to the presence of various impurities. In nature, there are no completely pure substances. Due to the presence of a unique fractal discontinuity in various analyzed objects of taste there is a possibility of existence of such a large (infinite) variety of flavors.
The smallest indivisible unit of a fractal, as the taste buds, and analyzed the object of taste is an electron. It is this elementary particle (electron) that determines the General geometry of fractals of taste analyzers and the analyzed object of taste. In addition, the number of electrons at the last energy level in atoms determines the complementarity of taste analyzers and the analyzed object of taste.

Currently, it is not known what an electron is and what geometry it has. So, once S. Berkovich admitted to L. Landau that no matter how «hollows» quantum mechanics, and the very essence of it can not grasp [35].

If our assumption is correct, taste receptors and analyzed taste objects have a fractal-complementary structure, any type of taste and any flavor shade can be expressed by a mathematical formula.

It is now established that G-proteins are of great importance in the taste receptors of the tongue responsible for the perception of sweet and bitter taste [36]. So, G-proteins (persistent. G proteins) are a family of proteins related to GTPases that function as secondary mediators in intracellular signal cascades [37]. G-proteins are so named because in their signaling mechanism they use the replacement of GDP by GTP as a molecular functional «switch» to regulate cellular processes. G-proteins were discovered and studied by Alfred Gilman and Martin Rodbell, who received the 1994 Nobel prize in physiology or medicine for this discovery [38, 39]. G-proteins are divided into two main groups – heterotrimeric («large») and «small». Heterotrimeric G-proteins are proteins with Quaternary structure consisting of three subunits: alpha(α), beta (β) and gamma (γ). Small G-proteins are proteins from one polypeptide chain, they have a molecular mass of 20–25 kDa and belong to the superfamily of Ras small GTPase. Their single polypeptide chain is homologous to the α-subunit of heterotrimeric G-proteins. Both groups of G-proteins participate in intracellular signaling [37].

In the work of many G-proteins involved auxiliary proteins. GAPs (GTPase Activating Proteins, proteins-activators GTPase activity) accelerate the hydrolysis of GTP by accelerating the inactivation of G-proteins [37]. The function of GAPs is especially important for small G-proteins, because alpha subunits of heterotrimeric G-proteins often have sufficient GTPase activity themselves. Gap proteins are proteins of the RGS family.

GEFs (Guanine nucleotide Exchange Factors, guanyl nucleotide exchange factors), accelerate the exchange of GDF to GTP and thus activate G-proteins [37]. Typically, G-protein GEF-Ohm is activated by a ligand receptor, but in some cases, AGS proteins (Activator of G-protein signaling, g-protein signal transfer activators) can activate G-protein regardless of the effects of the receptor on it.

**Studies of milk proteins**

Many substances have a complex hierarchical structure and are able to «reveal» their taste characteristics stepwise, i.e. at each of the hierarchical levels of the organization of these substances have their taste characteristics. At the same time, it often happens that at the last hierarchical level the geometry of these substances tends to a spherical (neutral) form. To substances with complex and multilevel geometry can be attributed protein molecules (Figure 10 and 11).
Figure 10. Features of the structure of protein molecules:

- **a** – levels of protein molecule structure;
- **b** – microparticulated whey protein concentrate Promilk 630M;
- **c** – whey protein concentrate KSB-UV-10 (JSC «Shchuchinsky MSZ»).
Thus, protein molecules have primary, secondary, tertiary and quaternary structures [38, 39]:

1. The primary structure is the sequence of amino acid residues in the polypeptide chain of a protein molecule.
2. The secondary structure spatial configuration of the polypeptide chain:
   - the α-helix, stabilized by hydrogen bonds, has a step of 5.44 Å, a diameter of 10.5 Å, for each coil of the spiral accounts for 3.7 amino acid residue;
   - β-folded structure is a system of parallel or antiparallel segments of one or more polypeptide chains connected by hydrogen bonds; the basic identity period along the chain axis is 7.0 Å in the case of parallel chains and 6.5 Å in the case of antiparallel chains, and the distance between the chains is 9.5 Å.
3. Tertiary structure is the configuration of a polypeptide helix in space.
4. Quaternary structure – a set of polypeptide particles (subunits) representing a single molecular formation in structural and functional respect.

Proteins are conventionally divided depending on the shape of the molecule into two large groups: globular and fibrillar [38, 39]. Molecules of globular proteins are spherical or spindle-shaped; these proteins are soluble in water and aqueous solutions of salts. Fibrous proteins have elongated filamentous molecule and insoluble. In mammals, fibrillar proteins form the basis of supporting and covering tissues.
By chemical composition proteins are classified into simple proteins (proteins) and complex proteins (proteids) [40, 41]. Simple proteins contain only $\alpha$-amino acids. The composition of complex proteins, in addition to amino acids, includes a non-protein part, the so-called prosthetic group.

Simple proteins, for lack of other criteria, are divided into seven solubility groups [40, 41]:

1. **Albumins.** Albumins are soluble in water, precipitate when the solution is saturated with ammonium sulfate, easily subjected to thermal denaturation. These proteins are found in both animals and plants, such as egg albumin, blood plasma albumin, milk lactalbumin, plant albumins.

2. **Globulins.** Globulins are insoluble in water, but dissolve in dilute salt solutions, precipitate when the solution is saturated with ammonium sulfate, coagulate when heated. To this group of simple proteins include the globulins of blood plasma, myosin of muscle tissue, edestin from seed.

3. **Glutelins.** Glutelin – plant proteins, insoluble in water, but soluble in dilute solutions of acids and alkalis, e.g. wheat glutenin and oryzenin from rice.

4. **Prolamins.** Prolamins – vegetable proteins insoluble in water, salt solutions and absolute alcohol, but turning into a solution when treated with 80% aqueous alcohol. Basically these are proteins found in the seeds of plants (Zane, hordein, gliadin).

5. **Albuminoids.** Albuminoids (or scleroproteins) – simple proteins of animal origin, insoluble in water, salt solutions, alcohol and dilute acids and alkalis. Examples are proteins such as hair keratin, bone collagen, silk fibroin.

6. **Protamines.** The protamines – basic low molecular weight proteins with a high content of arginine. They are very soluble in water, insoluble in dilute ammonia solutions, do not coagulate when heated. Are composed of the sperm of fish, such as caprenin of sperm of common carp.

7. **Histones.** Histones dissolve in water and are insoluble in dilute ammonia; like protamines, do not denature when heated. Histones are also the main proteins, so in the cell they occur in the form of salt-like complexes with acidic components of it, most often with nucleic acids.

Complex proteins are classified depending on the nature non-protein component [40, 41]:

1. **Nucleoproteins.** Nucleoproteins consist of simple basic proteins (protamins or histones), which are connected by salt-like bonds with a non-protein component – nucleic acids. They are typical substances of cell nuclei and ribosomes.

2. **Glycoproteins.** Glycoproteins are complex proteins that contain carbohydrates, such as connective tissue proteins, blood group substances, and certain hormones (gonadotropin).

3. **Chromoproteins.** Chromoproteins are complex proteins consisting of a simple protein and a colored prosthetic group. Examples of chromoproteins include hemoglobin, cytochromes, catalase, containing metalloporphyrin as a chromophore, as well as rhodopsin (visual purple), whose chromophore group is 11-CIS-retinal isomer, and flavoproteins with a prosthetic group – Riboflavin.

4. **Phosphoproteins.** The composition of phosphoproteins includes phosphoric acid, and it is shown that it forms an ether with a hydroxyl group of serine. Typical phosphoproteins are casein of milk and vitellin eggs.

5. **Lipoproteins.** Lipoproteins are complex proteins containing lipids (in particular, phospholipids), widely distributed in animals and plants. Lipoproteinidny complexes are
included in the protein of brain, blood, milk, chloroplasts of plants, etc. Lipoproteidna structure are also components of intracellular membranes.

**Discussion of the results**

Hierarchy in the structure of organic matter is maintained by means of hydrogen bonds and electrostatic interaction between the functional groups of matter and between different substances [42]. The hierarchical structure of substances can be disturbed by physical, chemical or combined factors, i.e. cooking [43, 44].

It follows from the above that if a material object has taste, it means that it is ordered in a certain way. Thus, the taste characteristics of a material object can be expressed with the help of such a category as entropy. So, entropy (from others-Greek. ἐντροπία – turning, transformation) is a term widely used in the natural and exact Sciences [45]. The main value of entropy is a measure of disorderliness, randomness, disorder of the particles that make up the system [46, 47]. The category of entropy is related to information theory [48, 49].

It should be noted that both smell and taste are a form of chemoreception. Chemoreception – the ability of living things to perceive changes in the concentration of certain substances in the environment or in the body [50]. Therefore, we can assume that the features of the formation of sensations of smell will be similar to the formation of taste sensations.

**Conclusions**

As a result of our research it was found that:

1. In the formation of taste sensations of great importance belongs to the geometry of the taste buds of the language and the geometry of the analyzed objects of taste, which is created on the principle of complementarity (by type of lock-key). Taste analyzers of the tongue and analyzed objects of taste are universal in terms of size and have a fractal structure. The smallest indivisible fractal unit is the electron. The fractal structure of taste analyzers is continuous, and the analyzed taste objects are discontinuous and depend on the degree of purity of the object.

2. Among carbohydrates, glucose, fructose, sucrose, maltose, lactose and rhamnose have a crystalline structure, amorphous-crystalline (transitional or intermediate) structure – native starches, and amorphous structure – maltodextrins.

3. Many substances (protein molecules, etc.) have a complex hierarchical structure and are able to show their taste characteristics stepwise, i.e. at each of the hierarchical levels of the organization of these substances have their taste characteristics. At the same time, it often happens that at the last hierarchical level the geometry of these substances tends to a spherical (neutral) form.

4. Smell as well as taste is one of the types of chemoreception, so the features of the formation of sensations of smell are similar to the formation of taste sensations.

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Investigation of ejection process in mechatronic functional modules of packaging machines

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Keywords:
Ejector
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Simulation

Abstract

Introduction. The purpose of the research is to determine the influence of geometric, kinematic and technological parameters on the ejection processes in mechatronic functional modules of packaging machines.

Materials and methods. The modes of operation of pneumatic nozzle ejection systems with variable working environment were studied: compressed air, alcohol-containing solutions, gas-modified environment. The tasks set were solved on the basis of analysis and generalization of the literature material, conducting experiments to study the effectiveness of L-shaped ejectors, as well as bench studies of the process of creating and spraying the mixture on the product of processing.

Results and discussion. Problem solving for the proposed design of pneumatic nozzle ejection systems made possible to find optimal working technological and control modes for the processing of packing materials: dosed spraying of alcohol-containing substances on the surface of treatment with back pressure within 3–5 bar, jet velocity at the inlet of the ejector is adjusted by pressure regulator, working area irrigation with a diameter of 100–150mm, controlling the effect of turning the ejector on and off by a variable feedback signal on the inlet pressure both in the ejector and in the pressure line with a liquid jet of 0–10 V. Product processing above 6 bar causes the destruction of bakery products. For bakery products, the optimum pressure at the inlet of the ejector is 4 bars. Changing the geometry of the confuser and the diffuser makes it possible to reduce the flow of compressed air by 20%, which reduces the energy load for packaging machines.

Conclusions. Therefore, the optimal working modes of pneumatic nozzle systems for the treatment of flexible packaging materials and the surface of non-destructive bakery products are proposed.

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Introduction

In food packaging lines, when performing auxiliary technological operations, pneumatic nozzles devices with ejector systems are widely used [1,12,18]. On the basis of the analysis of the layout schemes of packaging machines, it was established that in a number of functional mechatronic mods (FMM) [1-3] are used with pneumatic systems. Examples of applications are surface coatings of packaging materials and consumer packaging, the introduction of a gas-modified medium (GMS) inside the package [4,7,18], the separation of the flow of consumer packaging on the conveyor, the creation of a vacuum, cleaning of the carton valves before applying an adhesive solution, etc. In order to choose the rational design and operating modes of the ejector, taking into account the various physical and mechanical properties of food products, packaging materials – it is necessary to be able to simulate the kinematic and dynamic characteristics of the working environment during the ejection process [16, 17, 18].

An effective method for modeling complex systems is simulation technology [5,6,13]. Which make it possible to take important technical solutions, accelerate the research and development processes, and shorten the time to create new packaging machines, while maintaining their competitive edge [8]. Solving the actual task of selecting and checking the rational parameters of ejectors in FMM packaging machines, – it is expedient to develop a generalized model for various working media (air, vacuum, GMS) [9,15,17]. Despite the rapid development of CFD-methods [10,14], the application of these methods does not always justify the expectations of the researcher. This is mainly due to the lack of a profile library of research environments and materials for CFD-engineers of scientific and production structures, as well as the lack of specialized literature [11,16].

Literature analysis has shown that there was a lack of information on adjusting the energy costs of PM due to the use of feeders with gaseous media. It has also been found that most PM consist of FMM lifting the gas medium to the packing area without a feedback control signal, which makes it impossible to adjust the accuracy of the feed and change the spray area [12,13,15]. To adjust the functionality of packaging equipment with pneumatic nozzle ejector systems, it is important to expand the study of optimal technological characteristics of pneumatic nozzle ejectors.

In this regard, the actual purpose is to create methodological foundations for CFD-calculations of pneumatic nozzle in functional modules of packaging machines. In well-known literary sources, particular attention is paid to the models of blown air and the cost characteristics of compressed air. In solving such problems, systematic analysis and synthesis of known literary sources was used [12], [13]. In view of this, the solution to the tasks of developing an ejector model and conducting a comparative analysis with theoretical studies of ejectors and the development of new structures is relevant, namely:

- development of CFD – model for reception of rational parameters of the ejector;
- synthesis of the ejector on the basis of the obtained results of imitative modeling;
- development of the structural control scheme of the ejector;
- substantiation of the proposed methodology for the analysis of pneumatic systems.

The analysis showed the need to study the structures and modes of operation of L-shaped ejectors to reduce their energy consumption in functional modules of packaging machines. There presented of the research is to study the effect of geometric, kinematic parameters on the technological characteristics of the proposed design of the pneumatic nozzle ejector in packaging machines.
Materials and methods

Materials

The object of the study is the hydrogasdynamic processes in the pneumatic nozzle ejector confuser-diffuser system. Particular attention is paid to changing the cost of the work environment and the recurrence of cycles to highlight the dose of the product [11, 14].

Despite the obvious advantages of semi-empirical methods over empirical methods, they have a number of disadvantages due to their limited scope and the need for a large amount of experimental data [16, 17]. As an alternative to empirical and semi-empirical methods, we have used approaches based on the solid-state mechanics, CFD methods (Computational Fluid Dynamics). That is, the system of Navier-Stokes or Reynolds equations is solved by numerical methods. [3,7,8]. The models developed can be used to analyze the operation of the packaging machine, to interpret the experimental results and to assist in the design and optimization of packaging lines. The research models were divided into two main categories:

1. Stable thermodynamic models that can be further divided into single-phase flow model and two-phase flow model;
2. Dynamic models, which are also divided according to phases [6,7].

