



ANTIOXIDANTS' EFFECT ON THE STORAGE OF DAIRY PRODUCTS WITH HIGH-FAT CONTENT

Olena GREK¹, *Tetiana PSHENYCHNA¹, Mariia NIKOLAIEVA¹

¹Educational and Research Institute of Food Technology, National University of Food Technologies, 01601, Volodymyrska str.68, Kyiv, Ukraine.

tanya5031@ukr.net

*Corresponding author Received 18th June 2021, accepted 28th September 2021

Abstract: The article presents the research results of the antioxidants' effect of various origins on the storage of dairy products with high-fat content. The quality change of such products was monitored by the oxidation product content. The antioxidants' effect of natural origin and human-made origin on the change in the peroxide and acid numbers in spreads with food fibers during storage period for 15 and 30 days at a temperature of (20 ± 2) ° C and $(0\dots 5)$ °C has been determined. A significant increase in the peroxide number occurs at a temperature of (20 ± 2) °C. It has been established, that after 6 storage days under the given conditions, the indicator for the control sample increases 4 times, while for products with high-fat content with the addition of antioxidants "NovaSOL COF" and "GRINDOX 109" -1.2 times. On the 12th storage day, the peroxide number in the spread without additives increased by 8.65 times, in the spread with the introduction of the natural flavoring agent "Caraway – elite flavor" – by 7.15, with the antioxidants "NovaSOL COF" and "GRINDOX 109" – by 4.45 and 4 times, respectively. There was a similar trend towards an increase in the acid number for the research samples of products with high-fat content. After 12 storage days, a significant increase in the value of the acid number has been found in the samples of spreads without antioxidants – 13 times, with the introduction of the natural flavoring agent "Caraway – elite flavor" – 7.8 times. Low acid number values are observed in the samples with the addition of the antioxidants "NovaSOL COF" and "GRINDOX 109", in comparison with other spreads. The obtained results are the basis for the development of recommendations for extending the storage life of products with high-fat content.

Keywords: *product with high-fat content, antioxidant, spread, storage period, peroxide number, acid number.*

1. Introduction

Modern industrial milk processing is a large complex of consistently interconnected chemical, physicochemical, microbiological, biochemical, thermophysical, and other labor-intensive and specific technological processes. They focused on the production of dairy products containing all the constituents of whole milk or its components.

Manufacturers desire to improve sensory properties and physicochemical indicators,

to achieve safety and products profitability in order to increase the competitiveness of the brand name sometimes leads to a change in traditional production methods, composition rationalization, and the use of other measures. in which economic feasibility does not always positively correlate with quality indicators, food and biological value of products. Relevant in the dairy industry is the simultaneous provision of traditional production methods using modern equipment and the development of new technologies for highquality dairy products with а multicomponent composition and an extended storage life [1-2].

Despite the current trends towards a decrease in the calorie content of dairy products, there is an expansion of the assortment range of products with a high-fat content – spreads and butter with fillers, drinking cream, sour cream products with non-dairy fats, desserts with a fat mass fraction of 15.0 to 46.0 % based on cottage cheese (chocolate glazed curd bar, pastes, sweet masses, cakes, creams).

Extending the storage life of the abovementioned products is a priority task, as the composition combination and the addition of the ingredients that are not traditional for products with high-fat content leads to defects and spoilage. To prevent the above-mentioned processes, it is advisable to use antioxidants capable of reacting with free radicals and thus breaking the oxidation chain and prolonging the storage life [3-4].

The aim of this work is to study the antioxidants' effect of various origins on the storage of products with a high-fat content – spreads with food fibers. According to DSTU 4445: 2005, a spread is a food fat product (water-in-fat emulsion), which consists of milk and vegetable fat with a total fat mass fraction of 50 % to 85 % and in which the milk fat fraction is not less than 25 % of total fat, with a heavy or soft consistency. Spreads can be manufactured with food additives, fillers, and vitamins.

