

The article discusses the issues of ensuring the safety and preservation of the biological activity of food products during processing and storage.

Undesirable Transformations of Certain Nutrients during Pre- processing and Protection against Them

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Abstract

This paper examines one of the most relevant aspects of food production in modern conditions – the issues of their processing and quality preservation, namely, the creation of high-quality feed for bees using inexpensive, non-traditional raw materials. When solving this problem, it turned out that previous technologies cannot ensure the production of safe products: compounds harmful to both humans and bees are formed: oxidized flavonoids, 5-hydroxymethylfurfural. At the same time, the organoleptic properties (color, odour, taste) of fruit-based products have sharply deteriorated. Moreover, these substances have pronounced toxic properties. To prevent these undesirable phenomena, the author has developed a new method for concentrating solutions and liquid mechanical mixtures at low temperatures ($<70^{\circ}\text{C}$) (Madzgarashvili, 6), which made it possible to avoid the formation of the above substances;

-Using modern biotechnological methods, in particular, through enzyme preparations, it was decided to create a fundamentally different way of producing one of the promising bee products – bee bread: It was obtained directly from pollen, by lactic acid fermentation in laboratory or industrial conditions, which eliminated of bee hive impurities, honeycomb damage, risk of residues of the embryo feed getting into finished products, and expanded the possibilities of bee bread production and export.

Key Words: Honey; Pollen; Bee Bread; Ferments; Fruit Concentrates; 5-Hydroxymethylfurfural; Flavonoids.

Introduction

Such transformations occur in the content of protein, simple carbohydrates, vitamins and other substances. The main reasons for them include improper thermal regime, atmospheric oxygen, various types of microbes, high water content, hydrogen ion concentration, sunlight, composition of packaging

material, etc., and the consequence is a change in the quality of food and the appearance of undesirable, and sometimes harmful substances. Such a wide variety of factors and completely different chemical composition of food make the researcher look for optimal solutions for processing and storing certain types of food. Based on the above, we approached this issue primarily taking into account their chemical composition, in particular, understanding the possible reaction of the factors listed above to the substances (protein, carbohydrates, excess moisture, etc.) included in their composition.

Materials used: dried pollen, with a residual moisture content of 10-12%; natural honey with excess water and acetic acid; natural fruits, with the possibility of canning; natural grape juice (Badagi), with a sugar content of 20-22% by weight; wheat flour, with residual moisture 12-13%; Potassium pyrosulfite, commercial preparation; carbon dioxide gas; enzyme preparations: α -amylase, β -fructofuranosidase.

Research methods

1. Technology of Drying of Pollen (Madzgarashvili, 2, Rus)
2. Preservation of Pollen in Bee Colony (in Honeycombs) (Tunikow et al , 11, Rus)
3. Method of Preparing of Bee Bread without Bee Colony (Honeycombs) (Madzgarashvili, 3, Geo)
4. Kirby-Bauer Disk-Diffusion Susceptibility Test Protocol. (Hudziki, 10, Eng)
5. Determination of HMF by Fiehe's Test. TU Latv. SSR 290-60 (9, Rus)
6. Method of Hydrolysis of Food Sugar in Concentrated Solutions. Patent of Former USSR # 578 341 C 13K 3/00, 1977 (Madzgarashvili G. et al, Rus).