Research materials include: compressed air, gas modified medium (GMC), packaging materials, alcohol solutions, pneumatic syringe systems, surface treatment operations, dosage systems, driver system. The design of the experimental ejector is designed taking into account the process of processing the surface of the packaging material during dosing-packing operations. The work of the ejector in the packaging machine for handling the packages is as follows. A high-pressure (working) gas with a full pressure \( p \) and a braking temperature \( T \) is brought through the coil 1 (Figure 1) into the mixing chamber 4. At the input channel of the mixer chamber static pressure is set below the full pressure of the low pressure gas ejection.

Under the influence of the pressure difference, low pressure gas (or a working fluid close to the Newtonian) is directed to the mixing chamber. At the end of the chamber 4 after the completion of the mixing process, the gas has averaged parameters of the emulsion. The geometry of the L-shaped ejector is most widely used in packaging machines. When modeling in the environment of the PP Flow Vision, the main geometric parameter of the ejector is the ratio of the areas of the output nozzle sections for the working flow and the flow of ejection:

\[
\alpha = \frac{F_1}{F_1} = \frac{F_1}{F_3 - F_1}
\]  

where \( F_1, F_2 \) — respectively, the area of the outlet nozzle sections for supplying work flow and ejection flow; \( F_3 \) — the intersection area of the cylindrical mixing chamber (cross section at the outlet of the diffuser 4).
Methods

The paper used analytical and numerical methods of calculation with the setting of experimental development experiments. The result of a complex analytical calculation (selection of coefficients, refinement during the calculation of the ranges of the operating mode and geometric parameters, etc.), in the best case, integral parameters are obtained that are close to the experimental ones [5,6]. In the course of numerical simulation, it is possible to obtain not only adequate integral parameters, but also flow parameters (pressure, velocity, temperature, etc.) at any point in the computational domain. This is especially true when designing ejectors in which processes of mixing the working substances occur.

The methods for calculating ejectors contain various empirical coefficients, specially selected for a specific design and range of operation of the ejector. The range of application of the equations to describe the characteristics of the ejector is limited. Various methods of reducing the dimensions of the ejector design based on the use of a multi-nozzle apparatus for supplying an active stream are considered. Mixing chambers and nozzles, characterized by an L-like shape for packaging machines, are poorly understood [8, 9, 11].

The calculation procedure is based on the use of numerical research results, namely, the obtained value of static pressure on the supply of working media to the ejector installation, followed by the assessment of changes in power and fuel consumption using analytical dependencies [17,18]. Numerical calculations of the structural and operational parameters of the ejector were carried out in a software package based on the finite element method. The calculations were performed in 2D and 3D statements as part of the solution of the stationary problem. In all calculations, the k-ε RNG turbulence model with a standard near-wall function was used [5, 8, 10]. The criterion for the effectiveness of each ejector circuit is the pressure field at the outlet of the diffuser. The adequacy of computational studies was compared with experimental data obtained during experimental studies. Studies are aimed at optimizing the design of the ejector, namely, determining the optimal geometry of its individual nodes: an active vortex nozzle, a mixing chamber, a diffuser, and an internal air supply channel. The main goal was to reduce hydraulic losses along the path in the ejector elements for energy efficiency.

Research simulation method. For a research simulation using a finite element method software package in Flow Vision [19] it is assumed that the ejector operates at a given static pressure at the outlet of the diffuser (for example, when it enters the atmosphere or inside a consumer packaging with constant pressure). The degree of expansion of the diffuser, was considered as a parameter that significantly affects the modes of the ejector. Confirmation of the adequacy of simulation models to the real process was carried out by experimental experiments on the developed stand. The parameters of the gas (working fluid) moving on the channel (nozzle system) can be changed by external influences, for example, due to heat supply, channel section changes, and the like. Often such physical actions are used to increase the flow rate of gas or increase in pressure. By the actions of external influence on pneumatic spray ejection systems are as follows:

1. Geometric – change in the cross-sectional area of the channel F.
2. Consumable – change of second consumption Ms.
3. Mechanical – supply or removal of mechanical energy lm.
5. Torting – the energy consumption of gas for friction lter.
6. Driver system – feedback control system.

The change (increase) of influences along the length of the channel is marked accordingly – dF, dMc dlm, dqe, dlter. Moreover, all these changes, except for dlrr, can be both positive and negative.
Results and discussion

Integration of pneumatic nozzle ejectors in FMM packaging machine

Analysis of the structure of packaging machines (PM) using a gas-containing medium in the package, showed the presence of complex FMM gas supply to the packaging area [5, 6]. Such modules are used in one layout with drives of linear and circular displacement [7, 9]. In order to expand the functionality of packaging equipment with pneumatic-emitting systems, it is necessary to provide for the search of rational technical solutions with optimal cost characteristics of FMM [8, 10, 11]. To improve the existing FMM by pneumatic-emitting systems for packaging food artificial and small-scale products, work was carried out with the involvement of simulation in PP Flow Vision [14, 15].

The basis of the arrangement of FMM with pneumo conducting ejection systems was selected PM for artificial products, processing of consumer packages and packing flexible materials based on ejectors with pneumatic or electropneumatic actuators for gas and Newtonian fluid media (technological environments). As a result of the topological analysis of the PM, a typical technological scheme of the FMM of the pneumatic plunger ejection systems is shown in Figure 2, which involves adjusting the magnitude of the effects on the ejector. For air blasting ejection systems, the work of which is directly related to the cost of compressed air and the working process environment, the system of precise direct control is related to the performance of a separate FMM and the entire packaging machine.

![Figure 2. Technological scheme of PM for packing in a package of type "Sandwich":
1 – functional device for feeding the packaging material; 2 – formation of blister packaging;
3 – moving the product into a blister; 4 – feeding roll material for packing sealing;
5 – sealing blister; 6 – supply of gas mixture; 7 – the formation of transverse seams;
8 – cutting off the finished package](image)

Proposed control system

During the study, the designs of the ejector of the packaging machine with control systems for dispensing the technological environment for food products were selected in Figure 3. Electropneumatic proportional control systems with the main technological parameters of the process were used. The greatest advantage is present in the arrangements with the electropneumatic automatic control system Figure 3. This involves connecting to the object of the regulating device (regulator) and input into the feedback system. The generalized block diagram is as follows:
Figure 3. Block diagram of the automatic regulating system of the pneumatic nozzle FMM of the food packaging machine

The input of the regulator is the inconsistency signal \( \varepsilon \) – the difference between the measured signal \( X \) and the set level \( W \) (setpoint). Despite the fact that they are part of the control system, the controller "does not know" the signals \( V \) and \( T \), directly related to the object. The task of the regulator is to control not only one object, but an entire system of three elements: an actuator, object, sensor. It complicates the management and reduces its quality. It turns out that the sudden expansion leads to hydraulic losses, that is, to loss of pressure (pressure), regardless of the losses caused by friction.

Development of a synthesis method for pneumatic nozzle ejection systems for FMM food packaging machines

Warehouse uncompressed Bernoulli equation for fluid that is when \( \rho = \text{const} \) [2-7] :

\[
\begin{align*}
    z_1 + \frac{p}{\rho g} + \frac{w_1^2}{2g} &= z_2 + \frac{p}{\rho g} + \frac{w_2^2}{2g} + h_{flow} \\
    z_1 &= z_2
\end{align*}
\]

That is, the flow is horizontal, multiply the resulting expression on

\[
\rho g: p_1 + \frac{\omega_1^2}{2} = p_2 + \frac{w_2^2}{2g} + \rho g h_{flow} \quad \rho g h_{flow} = p_{flow}
\]

Get a loss of full pressure as a result of sudden expansion.

\[
p_1 - p_2 = \frac{\omega_1^2}{2} - \frac{\omega_2^2}{2} + p_{flow}
\]

Apply the Euler equation

\[
p_1 - p_2 = \rho w_2 (w_1 - w_2), \text{ where } p_1 - p_2
\]

loss of statistical pressure resulting from fluid movement from a high-pressure area to a site with less pressure. Since the plot 1 – 2 is short, then the loss of liquid is not taken into account by the Carnot-Bordeaux theorem:

\[
\begin{align*}
    \rho w_2 (w_2 - w_1) &= \frac{\rho w_2^2}{2} + \frac{\rho w_1^2}{2} + p_{flow}, \\
    p_{flow} &= \frac{\rho w_1^2}{2} - \rho w_1 w_2 + \frac{\rho w_2^2}{2} = \rho \frac{(w_2 - w_1)^2}{2}, \\
    p_{flow} &= \frac{\rho}{2} (w_1 - w_2)^2.
\end{align*}
\]
With the help of this equation, you can make recommendations for eliminating the transition of sections of cylindrical cross sections with a smaller diameter to sections with large diameters on the coordinate system of the flow of the product. In a food dispenser close to rheology to Newtonian liquids, we have developed pneumorphic gas ejectors [3,5,9]. The resulting structure can be synthesized in functional mechatronic modules of packaging machines and used for moving gas or low pressure fluid through a high pressure gas jet.

**Investigation of the flow structure in the area of mixing jets**

The 3D ejector (Figure 4) consists of a nozzle 3 for high pressure gas (active or ejectable), 4 – nozzles for low pressure gas (passive or ejector), 1 – mixing chamber and 2 – diffuser. The active gas stream, having a high velocity at the outlet of the nozzle 1, and consequently, low pressure sucking from the nozzle 2 of the liquid (gas), and mixing with it in the chamber 3, transmits to it a portion of the energy that gives the mixture a certain speed. The nozzle 1 may be subsonic or supersonic (depends on the pressure drop and nozzle construction). Supersonic ejectors are more effective.

![Figure 4. Developed ejector for surface treatment of food products:](image)

1 – housing; 2 – diffuser; 3 – confuser

A feature is the change in the mass of a liquid product or gas moving at a speed $w_1$ in the nozzle and $w_2$ in the mixer chamber. The active jet injected into the ejector changes its speed from $w_1$ to $w_2$ speed in the mixer chamber. Changing the speed of the active jet $M_A (w_2 - w_1)$. Assume that the passive jet at the input to the ejector has a speed of $w = 0$. In the mixer chamber its speed becomes $w_2$. Changing the velocity of the passive jet $M_P (w_2 - w_1)$. Since there are no external forces acting on the gas, the total change in the amount of motion in accordance with the assumptions made is zero:

$$
\frac{M_P}{M_A} = w_1 - w_2 = n,
$$

$$
\frac{M_P}{M_A} = 1 - \frac{w_2}{w_1} = n
$$

As a result of the simulation, the tasks were set: to evaluate the flow characteristics of the proposed ejector model; determine the forces acting on the wall of the diffuser and the nozzle in the subsonic and sound modes of the ejectors in the dispenser; get results on the distribution of forces acting on the liquid (product) along the axis of motion in the projection on the horizontal axis. Accepted assumptions in the model: Gas flows, under some pressure. It creates the force of RD, acting from the inside of the diffuser wall, perpendicular to its surface. Assume that this force acts on a diffuser at some point. In turn, on the wall of the diffuser, the reactive power of the WG is applied to the gas, applied to the control surface of the gas. In fact, as you know, the point of applying force and reactive force coincide. PG force can be divided into two. Vertical component of R Du, "disperses" the diffuser and is perceived by the material of the wall. A similar vertical force of an OC is R Du, acting on gas, is counterbalanced by the force acting on the gas from the side of the diffuser on the opposite side. The results are shown in table 1.
Results of the influence of changes in the geometric characteristics of the nozzle on the kinematic parameters of the system

<table>
<thead>
<tr>
<th>Mode</th>
<th>Cut 1</th>
<th>Cut «narrowing»</th>
<th>Cut 2</th>
<th>Channel function</th>
<th>Addiction</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>M &gt; 1</td>
<td>M &lt; 1</td>
<td>w &lt; w_{cr}</td>
<td>Venturi tube</td>
<td>In &quot;narrowing&quot; speed does not reach critical value</td>
</tr>
<tr>
<td></td>
<td>w &lt; w_{cr}</td>
<td></td>
<td>P &gt; P_{cr}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>M &lt; 1</td>
<td>M = 1</td>
<td>w &gt; w_{cr}</td>
<td>Laval's nozzle</td>
<td>In &quot;narrowing&quot; speed reaches critical and growing rapidly</td>
</tr>
<tr>
<td></td>
<td>w &lt; w_{cr}</td>
<td></td>
<td>P &lt; P_{cr}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>P &gt; P_{cr}</td>
<td></td>
<td>P = P_{cr}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>M &gt; 1</td>
<td>M = 1</td>
<td>w &lt; w_{cr}</td>
<td>Supersonic diffuser</td>
<td>The rapid increase in pressure</td>
</tr>
<tr>
<td></td>
<td>w &gt; w_{cr}</td>
<td></td>
<td>P &gt; P_{cr}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>P &lt; P_{cr}</td>
<td></td>
<td>P = P_{cr}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>M &gt; 1</td>
<td>M &lt; 1</td>
<td>w &gt; w_{cr}</td>
<td>Difficult to implement</td>
<td>A shock wave arises and the gas flow turns into subsonic</td>
</tr>
<tr>
<td></td>
<td>w &gt; w_{cr}</td>
<td></td>
<td>P = P_{cr}</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>P &lt; P_{cr}</td>
<td></td>
<td>P = P_{cr}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

According to the modes of Table 1, it can be argued that one pneumatic nozzle channel can act as a Laval nozzle, a supersonic diffuser and a Venturi tube, depending on the parameters of the FMM working system at the inlet and outlet of the spray device. Therefore, to develop their own design of pneumatic nozzle ejecting device, the assumption is made: F1 = F2; the movement of the gas inside the nozzle is energy-isolated, isoentropic and stationary, the system operates with purified air under normal conditions.

**Experimental design pneumonozzle system**

Thus, the greater the velocity of the active gas and the less passive, the greater the rate of ejection. As can be seen from the CFD model, Figure 5, this calculation is very simplistic.

The methodology of the study is shown in Figure 5, with a detailed description of the input parameters of modeling, step-by-step evaluation of mathematical models, comparative characteristics of the obtained results, approaches to the choice of rational parameters to build a physical model of pneumatic nozzle ejection system in Figure 6.

As a result of modeling, in contrast to the well-known research approaches [5, 8, 11, 14], we take into account the OEE – as a general criterion for evaluating the operation of a pneumatic nozzle ejector in FMM packaging machine.
Figure 5. Structure of the algorithmic method of synthesis of a pneumatic plunger ejection functional mechatronic module for a packing machine
To determine the force acting on the wall of the diffuser or nozzle with subsonic motion and the absence of hydraulic losses. Consider the forces acting on the gas (liquid) along the axis of motion in the projection onto the horizontal axis (Figure 6, a).