During spreads' storage, vegetable and animal fats included in its composition, under the influence of atmospheric oxygen, light. especially direct sunlight or ultraviolet, moisture, gradually acquire an unpleasant taste and smell [5]. The reason for fatty foods' spoilage is the development of oxidative and enzymatic processes. Thus, the oxidative destruction of the fatty components in spreads, first of all, leads to the formation of peroxides, aldehydes, ketones, low molecular weight acids, and other compounds. Fats and oils, which contain desaturated fatty acids (linolenic, linoleic, oleic acids), when exposed to air, dissolve their components, including oxygen, and oxidize. As a result, the nutritional and biological value of fats decreases, and they may be unsuitable for consumption [6].

2. Matherials and methods

The object of research is products with high-fat content – spreads with food fibers and antioxidants. Considering theoretical information, an antioxidants' mixture based on vegetable fats: natural *origin* – "NovaSOL COF" or human-made origin – "GRINDOX 109", natural flavoring agent "Caraway - elite aroma" (TU U 24.6-22961668-007: 2007) based on the aromatic oil, have been used to extend the storage life of the spreads.

"NovaSOL COF" (Belagroleks, Belarus) is a highly effective liquid antioxidant, the main active substances of which are ascorbic acid (vitamin C) (E 300) and tocopherol (vitamin E) (E 306) [7-8].

"GRINDOX 109" (Danisco, Denmark) is a mixture of antioxidant substances: butylhydroxyanisolum (E-320) (10%), butylhydroxytoluenum (E-321) (10%), propyl gallate (E 310) (6%), citric acid with propylene glycol, food emulsifier and rapeseed oil (68%) as a basis [9].

The natural flavoring agent technology of caraway aromatic oil has been developed by NUFT scientists. This technology provides for vacuum fractionation of raw materials, obtaining fractions with desired aromatic properties. As the caraway aromatic oil is insoluble in water, therefore, the dosage is carried out with a 40 % alcohol-water solution.

The chemical composition is represented by the following main components: β myrcene, limonene, α -terpineol, carvone, p-cymene, cis-limonene oxide, translimonene oxide, caryophilene, etc. It is

known that this compound's class is extremely reactive due to the presence of active chemical centers (and bonds, carbonyl groups). These substances can play the role of antioxidants, as they are among the class of the same compound as vitamin E [10].

Obtaining research samples of spreads with food fibers

To determine the antioxidants' effect of various origins on the storage life of products with high-fat content – spreads with food fibers, research samples have been developed using a technology based on the separate preparation of a milk-fat emulsion (oil (15.0 %), Citri-Fi (0.3 %), skim milk), and mixing with cream [11]. The food fibers' addition is caused by their high fat-binding capacity, emulsifying, structure-forming properties.

The next technological operations were the introduction antioxidants into the emulsion, namely "NovaSOL COF"-0.04 %, or "GRINDOX 109" – 0.05 % or a natural flavoring agent based on aromatic oils "Caraway – elite aroma" – 0.05 % (the quantity is chosen according to the manufacturers' recommendations), mixing until complete dissolution, emulsification and pasteurization, intensive thermomechanical processing. During the the liquid last operation, fat/water emulsion is converted to a reverse type water/fat emulsion system. The finished samples were packed in 100 g parchment paper. Spreads were stored with no exposure to light for 15 days at a temperature of (20±2) °C and for 30 days at (0...-5) °C. Control samples were with food fiber spreads without antioxidants.

The quality change in spreads with food fibers during the storage period was controlled by the content of oxidation products (peroxide number) and fat hydrolysis (acid number). The peroxide number characterizes the content of primary oxidation products in the fat – peroxides and hydroperoxides, which have almost no effect on the sensory characteristics of the product but indicate significant changes in the research object [12]. Therefore, by determining the peroxide compounds accumulation during the storage period of the fat base of the spread, it is possible to establish its resistance to oxidation long before the change in its sensory characteristics.

Determination of peroxide and acid numbers in products with high-fat content

To determine the *peroxide number* in spreads with food fibers, 1 g of spread was weighed into a conical flask with a ground stopper with an accuracy of 0.2 mg.