Results of the research and discussion

Development of a safe technology for enzymatic hydrolysis of sugar syrup and removal of excess water from the solution. According to Hertzfeld (1), 5-hydroxymethylfurfural, produced during acid hydrolysis of sugar, even at its low concentration in solution (3 mg/%) negatively affects the life expectancy of bees. For this reason, our research (Madzgarashvili, 2) has for the first time determined the minimum temperature required for this substance to produce (70°C). Under normal conditions it significantly prolongs the evaporation of excess water from the hydrolysate. In the course of subsequent research, a simple and effective method of solvent evaporation from solutions and liquid mechanical mixtures was developed. It is carried out at atmospheric pressure, temperature 40-65°C, with high condensation intensity, depending on the type of substrate. In particular, in one series of experiments, the initial concentration of the solution was 12-23wt%, and the evaporation rate (decrease in water content) per hour was 11-12%. In the subsequent period (concentration 24-65%), the evaporation rate reached 16-17%. At the final stage (concentration 66-81 wt%), the evaporation rate decreased to 8-10%. In the next experiment, at an initial solution concentration of 67-68%, 90-100 minutes were enough to prepare the optimal composition of invert syrup for bees (78-81wt%). The content of 5-hydroxymethylfurfural in this product did not exceed 5 mg/kg (laboratory "Multitest", Tbilisi, 2017). This figure is significantly lower than the data for honey of the highest quality. This effect was achieved by using the microbial β -fructofuranosidase (Madzgarashvili, 4). Subsequently, the production and use

of invert syrup in this way became the basis for the development of safe technologies for the production of other products (bee bread, fruit concentrates, dried fruits).



Fig. I. Invert syrup additions



Fig. II. Candy (paste food) consists of: only simple sugars



with protein

Features of processing and storage of high-protein foods. In this case, the subject of our research was pollen - pollen grains, that bees collect as a source of basic nutrients (except carbohydrates), a product with high biological activity, perishable under natural conditions, with moderate (20-30%) moisture content and abundantly infected with yeast fungi. The bee itself solved this issue in the process of evolution by carrying out lactic acid fermentation in a product placed in honeycombs, but it is quite difficult for a person to remove the product stored in a honeycomb and already turned into bee bread, not to mention its ecological purity, the volume of a marketable product is reduced due to the sharp seasonality of work. Man has developed simple methods to collect raw pollen from bees and dry it (Fig. III). For the last operation, it is recommended to use a simple drying cabinet with a thermal regime of 35-40°C. Obviously, this regime makes the drying process much longer (20-48 hours, taking into account its initial humidity). A negative consequence of this process is the low stability of labile ingredients, especially in terms of preservation of carotene and amino acids (lysine, phenylalanine, arginine).



Fig. III. Pollen dryer



Pollen



Bee bread

During the comparative testing of drying units of different designs, we preferred a vacuum dryer. In addition, it was observed that: if the residual pressure does not exceed 0.05 kg/cm², and the temperature ranges from 60-65°C, then the drying process lasts 75-90 minutes, and the residual moisture content is

4 wt.% on average. It should be noted that under these conditions, the temperature in the material to be dried does not rise above 45°C, which is explained by the increased release of heat and water vapor from the vacuum dryer (Madzgarashvili, 2). The fact that the negative effect of atmospheric oxygen on the preservation of carotene and amino acids is significantly weakened in vacuum conditions can not be regarded as a factor contributing to the improvement of drying, in particular, the carotene content in the test sample of pollen (drying in vacuum) was 8.5 mg%, in the control of the sample (drying in a conventional drying cabinet 40-45°C) this indicator was 7.94 mg%, of Lysine- 3.23 and 2.55 mg%, respectively; of Arginine -4.21 and 1.27; of Phenylalanine -1.94 and 1.35. In the test group of bee colonies, which were given vacuum-dried pollen mixed with candy, the area of an adult brood at the end of the experiment was 29.4 dm², the same indicator of the control group was 25.5 dm². Furthermore, it should be noted that volatile essential oils - an important biologically active substance - are much more intensively lost in vacuum, which can be considered a disadvantage of this method.

At the next stage of the work, we made bee bread from dry pollen without a bee colony (honeycombs, Madzgarashvili, 3). The advantages of this step include: clearly the best ecological purity of the pollen, the opportunity to do work literally all year round, and for the collection of pollen - during 5-7 months of the active season, reduction of labor costs by almost 40%, the duration of conservation of bee bread has been reduced from 2.5 weeks to 50 hours, using selective strain of lactic acid bacteria. This was also due to the fact that the mixture created the necessary minimum of simple sugars (invert syrup by Madzgarashvili et al, 4) for the functioning of lactic acid bacteria, and also used a neutral gas-carbon dioxide was used both during incubation and storage of the finished product. Accordingly, the market price of finished bee bread has decreased from \$100 to \$64 per kg, which will significantly increase the consumption of the product by the population with the results obtained.