General scheme in the expected load on the wall pressure diffuser, (Figure 6,b):

Figure 6. Analysis of the experimental system:

a – general scheme of the expected load on the wall of the pressure diffuser for the developed model ejector;
b – General scheme of the dispenser of the pneumo-ejecting system with supplying the spray jet to the FMM of the packaging machine:
DI – discrete inputs; DO – discrete outputs; MPR – mechatronic pressure regulator (analog inputs / analog outputs), proportional to the input signal; ITL – information transmission line; PS – pressure sensor; LS – location sensor; DAC – digital-to-analog converter; ADC – analog-to-digital converter.
The horizontal components of the RSU and Rd are not balanced. These forces are created by pressure of gas P1 from left to right in section 1 and pressure P2 from right to left in section 2. These pressures arise from the mass of gas surrounding the allocated volume. Pressure p2 prevents gas propagation in the direction of its movement from left to right

\[ P_1 = p_1 F_1; \quad P_2 = p_2 F_2, \]

where: F1 and F2 are the cross-sectional areas of the input and output. As a result of the analysis of the developed ejector model, results have been obtained that prove that the dynamic models have a higher accuracy of prediction and provide more information in comparison with stable thermodynamic models.

For research, a special stand has been designed and manufactured on which it is possible to simulate different modes of operation of the piston microdoser within FMM processing of consumer packaging.

The block diagram of the experimental stand is shown in (Figure 6b).

When testing the stand for the operation of the piston micrometer, the tolerance limit for the nominal weight of the liquid product dose is 50 ml, not more than 1.5%.

The transmission ratio for the pressure regulator is calculated by the formula:

\[ K = \frac{P}{U} = 9 \cdot 10^4 \text{ (Pa/W)} \]

DAC with U = 0...10V output signal was used to control the MRI. The DAC channel transmission ratio is the ratio of the output voltage to the input code R will be: \( K' = \frac{U'}{R'} = \frac{1}{409.6} \text{ (V / disc unit)} \). The minimum value of the pressure at the fixing corresponds to the signal of the reference \( \Delta R = 1 \text{disc} \). Will be: \( \Delta P = \Delta R \cdot K' \cdot K = 1 \cdot (10/4096) \cdot (900000/10) = 220 \text{Pa} \). This value of \( \Delta P \) is 0.022% of the range of change in initial pressure, that is, sufficient from the point of view of the accuracy of pressure measurements during the experiments. The controls for the micro-dosing module were formed according to sinusoidal and stepped laws, using the software FluidLab-P, Version 1.0. SWCN-P-10 (Camozzi) was used to obtain information on the pressure values of the product receiver.

The study monitored the stability of the pressure in the receiver, which depends on the error of dosing at the exit of the microdosage. The general view and drawings of the design of the extractor microdosage are shown in Figure 6. The general view of the experimental stand with FMM supplying the microdose in the area of packaging and processing of consumer packaging.

The results of experimental studies have established the nature and duration of transient regulation of the pressure at the outlet of the MRI, and its subsequent impact on dose separation from the receiver. The amount of product formed and the velocity of the jet at the outlet of the nozzle portion of the dispenser depend on the regulation of the inlet pressure, the throughput of the working channel, and the operating pressure in the control part of the module. The characteristics of the control signal change are shown in (Figure 7).

The following results of the deviation of the repetition of the dose of the product were obtained, with the operation of the FMM microdoser according to the sinusoidal law of filing for spraying:

- product – Dewar’s12 (wiskey) – density 942kg/m^3; diameter of the pipeline 0.004m, pressure – 1.8 bar, pressure amplitude 1.2 bar; frequency varies within: 18–36 Hz; deviation of the product dose within 2.2% (Figure 7, a);
- product – Southern Comfort (liqueur) – density 994 kg/m^3; diameter of pipeline 0.004m, pressure – 1.8 bar, pressure amplitude 1.2 bar; frequency varies within: 18–36 Hz; deviation of the product dose within 1.5% (Figure 7,b);
- product – Monin (syrup) – density 1300 kg/m^3; diameter of pipeline 0.004m, pressure – 1.8 bar, pressure amplitude 1.2 bar; frequency varies within: 18–36 Hz; deviation of the product dose within 1.0% (Figure 7,c).
Figure 7. Generalized characteristic of the FMM microdosage
Conclusions

1. When the correction parameters of the differential pressure feedback and its derivatives with the external mechatronic pneumatic controller in the microdetector are entered – improved performance of the dosing module is obtained. The error in the formation of the dose of the product is significantly reduced and does not exceed the rules on the regulation of the technological process in packaging machines.

2. Based on the results of a series of simulation experiments, one can assume that the defining elements of the ejector's operating characteristics are:
   − a nozzle that provides the required flow;
   − mixing camera with the necessary parameters;
   − the location of the nozzle and its form of communication with the surface of the ejector, providing the necessary pressure distribution and turning the jet.

3. The results of the simulation experiment confirmed the correspondence of the coupling model between pressure and velocity, presented in the course of the mathematical description. The obtained data showed a sharp change in the nature of the distribution of pressure and velocity inside ejection systems when changing the type of working environment in single-phase pneumatic systems. This is one of the criteria to take into account when choosing the type of control system of the FMM of the packaging machine.

4. Problem solving for the proposed design of pneumatic nozzle ejection systems made it possible to find optimal working technological and control modes for the processing of packing materials: dosed spraying of alcohol-containing substances on the surface of treatment with back pressure within 3-5 bar, jet velocity at the inlet of the ejector is adjusted by pressure regulator, working area irrigation with a diameter of 100-150mm, controlling the effect of turning the ejector on and off by a variable feedback signal on the inlet pressure both in the ejector and in the pressure line with a liquid jet of 0-10 V.

5. Product processing above 6 bar causes the destruction of bakery products. For bakery products, the optimum pressure at the inlet of the ejector is 4 bars. Changing the geometry of the confuser and the diffuser makes it possible to reduce the compressed air flow rate by 20%, which reduces the energy load for packaging machines. The digital controllers and flowmeter in the ejector system with 0-10V feedback enable 0.1 – 0.5s to change the performance of a separate functional mechatronic module of the packaging machine.

6. The 3D simulation model of a gas or liquid displacement ejector using a high pressure gas jet was synthesized. Deviation of the repeat dose of the product, when sprayed on biscuits: Dewar’s12 (whiskey) frequency varies within: 18– 36Hz; product dose variation within 2.0%; product – Southern Comfort (liqueur), product dose deviation within 1.3%.

References

Influence of discrete-pulse energy input on the distribution of plant biomass

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2 – Institute of Engineering Thermophysics of the National Academy of Sciences of Ukraine, Kyiv, Ukraine

Abstract

Introduction. The aim of this work is to determine the influence of dispersion modes of plant biomass of raw materials in the rotor-pulsating apparatus by the method of discrete-impulse energy input

Materials and methods. The material of the studies was wheat straw and corn stalks, grinded on a disintegrator, which were mixed with water in certain proportions. The suspension was treated in a rotor-pulsating apparatus under different modes. The particle size distribution of the obtained particles was determined by the sieve method and the laser diffraction method.

Results and discussion. It is determined that under the same conditions of treatment granulometric composition of the mixture of milled biomass of corn stalks with water after milling in the rotor-pulsating apparatus has a dispersity of 3–5% lower than the mixture of wheat. This can be explained by the different strengths of lignocellulosic fibers in the investigated plants.

It was found that with the increase of a solid/water ratio from 1: 5 to 1:15, a dispersity of particles is reduced by 35–40%, and from 1: 5 to 1:10 by 3–5%. According to the authors, this is due to changes in the viscosity of the solution. Reducing the solid/water ratio from 1:15 to 1:10 for 10 cycles of the dispersion treatment in the rotor-pulsating apparatus leads to a decrease in temperature from 47 to 42º C (≈ 10%), but the productivity of the equipment increases 1.5–2 times, energy consumption decreases by 25–30%. The optimum parameters for milling of wheat straw or corn stalks in a rotor-pulsating apparatus are: the solid/water ratio is 1:10; the shear flow rate is $40 \cdot 10^3$ s$^{-1}$; the frequency of flow pulsations is 3 kHz. The number of processing cycles is 25–30. It was determined that the granulometric composition of an aqueous dispersion of wheat straw or corn stalks at a solid/water ratio of 1:10 and treated in the rotor-pulsating apparatus with the frequency of pulsations of 3 kHz, shear flow rate $40 \cdot 10^3$ s$^{-1}$ for 25–30 cycles allows the conclude that about 50% of the particles have a size in the range of 30–50 μm.

Conclusions. Dispersion of plant biomass by the method of discrete-pulse energy input provides for obtaining 80% of particles with a size of 1–50 μm.
Introduction

In the technology of acid or enzymatic hydrolysis of lignocellulosic feedstock, a pretreatment of plant raw materials for hydrolysis involving the grinding of plant raw materials is a necessary but most energy-consuming step [1]. Mechanical pre-treatment of plant raw materials before the hydrolysis proves mechanical comminution can afford 5–25% improvement of hydrolysis product and boosts 23–59% rate of hydrolysis, depending on the milling techniques [2]. A comparison study was performed and it showed that smaller size of corn stover (about 53–75 mm) produced greater outcome by 1.5-fold than the larger size substrate [3]. The effect of particle size on enzymatic hydrolysis of pretreated Miscanthus x giganteus was determined by Esha Khullar with colleagues. An increasing trend in percent total conversion was observed with decreasing mean particle size. Enzyme hydrolysis of unpretreated biomass samples also resulted in increased total conversions as particle size decreased, although mean conversions (10–20%) were much lower than for pretreated biomass samples (53–94%) [4].

The effect of feedstock particle size on dilute acid hydrolysis using Giant Reed (Arundodonax) was studied in the work [5]. Results clearly show a selective hydrolysis of the hemicellulose regardless of the particle size fractions assayed.

Shredded plant biomass is widely used in various fields: for the bioethanol production, fuel pellets, composite building materials, as the filler for filters, for paper production, in agriculture in the form of fertilizers, vitamin and protein feed additives, as well as in the form of biologically as active additives in the food and cosmetics industry [6–10]. Vegetable flour is obtained by grinding of agricultural waste on various types of grinders [11]. Mechanical milling destroys the crystalline structure of cellulose, increases the surface available to cellulolytic enzymes and, as a result, leads to a significant increase in the reactivity of plant raw material [12,13]. Fine milling of straw allows increasing the yield of reducing substances in its hydrolysis [14–16]. Milling of plant raw materials can be carried out both in dry and in wet form [17]. Also, using the apparatus is further improving, in particular, the fermentation, the separation of the biomass of yeast, the production of bioethanol.

In order to preserve the quality of the product obtained, it is advisable to use less power-consuming equipment. Consequently, the intensification of the milling of plant material while simultaneously reducing the power of mechanical impact is an urgent task.

The application of the method of discrete-pulse energy input in the process of dispersion of plant material allows to optimize the technology of bioconversion of lignocellulose with the production of bioethanol and other products.

The idea of the method discrete-pulse energy input is to accumulate (concentrate) in advance the energy permanently introduced and arbitrarily distributed in the working volume at the local discrete points of the system for further impulse realization to achieve the necessary thermophysical effects [18].

Most often, the discrete-pulse energy input method is implemented in rotor-pulsating apparatus of various modifications [19]. They are widely used in various industries, such as food, pharmaceutical, chemical, microbiological, agriculture, etc [20–24].

The use of this equipment in the milling of lignocellulosic raw material may intensify the process, namely, reduce the duration of pretreatment, hydrolysis, and fermentation, increase the amount of reducing substances, reduce energy costs and, in general, make the technology more efficient.

The aim of research is to determine the influence of dispersion modes of plant biomass of raw materials in the rotor-pulsating apparatus by the method of discrete-impulse energy input.
Materials and methods

Plant raw materials

The materials under study were wheat straw and corn stalks pre-grinded in a disintegrator. The particle size of 400 μm after grinding was 69 and 75% wt. in accordance. The resulting mass was mixed with water in the proportions determined by the experimental conditions. The resulting suspension was treated in a rotor-pulsating apparatus under the modes determined by the experimental conditions with subsequent filtration, after which the granulometric composition was determined.

Methods

Sieve method. Determination of the granulometric composition of straw was carried out by sieve analysis. The weight of the test material was sifted through a set of sieves, and then the percentage content of the residue on each of the sieves relative to the mass of the initial weighting was determined [25, 26].

Microscopy. The particle size distribution in the range 1-80 μm was determined by the method of laser diffraction using the laser particle size analyzer Microsizer 201 A. References to the relevant standards in the order of measurements are given in the sources [27, 28].

Experimental setup. To prove the proposed assumptions, an experimental rotor-pulsating setup for the milling of plant raw materials was designed. The technological scheme of the setup is presented in Figure 1.

![Figure 1. Technological scheme of dispersing of plant raw materials:](image)

The milling of plant raw materials according to the proposed scheme is as follows. The receiving tank 1 is filling with water. The two-way valve 2 is opening and the prepared solution is fed into rotor-pulsating apparatus 5, which is also a pump. Then, the three-way cock 7 is opened so that the solution returns to the receiving tank 1. For 3-4 cycles of pumping, the dispenser 4, which in specific proportions feeds the raw material into the solution flow, is turned on.

Solid raw materials are straw, shredded in a disintegrator to particles of not more than 1000 microns in size.

Mixing with the flow, the solid raw material is passing through the rotors and the stator of the rotor-pulsating apparatus, where simultaneously processes of dispersion, dissolution, heating, and hydrolysis occur. These processes occur simultaneously due to the impact of shock waves, interphase turbulence, cavitation, and vortices. It allows destroying the structure of lignocellulose with the removal of lignin and the transfer of crystalline cellulose into an amorphous state, suitable for further processing.

A mixture of liquid solution and plant raw material circulates through the circle: receiving tank 1 – rotor-pulsating apparatus 5 for a few minutes to several hours. During this time, the mixture undergoes dispersing, stirring, dissolving, heating. The complex of such operations prepares the plant material for hydrolysis. The prepared milled mass is sent to collector 9 for further use.

The rotor-pulsating unit of the rotor-pulsation apparatus consists of two rotors connected by screws and representing a single rotor unit, the stator and the impeller of the centrifugal pump.

The rotors have the following design characteristics: the inner radius of the small rotor is 56 mm, the inner radius of the large rotor was 66 mm, the width of the slots is 3.0 mm, the angle between the slots in the shell of 6º, the height of the slot is 5 mm, and the number of slots of rectangular shape is 60. The range of gap variation between the rotor and the stator is \( \delta = 0.3–0.5 \) mm. Structural characteristics of the stator are as follows: the radius of the stator is 61 mm, the width of slots is 3.0 mm, the height of the slots is 5 mm, and the number of slots of rectangular shape is 60.