The spread was melted in a water bath and 10 cm^3 of chloroform and 10 cm^3 of glacial acetic acid were added along the wall, washing off the residues. Then 0.5 cm³ of a saturated freshly prepared aqueous solution of potassium iodide was introduced. The flask was closed with a stopper, the contents were mixed and left in a dark place for 3 min. Then 100 cm³ of water was added, to which 1 cm³ of 1 % starch solution was previously added, and titrated by 0.01 N thiosulfate solution until the blue color disappeared. Peroxide number (X), mmol 1/2 O/kg, was calculated by the formula:

$$X = \frac{(V_1 - v) \cdot 0.00127 \cdot 100}{q}$$

where X – the peroxide number, mmol 1/2 O/kg;

 V_1 – the amount of 0.01 N thiosulfate solution, which was used for titration during the main experiment with a fat weight, cm³;

v – the amount of 0.01 N thiosulfate solution, which was used for titration of the sample without fat, cm³;

g - fat weight, g; 0.00127 – the gram number of iodine, equivalent to 1 cm³ of 0.01 N thiosulfate solution.

To determine the *acid number*, a spread with food fibers weighing 5 g was introduced into a conical flask with a volume of 100 cm3, heated in a water bath at 45...50 °C until melting, and dissolved in 20 cm³ of a neutralized mixture of ethyl alcohol and diethyl ether (1:1). Then 3 drops of 1 % phenolphthalein solution were added and, with constant stirring, titrated with an aqueous solution of 0.1 N alkali (NaOH). The titration was finished when a pink color appeared and did not disappear within 1 min. The acidity in the spread with food fibers was calculated by multiplying the amount of 0.1 N alkali solution, which was used to neutralize milk fat, by 2 [13].

3. Results and discussion

The antioxidants' effect of various origins on the change in the peroxide number of products with high-fat content – spreads with food fibers at a temperature of (20 ± 2) °C and (0...-5) °C is shown in Figure 1.

According to the research results presented in Figure 1, the auto-oxidation process of the fatty base of the spreads at different temperatures was different. A significant increase in the peroxide number occurs at a temperature of (20±2) °C. Thus, after 6 storage days under the given conditions, the indicator for the control sample increases 4 times, while for products with high-fat content with the addition of antioxidants "NovaSOL COF" and "GRINDOX 109" – 1.2 times. Intensive peroxides accumulation in spreads with food fibers has been found on the 12th storage day. In particular, the peroxide number in the spread without additives increased by 8.65 times, in the spread with the introduction of the natural flavoring agent "Caraway - elite flavor" - by 7.15, with the antioxidants "NovaSOL COF" and "GRINDOX 109" - by 4.45 and 4 times, respectively. In the control sample, the primary product accumulation of fat oxidation reached a maximum value of 20.3 1/2 O/kg after 12 storage days.

By the end of the storage period (15 days), the peroxide numbers in products with high-fat content decreased slightly in comparison with the corresponding values of this indicator on the 12th day. This is due to the subsequent transformation of primary oxidation products into secondary ones.



Fig. 1. The antioxidants' effect of various origins on the change in the peroxide number of spreads with food fibers during the storage period at different temperatures: a) $t = (20\pm 2)$ °C and b) t = (0... -5) °C

In this period, the difference between the peroxide numbers in the control sample and spreads with antioxidants of various origins ranged from 1 to 2.7 %, respectively (when stored at a temperature of (20 ± 2) °C).

So, the highest antioxidant activity during the storage period of spreads at a temperature of (20 ± 2) °C was shown by antioxidants of natural origin "NovaSOL COF" human-made and origin "GRINDOX 109". The value of peroxide number is less than 10 mmol 1/2 O/kg, the which is maximum permitted concentration according to the requirements of regulatory documents [14]. The antioxidants added to the product slowed down the course of oxidative processes in comparison with the control sample.