To determine the biological activity of the bee bread made by the above technology, the sample was incubated with *Clostridium botulinum* spores, placed in a thermostat at 37°C for 10 days, after which a sample of bee bread was given together with the main feed to an experimental group of white mice. The control group received regular food (without bee bread). During the experiment, all numbers of mice were maintained, i.e. the bee bread inhibited the ability of *Clostridium botulinum* to multiply and produce toxin (L. Malania, personal report from R.Lugar laboratory, Tbilisi, 2019).

This product was also tested in the Microbiological Laboratory of “Biotexi” LLC by including it in a meat-peptone agar (Hudziki, 10) on which strains of *Escherichia coli* and *Staphylococcus aureus* were incubated. Within 24 hours, the diameter of their inhibition zones was 33 and 31 mm, respectively. Unfortunately, we did not have the opportunity to determine the effect of bee bread made in this way on the condition of patients with the Covid-19. Due to technical difficulties, we were also unable to determine the level of carotene retention compared to the initial product using an improved research method (Biehler et al, 7). In addition, it would be very interesting to implement the entire process of product preparation (including final humidity conditioning) in the neutral gas zone.

Processing and storage of foods rich in simple carbohydrates. Such products include fruits and honey. The water content in fruits is very high, and the fructose-rich raw materials almost do not emit water

at low temperatures ($<45^{\circ}\text{C}$) during the drying process. Prolonged low-temperature drying and the same process in short-term, but high-temperature conditions dramatically worsen the appearance of the product; Due to the oxidation of phenolic compounds, Badagi (grape juice) darkens, and 5-hydroxymethylfurfural, harmful to health, is formed. Under these conditions, it is very difficult to produce high-quality canned fruits, and conditioning of unripe honey (concentration 75-79 wt.%) takes several hours (Tew, 5), which leads to a further increase in the above-mentioned harmful substances.



Fig. IV. Results of analysis (Fiehe's test) of churchkhela technology made: by new (left) and traditional (right) methods



Fig. V. Peach jam prepared by new (4) and initial material (5)



Fig. VI. White cherry jam by new (2) and the same to the traditional technologies (3)



Fig. VII. Quince puree by new (8) and by industrial technologies (9)

According to our observational data (certificate #5870, 6), the intensity of thickening of solutions or liquid mechanical mixtures increases dramatically due to an increase in the surface area of liquid evaporation (a decrease in water content by 16-17% every hour). In this case, the intrinsic temperature of the solution becomes a secondary factor, due to the installation of a special device in a standardized boiler, this area can be increased several times, which allows to achieve intensive evaporation of the solvent at a temperature of $40-65^{\circ}\text{C}$. Following this regime, at the beginning of the research, we developed a technology for the production of honey substitute - invert sugar for bees (Madzgarashvili et al, 3), in which the temperature required for concentration starts from 62°C and ends at 68°C , reaching a concentration of 82-83 wt.%. According to the testing laboratory "Multitest" (Georgia), the

content of 5-hydroxymethylfurfural in invert syrup made using this technology did not exceed 5 mg/kg. The same indicator ranged from 83 to 713 mg/kg in canned fruit brought from the International Food Exhibition in Istanbul (2017 y.), as well as from Georgian enterprises. Here are photos of jams and purees prepared using these technologies, clearly indicating a sharp increase the formation of 5-HMF (Fig. IV). Relatively low temperature used for canning (<70°C) excludes the possibility of the formation of caramelans.