### Results and discussion

#### Dry pre-treatment by disintegrator

In the first stage of studies, the straw of wheat and corn stalks were pre-treated in a disintegrator ДЗ-300/1 (operated at speed of 3000 rpm, power consumption 3 kW/h for half an hour) to particles of not more than 1000 \( \mu m \) in size. The granulometric composition of the plant raw material after treatment in the disintegrator is given in Table 1.

<table>
<thead>
<tr>
<th>Type of plant raw material</th>
<th>Particle size, ( \mu m )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&gt;80</td>
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<tr>
<td>Straw of wheat</td>
<td>2</td>
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<tr>
<td>Corn stalks</td>
<td>1</td>
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</tbody>
</table>
The granulometric composition of wheat straw and corn stalks after treatment in the disintegrator is almost unchanged. The content of particles larger than 400 μm is about 70%. In the course of further research, the resulting crushed mass from various types of raw materials was mixed with water at a solid/water ratio of 1:5; 1:10; 1:15.

**Wet milling by discrete-pulse energy input**

The resulting dispersions are processed by the method of discrete-pulse energy input in a rotor-pulsating apparatus consisting of one stator and two rotors.

The intensity of processing of water dispersion of wheat straws or corn stalk in the rotor-pulsating apparatus is determined by the following parameters:

Frequency of flow pulsations

\[ f = \omega \cdot n, \]

where \( \omega \) is the rotational speed of rotor unit, rps; \( n \) is a number of holes in the rotor and stator.

Flow shear rate

\[ \nu = \frac{\omega \cdot R}{\mu}, \]

where \( R \) is the internal radius of the rotor, m; \( \mu \) is the gap between rotor and stator.

The mechanisms of discrete-pulse energy input in a rotor-pulsating apparatus were the frequency of flow pulsations and the flow shear rate of the treated medium, which were respectively 1 kHz and 20·10³ s⁻¹.

An important value characterizing the passage of the medium through the rotor-pulsating apparatus is the number of cycles of treatment. One cycle is the time taken for the entire volume of the treated medium to pass through the working bodies of the rotor-pulsating apparatus.

Table 2 shows the granulometric composition of the aqueous dispersion of wheat straw in a solid/water ratio of 1:5; 1:10; 1:15 and treated in a rotor-pulsating apparatus for 10 cycles.

**Table 2**

<table>
<thead>
<tr>
<th>Solid/water ratio</th>
<th>Particle size, μm</th>
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<tr>
<td></td>
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<td>1:10</td>
<td>42</td>
</tr>
<tr>
<td>1:15</td>
<td>31</td>
</tr>
</tbody>
</table>

Similar studies have been conducted for the aqueous dispersion of corn stalks. The data is shown in Table 3.

**Table 3**

<table>
<thead>
<tr>
<th>Solid/water ratio</th>
<th>Particle size, μm</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>&lt;80</td>
</tr>
<tr>
<td>1:5</td>
<td>36</td>
</tr>
<tr>
<td>1:10</td>
<td>35</td>
</tr>
<tr>
<td>1:15</td>
<td>19</td>
</tr>
</tbody>
</table>
Under the same conditions of treatment granulometric composition of the mixture of milled biomass of corn stalks with water after milling in the rotor-pulsating apparatus has a dispersity of 3–5% lower than the mixture of wheat. This can be explained by the different strengths of lignocellulosic fibers in the investigated plants.

It was also found that with the increase of a solid/water ratio from 1:5 to 1:15, a dispersity of particles is reduced by 35–40%, and from 1:5 to 1:10 by 3–5%. According to the authors, this is due to changes in the viscosity of the solution. A aqueous dispersion of wheat straw at a solid/water ratio of 1:5 is a viscous suspension, which is difficult to pump by rotor-pulsating apparatus. In this connection, the dissipation of mechanical energy into heat is carried out.

For 10 cycles, the solution treated in the rotor-pulsating apparatus was heated from 17 to 47 °C.

The graph of the temperature change of the water dispersion of wheat straw treated in the rotor-pulsating apparatus from the number of processing cycles and the solid/water ratio is shown in Figure 2.

The change in the temperature of the aqueous dispersion of corn stalks from the number of processing cycles and the solid/water ratio when milling in the rotor-pulsating apparatus has a similar dynamics with wheat straw.

Reducing the solid/water ratio from 1:15 to 1:5 allows to increase the viscosity of the solution, and hence the temperature. This factor is important not only in the process of lignocellulosic raw materials milling, but also in its bioconversion.

Figure 2. Dependence of temperature change of water dispersion of wheat straw on dispersion in the rotor-pulsating apparatus from the number of cycles of treatment and the solid/water ratio:

♦ 1:15; ■ 1:10; ▲ 1:5.
Reducing the solid/water ratio from 1:15 to 1:10 for 10 cycles of the dispersion treatment in the rotor-pulsating apparatus leads to a decrease in temperature from 47 to 42 °C (≈ 10%), but the productivity of the equipment increases 1.5 – 2 times, energy consumption decreases by 25–30%.

The temperature of the water dispersion of wheat straw or corn stalks in a solid/water ratio of 1:15, treated in the rotor-pulsating apparatus in 10 cycles, rises from 17 to 22 °C, at the same time with a solid/water ratio of 1:10 from 17 to 42 °C, with a solid/water ratio of 1:5 from 17 to 47 °C.

The analysis and comparison of the resulted experimental data allow concluding, that further studies are appropriate to behave with a solid/water ratio of 1:10.

For a study 1 kg of milled in a disintegrator wheat straw or corn stalks was mixed with 10 liters of water and treated in a rotor-pulsating apparatus for 1 to 50 cycles at a constant flow shear rate (20×10³ s⁻¹) and a variable frequency of pulsations (1,3, and 5 kHz).

The change in the granulometric composition of the obtained straw wheat mass is shown in Figure 3.

![Figure 3](image)

**Figure 3.** Dependence of the content of the mass fraction of the milled wheat straw less than 80 μm on the number of processing cycles and the frequency of pulsations:

- ♦ - 1 kHz; ■ - 3 kHz; ▲ - 5 kHz.

When processing the water dispersion of wheat straw in a rotor-pulsating apparatus with a frequency of pulsations equal to 1 kHz, 42 cycles are required to reach 100% of the particles in less than 80 μm. With an increase in the frequency of pulsations from 1 to 3 kHz, the number of cycles decreases to 30 (≈30%).

When the frequency of pulsations is changed from 1 to 5 kHz, the number of cycles decreases to 27 (≈35%).
An increase in the frequency of pulsations from 3 to 5 kHz is associated with additional energy costs and practically does not affect the number of processing cycles. Given this, further studies were carried out at a frequency of pulsations of 3 kHz.

The dependence of the content of the mass fraction of the particle fraction of the dispersed mass of corn stalks is less than 80 μm on the number of processing cycles and the frequency of pulsations is similar to wheat straw.

Further studies have been conducted to study an influence of the flow shear rate in the rotor-pulsating apparatus and the number of processing cycles at the fractional granulometric composition.

The flow shear rate varied from $20 \cdot 10^3 \text{ s}^{-1}$ to $50 \cdot 10^3 \text{ s}^{-1}$.

The dynamics of change in the fractional composition of treated plant raw material is presented in Figure 4.

Figure 4 The dependence of the content of the mass fraction of the dispersed mass of wheat straw is less than 80 μm on the number of processing cycles and flow shear rate:

- $\textbullet$ - 20;
- $\textblacksquare$ - 40;
- $\texttriangle$ - $50 \cdot 10^3 \text{ s}^{-1}$.

The change in the flow shear rate significantly affects the particle distribution than the frequency of pulsations. The number of processing cycles decreases by 5–7%. The most efficient treatment of the medium in the rotor-pulsating apparatus for the flow shear rate is $40 \cdot 10^3 \text{ s}^{-1}$.

The optimum parameters for milling of wheat straw or corn stalks in a rotor-pulsating apparatus are: the solid/water ratio is 1:10; the shear flow rate is $40 \cdot 10^3 \text{ s}^{-1}$; the frequency of flow pulsations is 3 kHz. The number of processing cycles is 25–30.
The particle size distribution in the interval 1-80 microns was of interest. Data are presented in Table 4.

<table>
<thead>
<tr>
<th>Type of plant raw material</th>
<th>Particle size, μm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1-5</td>
</tr>
<tr>
<td>Straw of wheat</td>
<td>7</td>
</tr>
<tr>
<td>Corn stalks</td>
<td>6</td>
</tr>
</tbody>
</table>

Analysis of the granulometric composition of an aqueous dispersion of wheat straw or corn stalks at a solid/water ratio of 1:10 and treated in the rotor-pulsating apparatus with the frequency of pulsations of 3 kHz, shear flow rate $40 \cdot 10^3$ s$^{-1}$ for 25–30 cycles allows one to conclude that about 50% of the particles have a size in the range of 30–50 μm.

Such an extended interface contributes to the intensification of the process of bioconversion of the plant raw material.

The results obtained were compared with those of pre-treatment of a water dispersion of rice straw by techniques of wet disk milling (WDM), hot-compressed water treatment (HCWT), and dry ball milling (DBM) described in a work [29] and with data obtained during the processing of corn stover in the ball mill [30].

The results obtained in this work were also compared with results of dry pre-treatment of wheat straw by various techniques. A large range of wheat-straw powders was produced: from coarse (median particle size 800 μm) to fine particles (50 μm) using sieve based grindings, then ultra-fine particles 20 μm by jet milling and 10 μm by ball milling [31]. In another study, four mechanical deconstruction methods were compared at lab scale: BM (ball mill), VBM (vibratory ball mill), CM (centrifugal mill) and JM (jet mill) [32].

The results of the comparison indicate that the combination of dry pre-treatment of wheat straw or corn stalks in a disintegrator, followed by treatment of the aqueous suspension of the obtained biomass by the method of discrete-pulse energy input allows obtaining a higher degree of dispersion of the particles.

**Conclusions**

The use of the method of discrete-pulse energy input in the process of milling of biomass of plant raw material on the example of straw wheat and corn stalks provides for obtaining 77–80% of particles of dispersed biomass in the size of 1–50 microns.

**References**


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Development trends and risk factors of meat global exports

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Belarusian State Agrarian Technical University, Minsk, Belarus

Abstract

Introduction. The aim of the research was to identify and analyze the most significant factors of economic risk and to build an adequate mathematical model describing their impact on the volume of meat products exports.

Materials and methods. The object of the research was the world market of meat and meat products. The subject of the research was the factors of economic risk arising in the sphere of export relations. The assessment of risk factors impact is made on the basis of correlation and regression analysis.

Results and discussion. The volume of world exports of meat and meat products from 2013 to 2017 increased by 3.16 million tons. The increase in export volumes occurred mainly due to the main exporting regions: USA, Brazil, EU countries, Canada, Thailand and New Zealand. At the same time, there was a decrease in exports from Australia, India, China, Argentina. World pork exports in 2017 amounted to 8.23 million tons, which was 1.1 million tons, or 15.59%, higher than the level of 2013. The growth of beef’s export meat was established by 22.6% during the analyzed period. The world export volume of poultry meat increased, which over the analyzed period increased from 12.4 million tons in 2013 to 13.13 million tons in 2017 (an increase of 105.9%). Global volumes of mutton exports increased slightly from 2013 to 2017 by only 1.0%.

The main risk-forming factors limiting export volumes were identified and quantified: changes in animal feed prices, the spread of various epidemiological diseases in the territory of exporting countries, the level of state support for agriculture, and exchange rate volatility. A correlation analysis of export volumes of the European Union showed its strong dependence on the average feed cost per 1 kg of slaughter weight (correlation coefficient value -0.87) and the level of state support for agriculture (correlation coefficient value 0.56). These factors of variation are defined as significant and used for regression analysis. The constructed regression model describes the dependence of meat’s export volumes on changes in the most significant factors of variation as follows: an increase in the average feed cost (per 1 kg of slaughter weight) by $ 1 will reduce the export volume of European Union countries by 2.52 million tons; 1% increase in the level of state support for agriculture (% of GDP) will ensure the growth of export volume by 3.85 million tons.

Conclusions. The impact of risk factors on the export volume of the European Union countries has been assessed on the basis of the correlation and regression analysis, which allows to determine the variable factors having the greatest impact on the resulting indicator and to make an objective quantitative assessment of their impact.
Introduction

The global market of meat and meat products functions and develops under conditions of fierce competition [8], in which economic risk factors encourage investment [10], optimization [5], restructuring [6] and expansion [18] of the meat industry, thereby increasing its importance among other sectors of the global economy. The final results of production are largely predetermined by the ability of the producer to identify the economic risk factors accompanying his activities [12, 22, 32], and effectively manage them [15, 23, 26, 45]. Therefore, the analysis of development trends and risk factors of the world market of meat products is an actual economic task. According to the scientific hypothesis, the volume of meat products exports correlates not only with economic indicators, but also largely depends on the number of epidemiological outbreaks of infectious animal diseases [20, 34, 36]. To confirm this hypothesis, systematic scientific research is required. The analysis of literary sources has shown that at present there are no adequate mathematical models allowing to make scientifically grounded assessment of risk-forming factors impact on world meat products export. On this basis, the purpose of the study is to identify and analyze the most significant factors of economic risk and to build an adequate mathematical model describing their impact on the volume of exports of meat products.

Materials and methods

Object (and subjects) of research

The object of the research was the world market of meat and meat products. The subject of the study was the economic risk factors arising in the field of export relations of the European Union countries.

Analysis of development trends of the global meat products market

The statistical data of the Food and Agriculture Organization of the United Nations and the Organization for Economic Cooperation and Development have been used to analyze the volume and structure of meat and meat products production [14, 24].

Risk-forming factors of global meat export

Identification of risk-forming factors has been made on the analysis of fluctuation conditions of meat production export volumes on the basis of statistical data of the Food and Agriculture Organization of the United Nations, the Organization for Economic Cooperation and Development, the World Organization for Animal Health (MEB) [16, 25, 34, 36, 47].

Assessment of risk factors impact

The risk factors impact's assessment has been made on the correlation-regression analysis's basis [1, 21, 35, 48, 49], which provides identification of the dependence's degree of the output function on risk factors, the most significant ones selection and regression model's construction, which allows predicting the export volume's change at variation of analyzed parameters[11, 15].
Results and discussion

Analysis of development trends of the global meat products market

According to the results of the analysis, the main meat-producing regions did not significantly change their positions in the period from 2013 to 2017 (Table 1) [27–32, 37–41].

<table>
<thead>
<tr>
<th>Countries and regions</th>
<th>Years</th>
<th>Share in (2017), %</th>
<th>the region</th>
<th>the world</th>
</tr>
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<tr>
<td>Africa</td>
<td></td>
<td></td>
<td></td>
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</tr>
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<td>2013</td>
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<td>18,22</td>
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<td>6,70</td>
</tr>
<tr>
<td>Australia</td>
<td>4,54</td>
<td>4,88</td>
<td>4,97</td>
<td>4,69</td>
</tr>
<tr>
<td>New Zealand</td>
<td>1,36</td>
<td>1,38</td>
<td>1,43</td>
<td>1,44</td>
</tr>
<tr>
<td>WORLD</td>
<td>314,52</td>
<td>320,53</td>
<td>326,53</td>
<td>330,48</td>
</tr>
</tbody>
</table>

Footnote – The table is compiled by the author according to FAO data.

Thus, from 2013 to 2017, global production of meat and meat products increased by 6.3%, or 19.7 million tons, to 334.23 million tons. The share of Asian countries is the highest throughout the analyzed period, but it tends to decrease from 43% in 2013 to 42.4% in 2017. The share of European countries increased by 0.3% to 18.8% over this period. North and South America provided an increase of 0.2%, respectively. The share of African countries did not change significantly and amounted to 5.8% in 2017. The share of Oceania fell slightly to 1.9% in 2013-2017. The volume of meat production in the Republic of Belarus from 2013 to 2017 increased by 0.03 million tons, or 3.5%, and amounted to 1.21 million tons [1].

Since 2017 the main meat producers have been China (26%), 28 EU countries (14.4%), the USA (13.7%), Brazil (8.3%), Russia (3%), India (2.2%), Mexico (2%), Argentina (1.7%), Australia (1.3%). Meat production in the leading countries increased by 11.5 million tons over the past five years and amounted to 238.2 million tons in 2017, or 71.3% of the global volume.
Meat products are produced in almost all regions of the world and are the main source of animal proteins in the human diet [2]. The meat and slaughter products market is characterized by a relative homogeneity of its nomenclature (a small number of slaughter animal species). This segment is mainly represented by such types of meat as beef, pork, poultry and mutton (rabbit, horse meat and other types of meat occupy a small share in the production’s structure) (Table 2).

Table 2

<table>
<thead>
<tr>
<th>Countries and regions</th>
<th>Share of global production in 2017, %</th>
<th>Changes in 2017 by 2013, %</th>
<th>Countries and regions</th>
<th>Share of global production in 2017, %</th>
<th>Changes in 2017 by 2013, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beef</td>
<td></td>
<td></td>
<td>Pork</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>17,15</td>
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<td>China</td>
<td>46,30</td>
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</tr>
<tr>
<td>Brazil</td>
<td>13,72</td>
<td>98,7</td>
<td>The EU 28</td>
<td>19,78</td>
<td>105,1</td>
</tr>
<tr>
<td>The EU 28</td>
<td>11,31</td>
<td>106,4</td>
<td>The USA</td>
<td>9,69</td>
<td>110,4</td>
</tr>
<tr>
<td>China</td>
<td>9,93</td>
<td>107,8</td>
<td>Вьетнам</td>
<td>3,11</td>
<td>115,5</td>
</tr>
<tr>
<td>Argentina</td>
<td>4,08</td>
<td>100,7</td>
<td>Brazil</td>
<td>3,08</td>
<td>118,3</td>
</tr>
<tr>
<td>India</td>
<td>3,62</td>
<td>103,7</td>
<td>Russia</td>
<td>2,95</td>
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</tr>
<tr>
<td>Australia</td>
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<td>91,1</td>
<td>Canada</td>
<td>1,79</td>
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<tr>
<td>other countries</td>
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<td>119,3</td>
<td>Mexico</td>
<td>1,20</td>
<td>112,5</td>
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<td>other countries</td>
<td>10,56</td>
<td>105,2</td>
</tr>
<tr>
<td><strong>World</strong></td>
<td>100,00</td>
<td>104,1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poultry meat</td>
<td></td>
<td></td>
<td>Mutton</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Countries and regions</td>
<td>Share of global production in 2017, %</td>
<td>Changes in 2017 by 2013, %</td>
<td>Countries and regions</td>
<td>Share of global production in 2017, %</td>
<td>Changes in 2017 by 2013, %</td>
</tr>
<tr>
<td>The USA</td>
<td>18,20</td>
<td>110,8</td>
<td>China</td>
<td>30,89</td>
<td>114,7</td>
</tr>
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<td>China</td>
<td>15,52</td>
<td>100,4</td>
<td>The EU 28</td>
<td>6,34</td>
<td>99,0</td>
</tr>
<tr>
<td>The EU 28</td>
<td>12,08</td>
<td>114,7</td>
<td>Australia</td>
<td>4,82</td>
<td>110,6</td>
</tr>
<tr>
<td>Brazil</td>
<td>11,38</td>
<td>111,5</td>
<td>India</td>
<td>4,82</td>
<td>97,3</td>
</tr>
<tr>
<td>Russia</td>
<td>3,69</td>
<td>130,3</td>
<td>Pakistan</td>
<td>3,30</td>
<td>106,4</td>
</tr>
<tr>
<td>India</td>
<td>3,03</td>
<td>128,8</td>
<td>New Zealand</td>
<td>2,97</td>
<td>93,8</td>
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<tr>
<td>Mexico</td>
<td>2,73</td>
<td>117,2</td>
<td>Turkey</td>
<td>2,71</td>
<td>117,1</td>
</tr>
<tr>
<td>Indonesia</td>
<td>1,87</td>
<td>122,5</td>
<td>other countries</td>
<td>44,16</td>
<td>104,7</td>
</tr>
<tr>
<td>Turkey</td>
<td>1,84</td>
<td>125,0</td>
<td>WORLD</td>
<td>100,00</td>
<td>107,1</td>
</tr>
<tr>
<td>other countries</td>
<td>29,66</td>
<td>109,4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Footnote – The table is compiled by the author according to FAO data.
Production growth can be noted in all commodity groups: pork production increased by 4.16% (4.79 million tons), beef production - by 2.41% (1.65 million tons), poultry production - by 10.51% (11.6 million tons), mutton production - by 8.48% (1.2 million tons) [2].

The pork production leaders were China, the EU countries – 28, the USA, Vietnam, Brazil, Russia, Canada, the Philippines and Mexico in 2017. The output of these regions amounted to 107.12 million tons, or 89.4% of the global output.

Global beef production growth in 2013-2017 was mainly provided by increasing production in the USA, the EU countries – 28, China, Argentina, India and Mexico. At the same time, it was restrained by a decrease in production volumes of this product in Brazil and Australia. The beef production’s share in the largest beef-producing countries was 65.7%, or 45.71 million tonnes, of global beef production in 2017.

The increase in poultry production throughout the analyzed period was due to the growth in production volumes of major producing countries - the USA, China, the EU – 28, Brazil, Russia, India, Mexico, Indonesia and Turkey. In 2017, poultry output in these countries amounted to 86.07 million tonnes, or 70.34% of the global total [17].

The data analysis showed that China dominates the global production of mutton: in 2017, the share of this state in output was 30.89%. There are also EU countries – 28, Australia, India, Pakistan, New Zealand and Turkey among the main producers (Figure3) [7]. These countries produce 56% of this type of meat.

**Risk-forming factors of global meat export**

The volume of global meat export increased by 3.16 million tons in 2013–2017 [27–32, 37-41]. The increase in export was mainly due to the main exporting regions: the USA, Brazil, EU countries, Canada, Thailand and New Zealand (Figure1). Moreover, during the analyzed period, there was a decrease in exports from Australia, India, China and Argentina.

World pork exports in 2017 amounted to 8.23 million tons, which was 1.1 million tons, or 15.59%, higher than the level of 2013. At the same time we can note an increase in sales in the EU countries, the USA, Canada, Brazil and Mexico, while in China there was a significant decrease in exports (by 35.29%) (Figure2).

The main reason for the decline in exports from China was the restructuring of the pork industry and the consolidation of the meat and meat products market, which inevitably led to qualitative changes in the industry. It was associated with the redistribution of pork production in large industrial enterprises.

The need for this process was caused by the lack of the environmental safety’s necessary level, which the main subjects of the sector - private households, was not able to provide. [3]. As a result, ASF (African Swine Fever) was widespread throughout the country and was difficult to control with the current production structure. The primary meat-processing sector of China has been undergoing a restructuring process since 2008. However, the concentration of the industry remains at a low level. Private farms dominate the total pork production in China and occupy more than half of the market. Significantly, more stringent environmental standards were adopted to achieve the goal of meat sector concentration in the country, which led to a significant reduction in the sow’s number. In December 2016, the number of fattening sows and pigs decreased by 3.6% and 4.2%, respectively, compared to the same period last year. In 2017, the volume of imports to China accounted for 6% of total pork consumption. Unfortunately, this figure will amount to 7% by 2020, according to projections by FAO because the opportunities to increase domestic production will not be able to get ahead of sustainable consumption growth.
Table 1. Dynamics and structure of world meat and meat products exports by country

<table>
<thead>
<tr>
<th>Countries and regions</th>
<th>Years</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2013</td>
</tr>
<tr>
<td>The USA</td>
<td>7,57</td>
</tr>
<tr>
<td>Brazil</td>
<td>6,42</td>
</tr>
<tr>
<td>The EU –28</td>
<td>4,02</td>
</tr>
<tr>
<td>Australia</td>
<td>1,97</td>
</tr>
<tr>
<td>Canada</td>
<td>1,72</td>
</tr>
<tr>
<td>India</td>
<td>1,77</td>
</tr>
<tr>
<td>Thailand</td>
<td>0,8</td>
</tr>
<tr>
<td>New Zealand</td>
<td>0,92</td>
</tr>
<tr>
<td>China</td>
<td>0,71</td>
</tr>
<tr>
<td>Argentina</td>
<td>0,6</td>
</tr>
<tr>
<td>WORLD</td>
<td>29,67</td>
</tr>
</tbody>
</table>

Share of countries in world meat export in 2017, %

![Figure 1. Dynamics and structure of world meat and meat products exports by country](image)

Leading beef exporters, which accounted for 83.7% of world trade in 2017, included Brazil (18.2% of world beef exports), the United States (14.6%), India (16.6%), Australia (13.3%), New Zealand (5.3%), the EU (4.8%), Canada (4.3%), Uruguay (3.8%), Paraguay (3.4%), Argentina (3.0%) (Figure 3).

In the process of analysis, the growth of export deliveries of beef meat was established by 22.6% during the analyzed period. The increase in sales volumes of these products was observed from 2013 to 2017 in all major producing countries, except Australia and India, where a decrease in exports of this type of products by 6.2% and 2.3%, respectively, was observed.
The decrease in exports from Australia was a result of two-year drought period, partial herd liquidation, global competition strengthening, and also Australian dollar strengthening (predominantly against the USA dollar). In India a slight decline of exports was caused by the measures of state intervention of meat market, which resulted in introducing restrictions on cattle sale and purchase for slaughter on all cattle markets.

The world volume of poultry exports changed increasing in the analyzed period from 12.4 mln. tons in 2013 to 13.13 mln. tons in 2017 (the growth rate was 105.9 %). The main suppliers to export market in 2017 were: Brazil (32.6% from the world export of poultry meat), the USA (28.7%), the EU countries (11.8%), Thailand (8%), Turkey (3.4%), China (3.3%). As a whole their share amounted 87.7% of the world market (Figure 7). It should be noted that from the analyzed period the volume of exports reduces in the USA and China by 9.2% and 8.5% respectively.

The USA has been the leading exporter of poultry meat in the world for over a long period. However, the situation changed greatly due to the outbreak of Highly Pathogenic Avian Influenza (HPAI), which induced the importers to seek alternative sources of supply and, as a result, brought Brazil to the first place among exporters of poultry meat. Because of the restrictions imposed in the USA and spread of HPAI, China experienced lack of breeding material supply, which also made a significant impact on the export volume. According to the FAO data due to the continuous outbreaks of avian influenza in China further decrease in production volumes and poultry meat exports are forecasting.

---

**Table 1. Countries and Regions in World Pork Exports by Countries**

<table>
<thead>
<tr>
<th>Countries and Regions</th>
<th>2013</th>
<th>2014</th>
<th>2015</th>
<th>2016</th>
<th>2017</th>
</tr>
</thead>
<tbody>
<tr>
<td>The EU 28</td>
<td>2.29</td>
<td>2.21</td>
<td>2.42</td>
<td>3.12</td>
<td>2.85</td>
</tr>
<tr>
<td>The USA</td>
<td>2.17</td>
<td>2.13</td>
<td>2.19</td>
<td>2.29</td>
<td>2.44</td>
</tr>
<tr>
<td>Canada</td>
<td>1.21</td>
<td>1.18</td>
<td>1.19</td>
<td>1.26</td>
<td>1.3</td>
</tr>
<tr>
<td>Brazil</td>
<td>0.65</td>
<td>0.65</td>
<td>0.69</td>
<td>0.89</td>
<td>0.86</td>
</tr>
<tr>
<td>Mexico</td>
<td>0.12</td>
<td>0.13</td>
<td>0.14</td>
<td>0.15</td>
<td>0.18</td>
</tr>
<tr>
<td>Chile</td>
<td>0.16</td>
<td>0.16</td>
<td>0.17</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td>China</td>
<td>0.17</td>
<td>0.2</td>
<td>0.13</td>
<td>0.1</td>
<td>0.11</td>
</tr>
<tr>
<td>WORLD</td>
<td>7.12</td>
<td>6.97</td>
<td>7.24</td>
<td>8.28</td>
<td>8.23</td>
</tr>
</tbody>
</table>

**Figure 2. Dynamics and structure of world pork export by countries**

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---

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Table 3. Dynamics and structure of world beef exports by country

<table>
<thead>
<tr>
<th>Countries and regions</th>
<th>2013</th>
<th>2014</th>
<th>2015</th>
<th>2016</th>
<th>2017</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brazil</td>
<td>1.77</td>
<td>1.84</td>
<td>1.7</td>
<td>1.69</td>
<td>1.86</td>
</tr>
<tr>
<td>The USA</td>
<td>1.23</td>
<td>1.22</td>
<td>1.22</td>
<td>1.34</td>
<td>1.49</td>
</tr>
<tr>
<td>Australia</td>
<td>1.45</td>
<td>1.68</td>
<td>1.7</td>
<td>1.35</td>
<td>1.36</td>
</tr>
<tr>
<td>India</td>
<td>1.75</td>
<td>1.93</td>
<td>1.68</td>
<td>1.64</td>
<td>1.71</td>
</tr>
<tr>
<td>New Zealand</td>
<td>0.48</td>
<td>0.53</td>
<td>0.58</td>
<td>0.54</td>
<td>0.54</td>
</tr>
<tr>
<td>EC 28</td>
<td>0.28</td>
<td>0.32</td>
<td>0.45</td>
<td>0.46</td>
<td>0.49</td>
</tr>
<tr>
<td>Canada</td>
<td>0.31</td>
<td>0.34</td>
<td>0.38</td>
<td>0.42</td>
<td>0.44</td>
</tr>
<tr>
<td>Uruguay</td>
<td>0.32</td>
<td>0.31</td>
<td>0.34</td>
<td>0.38</td>
<td>0.39</td>
</tr>
<tr>
<td>Paraguay</td>
<td>0.3</td>
<td>0.36</td>
<td>0.35</td>
<td>0.36</td>
<td>0.35</td>
</tr>
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<td>0.22</td>
<td>0.2</td>
<td>0.23</td>
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</tr>
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<td>0.14</td>
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</tr>
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<td>0.32</td>
<td>0.45</td>
<td>0.46</td>
<td>0.49</td>
</tr>
<tr>
<td>Brazil</td>
<td>1.77</td>
<td>1.84</td>
<td>1.7</td>
<td>1.69</td>
<td>1.86</td>
</tr>
</tbody>
</table>