12



13

Fig VIII. Semi-dry Jams from: Quince (12) and musk strawberry (13)



Fig. IX. Pear Jam



Fig. X. Apple Jam

Grape juice processing. When using grape juice in production of Churchkhela, Georgian delicacy, by traditional technology, a radical change in its color is observed- intensive oxidation of phenolic compounds above a temperature of 50°C, which indicates a high content of these substances in juice. Below a number of substances successfully are used as antioxidants by various authors: sulfuric anhydride, polyacrylamide and others (Shatirishvili, 8), protected this product from darkening. Sulfuric anhydride, used by us for a similar purpose, effectively purified juice from sediment for 36 hours, although sometimes granular clinoptilolite (3-5 mm in size) had to be used for the same purpose. At the completion of this process, grape juice thickened to 82-83 wt.% at a temperature of 52-57°C was characterized by sufficient transparency and crystallized in a short time (2 weeks) (the result of excess

glucose) to form a gray-white, fairly dense dough (fig. XI left). This gives us an opportunity to make the Churchkhela production process permanent, that is, to get rid of seasonality (more equal provision of the market), while hydrogen ion concentration in juice before treatment and after concentration was almost the same and was pH 4,0- 3.9. This indicates that SO₂ is removed along with water vapor during the concentration of juice. As for 5-hydroxymethylfurfural, we conducted a qualitative analysis of it by the effect of hydrochloric acid resorcinol on diethyl ether extract (after evaporation of the ether) (Fiehe's test, 9)). The control sample was presented by the Churchkhela dough prepared in the traditional way (50% juice+ a mixture of wheat flour as a result of prolonged cooking). The results of the analysis are given above (Fig. IV).



Fig XI. Grape juice processed by new (left) and traditional (oxidated) methods

In the production of Churchkhela, it is worth noting that the product made in the traditional way, after drying in natural conditions, becomes very dense, which negatively affects its commercial qualities. It can be seen that there is no substance in grape juice that can break down starch, which is present in large quantities (48-57%) in wheat flour. The enzyme α -amylase was used to correct the condition. As a result of carrying out a certain amount of experimental works, we achieved the formation of saccharides of a simpler structure in the required amount in the flour suspension maintaining sufficient elasticity of the dough in the finished product without violating the integrity of the surface: The internal rotation angle of the product was reduced from 180° to 146°, which turned out to be a satisfactory indicator in terms of increasing the attractiveness of the product for the consumer.

Reducing the content of simple sugars in canned fruits has become very relevant in the current century, because their excess in the human body is accompanied by undesirable complications, especially when using folk methods: as a rule, the proportion of food sugar in the finished product significantly exceeds the amount of dry matter of the main raw material. In our research, we focused on the use of invert syrup (>67 wt.%) instead of crystal sugar, given that invert syrup penetrates more easily into the product to be processed, thereby contributing to the removal of excess water from the fruit. Immediately after the initial processing of the fruits, they were carefully put into a heated (> 40°C) syrup, to which the antioxidant SO₂ was previously added, the mixture placed in a container was kept in a thermostat at 65 ± 2°C for 2 hours, after which the syrup concentration was reduced to 50-54 wt.%. The syrup drained from the container was condensed to 70-72% and poured back onto the fruit

in the container. Through such step-by-step processing (with an increase in the concentration of syrup in the intervals up to 83-84%), the total concentration of jam increases to 81-82 wt.%, not accompanied by a decrease in the quality of jam during the shelf life. At the end of the process, the fruits were separated from the syrup and dried by enhanced aeration, and after transfer to the commercial vessel, the atmospheric air was replaced by carbon dioxide, providing complete preservation of the appearance, taste properties, absence of 5-HMF (fig. IV left) and excessive sweetness) of the finished products.

For our part, we will ensure the unhindered use of the proposed technologies at interested enterprises. To get more information contact the author at: G. Saakadze str. 45, 0180, Tbilisi, Georgia. E-mail: gmadzgarashvili@yahoo.com; Tel.: (+995) 555 39 07 56.