Figure 3. Dynamics and structure of world beef exports by country

World volumes of mutton exports increased slightly from 2013 to 2017 by only 1.0% (Figure 5). We have identified the main mutton exporting countries where exports of this product increased or decreased. The increase in mutton exports occurred in Australia (+4.7%), while the decrease was observed in New Zealand (-2.5%) and the EU countries (-3.2 thousand tons). In India, exports remained at the same level.
Having analyzed the main tendencies of development of the world meat market export, it can be concluded that its limitations is mainly due to the following risk-forming factors:

− increase in prices for animal feed, the growth of costs for raw materials production and processing, auxiliary materials, electricity, etc. [4, 23, 42, 43];
− the spread of various epidemiological diseases in exporting countries (e.g., African Swine Fever, Highly Pathogenic Avian Influenza) [20];
− state stimulation of domestic consumption growth, as well as development and implementation of targeted state programs aimed at increasing consumption of meat products;
− fluctuation in rates of exchange;
− actions of state authorities in the country of the counterparty and changes in legislation in the spheres affecting the activities of business entities;
− difficulties in predicting climate conditions in major exporting regions;
− conditions for the transportation and storage of meat products largely determine the regional features of product sales. This is a limiting factor of export even in case of increased production and increased demand in remote markets.

The research component was as follows:
- systematization and grouping of initial data;
- determining the connection's closeness between effective and factor features in relevant period [9, 45];
- construction of a regression model [13, 44];
- analysis of obtained dependencies.

The resulting indicator (Y) was the export volume of the European Union countries for the period 2012-2017 (million tons).

Factor features were:
- \( X_1 \) – average feed cost (per 1 kg of slaughter weight), (USD);
- \( X_2 \) – number of epidemiological outbreaks of animal diseases (once a year);
- \( X_3 \) – level of state support for agriculture (% of GDP);
- \( X_4 \) – exchange rate volatility against the US dollar (%).

The use of these factors of variation for correlation and regression analysis is caused by their impact on fluctuations of export volumes and the maximum frequency of manifestation.

The boundaries of factors changes are presented in Table 3.

On the basis of the conducted correlation analysis, the values of correlation coefficients for each type of correlation between the resulting indicator and the factors of variation were determined, as well as the characteristic of connection's closeness. The degree of each factor feature impact on the resulting indicator is presented in Table 4.
### Table 3

Boundaries of changes in the resulting indicator and variation factors

<table>
<thead>
<tr>
<th>Indicator name</th>
<th>Boundaries of variation</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum value</td>
<td>Maximum value</td>
</tr>
<tr>
<td>Export volume (Y), mln. t</td>
<td>3,99</td>
<td>5,16</td>
</tr>
<tr>
<td>Average feed cost (per 1 kg of slaughter weight)</td>
<td>0,98</td>
<td>1,58</td>
</tr>
<tr>
<td>(X1), USD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of epidemiological outbreaks of animal</td>
<td>1388</td>
<td>9929</td>
</tr>
<tr>
<td>diseases (X2), once a year</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Level of state support for agriculture (X3), % of</td>
<td>0,645</td>
<td>0,777</td>
</tr>
<tr>
<td>GDP</td>
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<td></td>
</tr>
<tr>
<td>Exchange rate volatility against the US dollar</td>
<td>-3,22</td>
<td>+19,64</td>
</tr>
<tr>
<td>(X4), %</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 4

Characteristics of the connection’s closeness between the indicators

<table>
<thead>
<tr>
<th>Interrelated indicators</th>
<th>Symbol of relationship</th>
<th>Correlation coefficient value</th>
<th>Characteristics of connection’s closeness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Export volume (Y), mln. t Average feed cost (per 1 kg of</td>
<td>Y→X1</td>
<td>-0,87</td>
<td>Very strong</td>
</tr>
<tr>
<td>slaughter weight) (X1), USD</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Export volume (Y), mln. t Number of epidemiological</td>
<td>Y→X2</td>
<td>0,37</td>
<td>Weak</td>
</tr>
<tr>
<td>outbreaks of animal diseases (X2), once a year</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Export volume (Y), mln. t Level of state support for</td>
<td>Y→X3</td>
<td>0,56</td>
<td>Strong</td>
</tr>
<tr>
<td>agriculture (X3), % of GDP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Export volume (Y), mln. t Exchange rate volatility against</td>
<td>Y→X4</td>
<td>0,17</td>
<td>Too weak</td>
</tr>
<tr>
<td>the US dollar (X4), %</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The analysis of correlation coefficient values has shown a very strong and strong dependence of export volumes (Y) on the average feed cost (X1) and the level of state support of agriculture (X3). Therefore, these factors of variation can be determined as significant and used for regression analysis. The relationship between the number of epidemiological outbreaks of animal diseases (X2), the volatility of the national currency exchange rate (X4) and the volume of meat and meat products export from the European Union is assessed as weak and very weak, respectively.

In order to be able to predict changes in the export volume of the European Union (EU) countries with the variation of the average feed cost (X1) and the level of agriculture’s state support (X3), the mathematical dependence has been obtained, which also allows us to assess the impact of factors on the output function. The multifactor regression equation has the following form:

\[ Y = 4,96 - 2,52X_1 + 3,85X_3 \] (1)
This correlation model reflects the close dependence of the resulting indicator on the factor ones. Multiple correlation coefficient is close to one and equal to 0.92. The reliability of the model is estimated on the level of importance of Fisher’s criterion (\( p \)), which should be less than 0.05 (\( p = 0.0443 \), so the model is significant). The accuracy’s degree of the process model description is characterized by the value of the determination coefficient (R-square). Since R-square = 0.85, we can talk about a satisfactory approximation (the model as a whole is adequate to the described phenomenon).

The regression equation’s coefficients show the quantitative impact of each factor on the resulting index, while the others remain unchanged. The analysis shows the following trends: an increase in the average feed cost (per 1 kg of slaughter weight) by $1 will reduce the export volume of European Union countries by 2.52 million tons; 1% increase in the level of agriculture’s state support (% of GDP) will ensure the growth of export volume by 3.85 million tons.

**Conclusions**

The analysis of development trends and risk factors of the world export of meat products has shown that fluctuations in export volumes are influenced by many factors: changes in prices for animal feed, spread of various diseases of epidemiological nature in the territory of exporting countries, state support for agriculture, stimulation of domestic consumption growth, fluctuations of exchange rates, etc.

The assessment of risk factors impact on the export volume of the European Union countries on the basis of correlation and regression analysis allowed us to determine that the average feed cost per 1 kg of slaughter weight (very strong feedback) and the level of agriculture’s state support (strong direct dependence) have the greatest impact on the resulting indicator. Changes in the number of epidemiological outbreaks of animal diseases have little impact on the European Union meat exports. The correlation between the volatility of the national currency exchange rate and the volume of exports is assessed as very weak. The regression model, which describes the meat exports volume dependence on the change in the average feed cost per 1 kg of slaughter weight and the level of agriculture’s state support, is adequate and allows predicting the change in the resulting indicator when the factors of variation change.

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Анотації

Харчові технології

Вплив високого тиску на м'ясо та м'ясні продукти. Огляд

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Вступ. Переробка м'яса високого тиску вважається найкращою технологією нетермічної обробки для продовження терміну зберігання та безпеки м'яса, напівфабрикатів із м'яса і готових до вживання м'ясніх продуктів, оскільки зберігає сенсорні та харчові властивості.

Матеріали і методи. Предметом статті є властивості м'яса, м'ясних продуктів, гелевої та білкової конформації міофібрилярних білків, оброблених високим тиском. Метод дослідження – аналіз та узагальнення останніх досліджень провідних світових наукових журналів.

Результати і обговорення. Під час обробки високим тиском рівень тиску становить 100-1000 МПа, а температурний діапазон – від -20 °C до 90 °C. Актуальність і перспективність дослідження використання технології високого тиску в м'ясній промисловості доведено на основі аналізу принципу переробки м'яса та м'ясніх продуктів високого тиску, впливу високого тиску на: властивості м'язів (pH, колір, текстура, ніжність, вологоутримуюча здатність); подрібнені м'ясні продукти (вологоутримуюча та жироутримуюча здатність, текстура); особливості гелевої та білкової конформації міофібрилярних білків (водно-жирова здатність міофібрилярних білків, ковалентні та нековалентні зв'язки, білкова конформація міофібрилярних білків).

Обробка високим тиском покращує властивості м'язових, м'ясних продуктів та міофібрилярних білків. Застосування помірного тиску до настання посмертного заклікання м'яса збільшує його ніжність і тривале зберігання кольору. Обробка високим тиском може підвищити вологоутримуючу та жироутримуючу здатність і покращити текстуру подрібненого м'яса. Високий тиск також впливає на ковалентні та нековалентні зв'язки і білкову конформацію міофібрилярних білків, розвиває здатність до утримання води, покращує структуру білків міофібрили.

Висновок. Застосування технології високого тиску в м'ясній промисловості є важливим і перспективним. Однак вплив факторів на м'язові властивості, фарш та міофібрилярні білки при використанні високого тиску дуже складний, і його слід вивчати далі.

Ключові слова: тиск, м'ясо, текстура, протеїн, гель.
Порівняння жирокислотного та амінокислотного складу м’яса та ікри мерланга (*Merlangius merlangus euxinus Nordman, 1840*) під час риболовного сезону в Чорному морі

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Вступ. Метою дослідження є визначення жирокислотного і амінокислотного складу м’яса та ікри мерланга, які виловлені в різні місяці року в Чорному морі.

Матеріали і методи. Мерланг (*Merlangius merlangus euxinus Nordman, 1840*) виловлений в районі Синопу у середньому Причорномор’ї. Відбір проб проводився двічі на місяць. М’ясо мерланга та іку порівнювали за жиркислотним (ЖК) та амінокислотним (АК) складом під час риболовного сезону в Чорному морі.

Результати і обговорення. Протягом шести місяців довжина та вага мерлангів, що виловилися у дослідженнях, коливались між 14,15–16,60 см та 24,49–29,68 г відповідно. Мінімальну довжину і вагу зафіксували в березні. Максимальна довжина та вага відповіли у травні (18,61 г/100 г) та у квітні (16,30 г/100 г).

Вміст НЖК (насичених жирних кислот), МНЖК (мононенасичених жирних кислот) та ПНЖК (поліненасичених жирних кислот) в рибному м’ясі та ікрі протягом сезону відрізняється. Мінімальний і максимальний вміст ейкозапентаєнової кислоти (ЕПК), докозагексаєнової кислоти (ДГК) було виявлено на рівні 7,42–10,72 г/100 г у м’ясі та 0,03–0,37 г/100 г в ікрі відповідно. Максимальне та мінімальне значення ω3/ω6 було виявлено у квітні 14,01 та у березні 4,47 г/100 г в рибному м’ясі відповідно.

Найвища кількість незамінної амінокислоти (НА) лізину була як у м’ясі, так і в ікрі протягом усіх місяців. Кількість лізину і глутамінової кислоти у рибному м’ясі була вищою, ніж у записаних значеннях для ікрі. Вміст глутамінової кислоти в рибному м’ясі був вищим, ніж у рибній ікрі протягом усього терміну дослідження. Співвідношення НА/ЗА було максимальним (0,9) в березні в рибному м’ясі. Співвідношення НА/ЗА ікри риби було виявлено у межах 0,7–0,9 протягом усього риболовного сезону.

Було встановлено, що м’ясо та ікра мерланга містять велику кількість незамінних жирних кислот і амінокислот.

Висновок. Харчова цінність рибного м’яса та ікри змінюється сезонно. Але вміст ароматичних амінокислот в рибному м’ясі вищий, ніж в ікрі.

Ключові слова: мерланг, ікра, амінокислота, жирні кислоти, ейкозапентаєнова кислота, докозагексаєнова кислота.

Вплив виду упаковки та температури на якісні характеристики поперекових м’язових волокон і трицепсу стегна яловичини при тривалому зберіганні

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Вступ. Метою дослідження є кількісне дослідження впливу виду упаковки, температури зберігання і тривалості зберігання з метою підвищення органолептичних показників та стабільність забарвлення поперекових м’язів і трицепсів стегна яловичини, які становлять основну частину сьогоднішнього постачання.
Матеріали і методи. Парні м’язи поперекових м’язових волокон і трицепсів стегна були відібрани з 27 та 54 яловичих туш зрілості 2 та 4 °C відповідно протягом 21, 32 та 42 діб для поперекових та 21, 28 та 35 діб для трицепсів стегна в одному з трьох варіантів упаковки: DryBag®, традиційний вакуумний пакет і без упаковки.

Результати і обговорення. Вихід готової продукції був аналогічним при зберіганні в упаковці DryBag® та без неї. Температура зберігання та тип упаковки мали незначний вплив на якісні показники м’яса. Стейки з поперечних м’язів, які зберігалися протягом 42 діб, мали нижчі значення граничного напруження зсуву і більш ніжні органолептичні показники, ніж стейки з поперечних м’язів, які зберігалися протягом 21 доби, хоча фактична різниця була незначною. Ніжність стейків трицепсу стегна була однаковою, незалежно від тривалості зберігання. Тривалість зберігання мала більший вплив на вихід, ніж на органолептичні показники, а температура зберігання й упаковка мала незначний вплив на показники якості всіх зразків.

Висновок. Якісні показники поперекових м’язових волокон і трицепсів стегна, які визначені у сортових відробках, що зберігалися в упаковці DryBag® і без упаковки, суттєво не відрізнялися. Вид упаковки мав незначний вплив на органолептичні показники, а температура зберігання вплинула на всі показники якості зразків.

Ключові слова: яловичина, зберігання, упаковка.

Делігніфікація лігніно-целюлозної біомаси для виробництва етилового спирту

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Вступ. Молекули цукрів лігніно-целюлозної біомаси є малодоступними для здійснення деполімерізації полісахаридів. Метою дослідження є визначення впливу фізико-хімічних параметрів на перебіг органосольвентної делігніфікації лігніно-целюлозної біомаси.

Матеріали і методи. Об’єкт дослідження — спосіб органосольвентного розчинення лігніну. Як сировину використовували пшеничну солому, післязбиральні відходи кукурудзи та стебло цукрового сорго. Вміст лігніну визначали шляхом гідролізу сумішшю концентрованої соляної та 72% сірчаної кислоти, полісахариди — за кількістю моносахаридів методом Макена та Шoorля.

Результати і обговорення. Для досягнення максимально можливого розчинення лігніну досліджено склад розчинника, ступінь подрібнення сировини, температуру обробки і тривалість процесу. Залежності від змінення концентрації сірчаної кислоти (z 1 до 3,9 %) в розчиннику вихід лігніну зі соломи відрахувався від 14,4 до 29,2%, а вміст нерозчиненої кислоти зменшувався з 66,7 до 25,4%. Для стебел цукрового сорго з 70 до 100С змінений вихід хвилку змінювався, відповідно, від 19,3 до 32,4%. Підвищення температури обробки з 70 до 100С полісахариди зменшили збільшення добавлення кислоти в 3,0, для стебела цукрового сорго з 70 до 100С полісахариди сприяли збільшенню вихід конверсії лігніну на 3%, а для стебел цукрового сорго з 70 до 100С змінювався, з 6,8 до 17,1%. Незалежно від типу рослини сировини максимальне
розчинення лігніну відбувається за температури 100°C, при цьому найбільший вихід редукуючих речовин досягається впродовж 1 години. Збільшення тривалості обробки до 6 годин підвищує ступінь конверсії лігніну, але при цьому спостерігається руйнування молекул цукрів, вміст яких зменшується майже вдвічі.

**Висновки.** Ступінь гідролізу лігніну органосольвентним розчинником можна регулювати шляхом вибору раціональних режимів подрібнення сировини, температурою й тривалістю процесу.

**Ключові слова:** спирт, целюлоза, біомаса, сольвент, лігнін, конверсія.

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**Вплив пошкодженого крохмалю на якісні показники пшеничного тіста і хліба**

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**Вступ.** Незначне пошкодження гранул крохмалю є бажаним, але надмірний рівень пошкодження крохмалю негативно впливає на якість хлібних виробів.

**Матеріали і методи.** Пшеничне борошно з більш низьким (3,15%) і більш високим ступенем пошкодження крохмалю (6,13%) було отримане шляхом повторного подрібнення (в два етапи) в млині лабораторного типу. Реологічні дослідження зразків тіста проводилися із використанням фаринографа і екстензографа, а властивості клейстеризації визначені за допомогою диференціальної скануючої калориметрії і мікровіскоамілографа. Дослідження пористості зразків хліба проводилося з використанням аналізатора структури, а питомий об’єм – методом лазерної топографії.

**Результати і обговорення.** Властивості тіста були кращими для зразків з більш високим рівнем пошкодження крохмалю, і значне покращення було помічено при збільшенні водопоглинання від 60,7 до 63,8%. Підвищення водопоглинання може бути пов’язане з впливом пошкодженого крохмалю, а також із впливом розміру часток борошна, оскільки дрібніші частинки мають велику загальну площу поверхні. Пошкодження крохмалю несуттєво впливає на більшість екстензографічних показників, хоча спостерігалося невелике зниження стійкості й еластичності. Зразки з більш високим ступенем пошкодження крохмалю показали знижену здатність до клейстеризації. Ентальпія клейстеризації (ΔHg) знизилася від 1,41 до 1,31 Дж/кг, а в’язкість амілографічного піку – від 582,5 до 505,0 BU. Це пояснюється обмеженим набуханням пошкоджених гранул крохмалю через втрату організованої структури. Не було встановлено істотних відмінностей у змісті вологи і активності води між зразками з різним вмістом пошкодженого крохмалю. Пошкодження крохмалю значно впливає на якість якісних показників хліба, але збільшення твердості і питомий об’єм були найбільш вираженими. Збільшились твердість від 4,09 Н до 5,25 Н і питомий об’єм від 4,04 cm³/g до 3,53 cm³/g) при використанні борошна з більш високим ступенем пошкодження крохмалю.

**Висновки.** Ступінь пошкодження крохмалю має значний вплив на реологічні властивості тіста, клейстеризацію крохмалю, а також на якісні показники хліба.

**Ключові слова:** хліб, тісто, крохмаль, якість.
Ефективність натуральних рослинних екстрактів у технології комбінованих м’ясомістких хлібів

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Вступ. Метою досліджень є аналіз ефективності застосування екстрактів розмарину та журавлини в технології комбінованих м’ясомістких хлібів із м’ясом прісноводної риби, яке відрізняється високим вмістом поліненасичених жирних кислот.

Матеріали і методи. Модельним зразком для вивчення ефективності екстрактів розмарину і журавлини послужив м’ясомісткий хліб із м’ясом прісноводної риби. Під час зберігання м’ясомістких хлібів із внесенями екстрактами визначали загальноперіодичні методами кислітне, перекисне числа, тіобарбітурове число.

Результати і обговорення. Екстракт розмарину має високу антиоксидантну активність та ефективно гальмує процес окислення ліпідів у м’ясомістких комбінованих хлібах з м’ясом мускусної качки і фаршем товстолобика.

Екстракт журавлини не гальмує гідроліз жиру під час зберігання м’ясомістких комбінованих хлібів і має незначний позитивний вплив на утворення первинних продуктів окислення та накопичення вторинних продуктів окисного псування ліпідів. Внесення екстракту розмарину в кількості 0,02—0,06% дає змогу уповільнити гідролітичне окислення ліпідів фаршу на 36,19—36,36%.

Внесення екстракту розмарину в концентраціях 0,02—0,06% до маси фаршу сприяє збільшенню окислення ліпідів у м’ясомістких комбінованих хлібах з м’ясом мускусної качки та фаршем товстолобика в кількості 0,02—0,06% до маси сировини. ПЧ в цьому зразку в кінці терміну дорівнювало 0,013±0,001%J2, тоді як у контролі цей показник становив 0,05±0,001%J2, що практично в 4 рази вище.

Стабілізація перекисного окислення ліпідів у м’ясомістких хлібах з м’ясом мускусної качки та фаршем товстолобика як наслідок має гальмування утворення вторинних продуктів окислення, що підтверджується отриманими результатами. Кількість альдегідів і кетонів була найдошішою в кінці терміну зберігання готових хлібів з екстрактом розмарину і становила 0,74—0,76 мг МА/кг, що нижче, ніж у контрольному зразку на 17—20 %. Продукти містять значну кількість вологи в активній фазі, що унеможливлює довготривале зберігання продуктів без використання речовин, що сповільнюють процеси псування.

Висновки. Доведено, що додавання екстрактів розмарину і журавлини сприяє гальмуванню окислення ліпідів при зберіганні м’ясомістких хлібів з комбінованим складом сировини.

Ключові слова: м’ясо, риба, хліб, екстракт, розмарин, журавлина.
Вплив гідроколоїдів на властивості тіста і якість безглютенового хліба, збагаченого сироватковим білковим концентратом

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Вступ. Вивчено вплив гідроколоїдів (ксантанової смоли та гуарової смоли) на властивості тіста та якість безглютенового хліба з рисового і кукурудзяного борошна, збагаченого концентратом білкової сироватки.

Матеріали і методи. Для приготування концентрату сироваткового білка було використано лабораторну систему зі змінним модулем плоскої ультрафільтраційної мембрани. Консистенцію тіста вимірювали за ступенем занурення за допомогою автоматичного пенетрометра.

Результати і обговорення. На основі попередніх експериментів (з 5, 10 та 15%) було встановлено, що оптимальна кількість концентрату сироваткового білка становила 10%. Тому для подальших експериментальних досліджень для контрольного хліба додавали 10% концентрат сироваткового білка. Додавання більшої кількості ксантованої смоли призводило до слабкої консистенції тіста. Щодо консистенції тіста можна зробити висновок, що додавання ксантованої смоли призводить до вивільнення тіста, незалежно від її кількості. Найкращий результат був отриманий при додаванні 1,5% гуарової смоли. Максимальне збільшення об’єму хліба було отримано при додаванні 1,5% гуарової камеді. Питомий об’єм хліба значно покращився при додаванні гідроколоїдів. Було встановлено, що контрольний зразок мав менший питомий об’єм. Зразки, що містять гідроколоїд, мали більший об’єм, ніж контрольний. Додавання 1% ксантованої смоли призяло до збільшення індексу H/D на 50% порівняно з контрольним зразком. При додаванні 1,5% гуарової смоли отримано найвищі результати – збільшення порівняно з контрольним зразком становило 100%. Гуарова смола мала більший вплив на органолептичні властивості безглютенового хліба з рису і кукурудзяного борошна, ніж ксантована камедь. Додавання 1,5% гуарової смоли призяло до найкращих результатів майже для всіх органолептичних властивостей (без пористості та післясмаку).

Результати, що стосуються пористості та післясмаку, не відрізнялися від отриманих з додаванням 1% гуарової смоли. Додавання 1,5% гуарової смоли у рецептурі безглютенового хліба з рису і кукурудзи, розмілених до найбільшого обсягу, призяло до рівномірного кольору шкоринки і мякуша, з відсутністю іржавих та інших нетипових відтінків. Аромат був слабшим, коли використовували 1% гуарової смоли. Зразки хліба з гуаровою смолою були оцінені як більш хрусткі, з дуже приємним смаком і післясмаком.

Висновок. У технології безглютенового хліба з рису і кукурудзяного борошна, збагаченого концентратом сироваткового білка, найбільш доцільним є додавання 1,5% гуарової смоли.

Ключові слова: хліб, гідроколоїди, кукурудза, рис, борошно.
Хімічні аспекти складу продуктів з насіння промислових конопель

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Вступ. Мета роботи – дослідження теоретичних і експериментальних аспектів хімічного складу та якості продуктів з насіння конопель, включаючи процеси окиснення в оліях, насінні та продуктах переробки.

Матеріали і методи. Матеріали дослідження – насіння промислових конопель сорту «Глесія», пресова олія та олійні композиції, обрушене насіння конопель. Показники якості досліджуваних матеріалів оцінювали за загальнодержавними методиками та Кодексом Аліментаріус.

Результати і обговорення. Отримані конопляні олії за вмістом жирних кислот, фосфоліпідів, вітамінів А і Е володіють підвищеною біологічною цінністю, а за вмістом токоферолів суттєво переважають соняшникову, кунжутну та амарантову олію. За антиоксидантною стійкістю кращим є зразок пресової олії ММ60. Співвідношення есенціальних жирних кислот наближено до ідеального: Омега-6 і Омега-3 як 3,0:1 – 3,7:1, тоді як в лляній олії – 1:3,6. Конопляна олія також містить біологічно цінну гамма-ліноленову кислоту. Методом спектрофотометрії підтверджено наявність каротиноїдів і хлорофілів у пресовій конопляній олії. Вміст вітаміну А в олії становить 78 мг/кг, вітаміну Е (сумарного) – 562,8 мг/кг. За хімічними показниками конопляна олія краще зберігається за температури 8±2 °С без доступу світла. Отримані конопляна олія та олійні композиції мають хорошу якість. Кращею шляхом підвищення якості насіння конопель без оболонки покращується, якщо порівняти з вихідним насінням.

Висновки. Конопляну олію та обрушене насіння конопель доцільно використовувати у виробництві функціональних харчових продуктів.

Ключові слова: коноплі, насіння, олія, амінокислота, функціональний.
Матеріали і методи. Приготували та вивчали желе, що містять сік фізалісу та сахарози (зразок S), фруктозу (зразок F) або мальтитол і сироп мальтитолу (зразок M) відповідно.

Результати і обговорення. Не було суттєвих відмінностей між зразками за вмістом сухої речовини і титрованою кислотністю. Найвищий загальний вміст цукру виявлений у зразку S (72,68%), а найнижчий – у зразку M (7,12%). Зразок M мав приблизно на 90% нижчий загальний вміст цукру, ніж зразок S, і приблизно на 83% нижчий, ніж зразок F. Отже, желе з сиропом мальтитолу можна класифікувати як "Харчовий продукт без додавання цукрів". Завдяки своєму складу така ж заява може бути віднесена до зразка F. Зразок F мав найбільшу сорбційну здатність, при якій спостерігався процес поглинання, а вміст вологи в желе зріс з 28,23% до 32,65% через 120 год. Зразки S і M виявили процес десорбції (зменшення приблизно на 2–3%, 120 год), тобто більшу стабільність у плані зберігання. Профіль текстури зразка M був більш сприятливим до подальшого використання желе, оскільки мав найвищу твердість (120 ±2) °C протягом 24 годин.

Висновок. Желе із соком фізалісу та сиропом мальтитолу можна класифікувати як "Низькоалорійний продукт" і "Харчовий продукт без додавання цукрів".

Ключові слова: фізаліз, мальтитол, фруктоза, желе, функціональний.
контролю значення зафіксоване на рівні 62,84%. Коефіцієнт раціональності амінокислотного складу становить 0,74±0,12, що на 3% вище ніж для молочно-білкового концентрату, виробленого за традиційною технологією.

Інтенсивність перетравлюваності білків in vitro під дією ферментів (пепсин + трипсин) з введенням у молочно-білкові концентрати солодових інгредієнтів прискорюється. Це пояснюється попереднім гідролізом і деструкцією білкових речовин при солодощені зернових.

Висновок. Результати дослідження згустків методом високорозчинної хроматографії підтверджують, що молочно-білкові концентрати із солодовими інгредієнтами мають підвищену біологічну цінність на 1,11–2,98%.

Ключові слова: молоко, білок, солод, амінокислота.

Вплив хлористого кальцію і альгінату натрію на реструктуризацію рибної продукції

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Вступ. Метою досліджень є визначення механізму реструктуризації рибної продукції при застосуванні хлористого кальцію та альгінату натрію.

Матеріали і методи. Рибний фарш з філе маломірних екземплярів коропа (білки – 16,5±0,2%; жири – 1,2±0,03%, мінеральні речовини – 1,3±0,03%); структуроутворювачі – альгінат натрію (C₆H₇O₆Na)n, хлорид кальцію (CaCl₂). Метод ротаційної віскозиметрії – реологічні характеристики; метод енергетичної абсорбції у діапазоні середніх довжин хвиль інфрачервоного спектра – енергетичні речовини; метод спектрофотометрії та рентгенофлуоресцентний метод – мінеральний склад; описувальний і профільний метод – органолептичні показники.