Conclusions

1. The use of the microbial β -fructofuranosidase for the preparation of invert syrups for various purposes made it possible to avoid the formation of the harmful 5-hydroxymethylfurfural, and temperatures from 40 to 65°C are sufficient for effective thickening of solutions of various concentrations, providing an increased evaporation surface area in batch / preparation vessels. Inverted syrup made in this way is much more environmentally friendly than high-quality honey, and, in addition to feeding bees, it can be used to make fruit concentrates (jam, fruit puree, dried fruits);
2. To remove excess moisture from a food product with low heat resistance, solid, granular structure, it is preferable to limit the drying process to vacuum drying, with a residual pressure of no more than 0.05 kg/cm² in a mode that provides the desired temperature within 45-50°C and a duration of 75-90 minutes. This makes it possible to preserve biologically active substances (carotene, amino acids), antimicrobial properties of the product as much as possible, to use neutral gas (for example, CO₂) for the incubation of anaerobic microbes for the same purpose, during the drying and storage of the finished product;
3. To process liquid low-concentrated fruit juices containing simple sugars and phenolic compounds, it is advisable to use an antioxidant (sulfur anhydride), for concentration - innovative technology based on an increased evaporation surface area that prevents the formation of substances harmful to health (5-hydroxymethylfurfural, oxidized flavonoids, caramelans);
4. To preserve a product with a high protein content and a relatively low water content while maintaining its biological activity, it is advisable to use lactic acid fermentation by specific bacteria, with the necessary minimum of simple sugars, with their further conversion into organic acids, which makes it possible to create the necessary amount of hydrogen ions (pH) in the product to be canned to avoid the process of protein decomposition.
5. Making jams from various fruits with minimal consumption of food sugar is facilitated by using concentrated (>67% by weight) invert syrup, which more easily replaces the water in the fruit. By gradually concentrating the syrup used, the total concentration of jam increases to 81-82 wt.%, which ensures the shelf life of fruits by preserving their presentation without syrup and is enhanced by placing fruits in an oxygen-free vessel.

Compliance with ethical standards

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Disclozure of conflict of interest

The author declares that there is no conflict of interest regarding the publication of this article.

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საზრდო ნივთიერებების არასასურველი გარდაქმნები კვებისწინა სითბური გადამუშავების პროცესში და მათი თავიდან აცილება

გიორგი მაძღარაშვილი

სოფლის მეურნეობის მეცნიერებათა დოქტორი, შპს „დემეტრას“ დირექტორი

ნაშრომი ეხება თანამედროვე პირობებში საკვები პროდუქტების წარმოების ერთ-ერთ აქტუალურ მხარეს- მათი გადამუშავებისა და ხარისხის შენარჩუნების საკითხებს, კერძოდ: იაფი, არატრადიციული ნედლეულიდან ფუტკრისათვის მაღალხარისხიანი საკვები საშუალებების შექმნას. ამ პრობლემის გადაჭრის დროს აღმოჩნდა, რომ ადრე შექმნილი ტექნოლოგიები ვერ უზრუნველყოფენ უსაფრთხო პროდუქტების მიღებას: წარმოიქმნება როგორც ადამიანისათვის, ისე ფუტკრისათვის მავნე ნაერთები: დაჟანგული ფლავონოიდები, 5-ჰიდროქსიმეთილფურფურალი. გარდა ზემოაღნიშნულისა, მკვეთრად გაუარესებულია ხილეულიდან მიღებული პროდუქტების ორგანოლექტიკური მაჩვენებლები (ფერი, სუნი, გემო). უფრო მეტიც, ეს ნივთიერებები ამჟღავნებენ აშკარად გამოკვეთილ ტოქსიკურ თვისებებს. ამ არასასურველი მოვლენების აღსაკვეთად ავტორის მიერ შემუშავებულ იქნა დაბალ ტემპერატურაზე (<70°C) ხსნარებისა და თხევადი მექანიკური ნარევების კონცენტრირების ახალი ხერხი (საქპატენტი, საავტორო უფლება # 5870, 2014), რამაც საშუალება მოგვცა, თავიდან აგვეცილებინა ზემოაღნიშნული ნივთიერებების წარმოქმნა;

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