Результати і обговорення. Досліджено функціональні та технологічні властивості рибної продукції в процесі реструктуризації альгінатом натрію та хлоридом кальцію. Додавання у рибний фарш до 1,0% альгінату натрію призводить до збільшення ефективної в'язкості системи до 3,60·10⁻³ Па·с (швидкість зсуву ε=1,8 с⁻¹). Збільшення концентрації альгінату натрію від 2,0 до 3,0% призводить до аналогічного збільшення ефективної в'язкості від 6,9·10⁻³ до 12,6·10⁻³ Па·с. При цьому, доведено, що додавання альгінату натрію з концентрацією 2,0% забезпечує повноту утворення структури рибної продукції у процесі її формування.

Встановлено, що інтенсифікація процесу структурування рибної продукції відбувається завдяки тривалості витримки системи рибний фарш/альгінат натрію у 5-відсотковому розчині хлориду кальцію (CaCl₂) впродовж 6–7·60 с при необхідному рівні ефективної в'язкості. Збільшення часу структурування (>7·60 с) і подальше формування призводять до погіршення органолептичних показників – появи гіркого смаку, за наявності вільних іонів кальцію.

У діапазоні концентрації альгінату натрію 1–3% відбувається збільшення водоутримувальної здатності рибної продукції у 1,27–1,45 раза. Максимальне значення органолептичних показників – 5 балів – отримала рибна продукція з концентрацією альгінату натрію 2,0–2,5%. Подальше збільшення концентрації альгінату натрію від 2,5 до 3,0% призводить до збільшення ефективної в'язкості та
інтрогуєючої здатності системи та характеризує зразки зі зниження органолептичним показниками, які характеризуються жорсткістю структури.

**Висновки.** Рациональні значення технологічних параметрів: концентрації альгінату натрію в рецептурній суміші – 2,0–2,5%; концентрація хлориду кальцію в розчині – 5,0%; час обробки утворених зразків у розчинах хлориду кальцію – (6–7)·60 с.

**Ключові слова:** короп, реструктурований, напівфабрикат, альгінат натрію, риба, філе.

**Особливості формування смакових відчуттів**

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**Вступ.** Важливою характеристикою, яка відображає якість і формує цінність харчового продукту, є його органолептичні властивості, наприклад, смакові відчуття. Однак даних, які достовірно описують механізм виникнення смакових відчуттів, недостатньо.

**Матеріали і методи.** Предметом досліджень були вуглеводи, білки та кухонна сіль. Фазова структура досліджена методом рентгенографії. Дифракційні криві реєстрували на рентгенівському дифрактометрі HZG 4A (Carl Zeiss, Jena) з використанням випромінювання міді (CuKα), фільтрованого нікелем. Сканувальні електронні мікрофотографії нативних гранул крохмалю були отримані з використанням сканувального електронного мікроскопа LEO 1420.

**Результати і обговорення.** Досліджено фазову і морфологічну структуру вуглеводів (моносахаридів, дисахаридів і полісахаридів) і хлориду натрію, а також морфологічну структуру білків молока. Серед вуглеводів глюкоза, фруктоза, сахароза, мальтоза, лактоза і рамноза мають кристалічну структуру, нативні крохмали мають аморфно-кристалічну (перехідну або проміжну) структуру, а мальтодекстрини – аморфну. Кухонна сіль має кристалічну структуру.

Показано, що при формуванні смакових відчуттів велике значення має геометрія смакових рецепторів язика і аналізованих смакових об’єктів, яка створюється відповідно до принципу взаємодоповненості (наприклад, замком). Аналізатори смаку язика й аналізовані об’єкти смаку універсальні за розміром і мають фрактальну структуру. Найменша неподільна фрактальна одиниця – це електрон. Фрактальна структура аналізаторів смаку є безперервною, а аналізовані смакові об’єкти – переривчастими і залежать від ступеня чистоти об’єкта. Багато речовин (білкові молекули та ін.) мають складну ієрархічну структуру і залежать від степенні чистоти об’єкта. Багато речовин (білкові молекули та ін.) мають складну ієрархічну структуру і залежать від степеня чистоти об’єкта. Багато речовин (білкові молекули та ін.) мають складну ієрархічну структуру і залежать від степеня чистоти об’єкта. Багато речовин (білкові молекули та ін.) мають складну ієрархічну структуру і залежать від степеня чистоти об’єкта.
Висновок. Висунуто гіпотезу про хеморецепцію, зокрема про формування смакових відчуттів, що дало змогу закласти основи математичного опису смаку.

Ключові слова: смак, хеморецепція, вуглевод, білок, фрактал, компліментарність.

Процеси і обладнання

Вплив дискретно-імпульсного введення енергії на дисперсність біомаси рослинної сировини

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Вступ. Метою роботи є визначення впливу режимів диспергування біомаси рослинної сировини в роторно-пульсаційному апараті методом дискретно-імпульсного введення енергії.

Матеріали і методи. Матеріалом досліджень були солома пшениці та стебла кукурудзи, подрібнені на дезінтеграторі, які змішували з водою в певних пропорціях. Суспензію обробляли в роторно-пульсаційному апараті за різних режимів. Гранулометричний склад отриманих частинок визначали ситовим методом і методом лазерної дифракції.

Результати і обговорення. Встановлено, що за однакових умов обробки в роторно-пульсаційному апараті, гранулометричний склад суміші подрібненої маси стебел кукурудзи з водою після подрібнення має дисперсність на 3–5% нижче, ніж суміш маси пшениці, що пояснюється різною міцністю лігноцелюлозних волокон у рослинах, що досліджувалися. Встановлено, що зі збільшенням гідромодуля від 1:5 до 1:15 дисперсність часток знижується на 35–40%, а від 1:5 до 1:10 на 3–5%, що пояснюється зміною в’язкості розчину. Зменшення гідромодуля від 1:15 до 1:5 дає змогу підвищити в’язкість розчину, а значить, і температуру, що має важливе значення не тільки в процесі диспергування лігноцелюлозної сировини, а й у його біоконверсії. Зменшення гідромодуля від 1:15 до 1:10 за 10 циклів обробки дисперсії в роторно-пульсаційному апараті призводить до зниження температури від 47 до 42 °C (=10%), але при цьому продуктивність обладнання збільшується в 1,5–2 рази, енерговитрати зменшуються на 25–30%.

Визначено, що оптимальними параметрами диспергування водної суспензії соломи пшениці або стебел кукурудзи в роторно-пульсаційному апараті є: гідромодуль – 1:10; швидкість зсуву потоку – 40·10³ c⁻¹; частота пульсацій – 3 кГц. Кількість циклів обробки – 25–30.

Визначено, що у водній суспензії соломи пшениці або стебел кукурудзи при гідромодуля 1:10, оброблений в роторно-пульсаційному апараті з частотою пульсацій 3 кГц, швидкості зсуву потоку 40·10³ c⁻¹ за 25–30 циклів, біля 50% часток мають розмір в межах 30–50 мкм. Визначено, що збільшення дисперсності частинок призводить до збільшення виходу редукуючих речовин у гідролізаті з 4% від а.с.р. при середньому розмірі часток 30–80 мкм до 5,5% при середньому розмірі часток 1–5 мкм.

Висновки. Диспергування рослинної біомаси методом дискретно-імпульсного введення енергії забезпечує отримання 80% частинок розміром 1–50 мкм.

Ключові слова: диспергування, біомаса, диспергатор, частота, гранулометрія.

Дослідження процесу ежекції в мехатронних функціональних модулях пакувальних машин

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Вступ. Мета досліджень – визначити вплив геометричних, кінематичних технологічних параметрів на процеси ежекції в мехатронних функціональних модулях пакувальних машин.

Матеріали і методи. Досліджувалися режими роботи пневмосоплових ежектуючих систем із змінним робочим середовищем: стиснене повітря, спиртовмісні розчини, газомодифіковане середовище. Зразки поверхонь для обробки: пакувальні матеріали, штучні хлібопекарські вироби. Поставлені завдання вирішувалися на підставі аналізу й узагальнення літературного матеріалу, проведення експериментів з дослідження ефективності L-подібних ежекторів, а також стендовими дослідженнями процесу створення і розпилювання сумішей на продукт обробки. Для проведення експериментів авторами був створений стенд для експериментальних досліджень, що дає змогу проводити експерименти в умовах близьких до промислових.

Результати і обговорення. Топологічним методом виділено типову технологічну схему ФММ пневмосоплових ежектуючих систем, у якій передбачено регулювання величини впливів на ежектор. Вирішення завдань для запропонованої конструкції пневмосоплових ежектуючих систем дало змогу знайти оптимальні робочі технологічні та керуючі режими щодо оброблення пакувальних матеріалів: дозволо розпилювання спиртовмісних речовин на поверхню обробки із магістральным тиском у межах 3–5 бар, швидкість струмини на вході в ежектор корегується тиском за сигналом від пропорційного регулятора, робоча зона зрошування діаметром 100–150 мм, керуючий вплив на ввімкнення та вимкнення ежектора за змінним сигналом зворотного зв’язку на вході в ежектор та у напірній лінії з різиною струмінною 0–10 В. Обробка продукту тиском понад 6 бар викликає деструкцію хлібопекарських виробів. Для хлібопекарських виробів оптимальний тиск на вході є в ежектор – 4 бари. Зміна геометрії конфузора та дифузора надає можливість знизити витрати стисненого повітря на 20%, що для пакувальних машин забезпечує зниження енергетичного навантаження. Цифрові керуючі регулятори і витратомір у системі ежектора із зворотним зв’язком 0–10 В дають змогу для змінювати продуктивність окремого функціонального мехатронного модуля пакувальної машини. Відхилення повторюваності дози продукції при розпиленні на печиво у межах 2,0%.

Висновки. Отримані дані показали різку зміну характеру розподілу тиску і швидкості всередині ежектуючих систем при зміні типу робочого середовища в однофазних пневмосистемах. Тому запропоновані робочі оптимальні режими пневмосоплових систем для оброблення гнучких пакувальних матеріалів і поверхні хлібопекарських виробів без деструкції.

Ключові слова: ежектор, режим, пакувальна машина, моделювання.
Економіка і управління

Тенденції розвитку та фактори ризику світового експорту м'яса і м'ясних продуктів

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Вступ. Метою дослідження є виявлення й аналіз найбільш значущих факторів господарського ризику та побудова математичної моделі, яка описує їхній вплив на обсяг експорту м'ясної продукції.

Матеріали і методи. Об'єктом дослідження був світовий ринок м'яса і м'ясопродуктів. Предметом дослідження – фактори господарського ризику, що виникають у сфері експортних відносин. Оцінка впливу факторів ризику проведена на основі кореляційно-регресійного аналізу.

Результати і обговорення. Обсяг світового експорту м'яса і м'ясних продуктів з 2013 по 2017 р. збільшився на 3,16 млн тонн. За цей період нараховування обсягів експорту відбулося переважно завдяки основним регіонам-експортерам: США, Бразилії, країнам ЄС, Канаді, Таїланду та Новій Зеландії. При цьому спостерігалося скорочення експорту з Австралії, Індії, Китаю та Новій Зеландії. Світовий експорт свинини в 2017 р. склав 8,23 млн т, що на 1,1 млн т, або 15,59% вище за рівень 2013 року. У процесі аналізу встановлено зростання експортиних поставок м'яса яловичини за аналізованій період на 22,6%. Збільшувся світовий обсяг експорту м'яса птиці, який за аналізованій період зріс з 12,4 млн т у 2013 р до 13,13 млн т у 2017 р. (зростання склало 105,9%). Світові обсяги експорту баранини зросли незначно – на 1,0%.

Виявлено та кількісно оцінено основні фактори ризику, що обмежують обсяги експорту: зміна цін на корми для тварин, поширення різних захворювань епідеміологічного характеру на території країн-експортерів, рівень державної підтримки сільського господарства, волантильність валютного курсу. Кореляційний аналіз обсягів експорту Європейського Союзу показав його залежність від середньої вартості кормів на 1 кг забійної ваги (значення коефіцієнта кореляції – 0,87) і рівня державної підтримки сільського господарства (значення коефіцієнта кореляції – 0,56). Ці фактори варіювання визначені як значущі і використані для регресійного аналізу. Побудована регресійна модель описує залежність обсягів експорту м'яса і м'ясопродуктів від зміні найбільш впливових факторів варіювання таким чином: зростання середньої вартості кормів (за 1 кг забійної ваги) на 1 дол. США знизить обсяг експорту країн Європейського Союзу на 0,87 млн тонн, а збільшення рівня державної підтримки сільського господарства (% від ВВП) на 1% забезпечить зростання обсягу експорту на 0,87 млн тонн.

Висновки. Зроблено оцінку впливу факторів ризику на обсяг експорту країн Європейського Союзу на основі кореляційно-регресійного аналізу, яка дала змогу визначити варіативні фактори, що найбільше впливають на результативний показник, і зробити об'єктивну кількісну оцінку їх впливу.

Ключові слова: м'ясо, експорт, ризик, кореляція.
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Вимоги до оформлення статей

Мова статей – англійська.
Мінімальний обсяг статті – 10 сторінок формату A4 (без врахування анотацій і списку літератури).
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Пункти 2–6 виконати англійською і українською мовами.

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   - Вступ
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За необхідності можна додавати інші розділи та розбивати їх на підрозділи.

8. Авторська довідка (Прізвище, ім’я та по батькові, вчений ступінь та звання, місце роботи, електронна адреса або телефон).
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Фон графіків, діаграм – лише білий. Колір елементів рисунку (лінії, сітка, текст) – чорний (не сірий).
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   Приклад:

2. Посилання на книгу:
   Автори (рік), Назва книги (курсивом), Видавництво, Місто.
   Ініціали пишуться після прізвища.
   Всі елементи посилання розділяються комами.

   Приклад:

Посилання на електронний ресурс:

Виконується аналогічно посиланню на книгу або статтю. Після оформлення даних про публікацію пишуться слова Available at: та вказується електронна адреса.

Приклади:


Список літератури оформлюється лише латиницею. Елементи списку українською та російською мовою потрібно транслітерувати. Для транслітерації з українською мови використовується паспортний стандарт, а з російської – стандарт МВД (в цих стандартах використовуються символи лише англійського алфавіту, без хвостиків, апострофів та ін).

Зручні сайти для транслітерації:

З української мови – http://translit.kh.ua/#lat/passport
З російської мови – http://ru.translit.net/?account=mvd

Додаткова інформація та приклад оформлення статті – на сайті http://ufj.ho.ua

Стаття надсилається за електронною адресою: ufj_nuft@meta.ua
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Тематика публікацій в Ukrainian Food Journal:

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Періодичність виходу журналу 4 номери на рік.

Результати досліджень, представлені в журналі, повинні бути новими, мати чіткий зв’язок з харчовою наукою і представляти інтерес для міжнародного наукового співтовариства.

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- CABI full text (2014)
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- Directory of Open Access scholarly Resources (ROAD) (2014)
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