It is known, as a result of hydrolysis, free fatty acids are disengaged, the content of which characterizes the acid number. By the value of the latter, the fat quality can be determined, an increase in acidity indicates spoilage. The change in the acid number of products with high-fat content – spreads with food fibers, depending on the antioxidants type during storage period at temperatures (20 ± 2) °C and (0...-5) °C is depicted in Figure 2. According to the research results (Fig. 2 a), the amount of free fatty acids in the spreads after 3 storage davs at a °C temperature of (20 ± 2) was insignificant. With an increase in the storage duration of the spreads, the acid number of their fat base - a mixture of milk fat and oil – gradually increased, most intensively in the control sample.

The increase in the acid number on the 9th storage day at a temperature of (20 ± 2) °C is noticeable only in the spread without antioxidants – by 6.25 times, while in the spreads with the addition of the natural antioxidant "NovaSOL COF" the amount of free fatty acids increased by 1, 3 times. A similar value is observed in the sample with the addition of the human-made antioxidant "GRINDOX 109" (an increase in the acid number by 1.25 %).

After 12 storage days, a significant increase in the value of the acid number has been found in the samples of spreads without antioxidants -13 times, with the introduction of the natural flavoring agent "Caraway – elite flavor" -7.8 times.

Regarding the samples of spreads, which were stored at a temperature of (0...-5) °C (Fig. 2 b), a similar tendency towards an increase in the acid number has been observed.



Fig. 2. The antioxidants' effect of various origins on the change in the acid number of spreads with food fibers during the storage period at different temperatures: a) $t = (20 \pm 2)$ °C and b) t = (0...-5) °C

However, due to low temperatures, the growth dynamic of this indicator is slow. Thus, the largest amount (0.18 mg KOH/g) of free fatty acids in the spread without antioxidants has been revealed on the 20th storage day. Low acid number values have been observed in the samples with the antioxidants' addition of natural origin and human-made origin "NovaSOL COF" and "GRINDOX 109", compared to other products with high-fat content.

4. Conclusions

While investigating the antioxidants' effect of various origins on the storage of products with high-fat content – spreads with food fibers for peroxide and acid numbers, it has been established that the most active are antioxidants of humanmade origin "GRINDOX 109".

By choosing antioxidants, it is possible to significantly reduce unwanted oxidative and hydrolytic changes in the fatty base of spreads. Food the storage at low temperatures inhibits these changes and, as a result, reduces the rate of radical reactions. In addition, it is possible to combine milk and vegetable fats with food fibers. Investigation of the intensity level of spoilage processes can be used to regulate the storage life of other dairy with multicomponent products а composition and high-fat content.

5. References

[1] GREK E., KRASULYA E., SAVCHENKO A., PETRINA A., Fatty acid composition of dairy fat products of vegetable origin. *Ukrainian journal of food science*. 2(1): 14-21, (2014).

[2] COMERT E. D., GOKMEN V., Evolution of food antioxidants as a core topic of food science for a century. *Food Research International*, 105: 76-93, (2018).

[3] GREK O. V. The use of antioxidants for dairy products with high-fat content. *Dairy industry*, 2: 28-30, (2013).

[4] CAROCHO M., MORALES P., FERREIRA I. Antioxidants: Reviewing the chemistry, food applications, legislation and role as preservatives. *Trends in Food Science & Technology*, 71: 107-120, (2018).

[5] MENDEZ-CID F. J., CENTENO J. A., MARTINEZ S. CARBALLO J., Changes in the chemical and physical characteristics of cow's milk butter during storage: Effects of temperature and addition of salt. *Journal of Food Composition and Analysis*, 63: 121-132, (2017).

[6] O' DWYER S. P., O'BEIRNE D., NI EIDHIN D., HENESSY A. A., O' KENNEDY B. T., Formation, rheology and susceptibility to lipid oxidation of multiple emulsions (O/W/O) in table spreads containing omega-3 rich oils. *LWT - Food Science and Technology*, 51(2): 484-491, (2013).

[7] KHANEGHAH A. M., An overview on some of important sources of natural antioxidants. *International Food Research Journal*, 23: 928-933, (2016).

[8] NECHAEV A. P., NIKOLAEVA Y. V., PILIPENKO O. V., DUBROVIN G. A., SAMOILOV A. V., Ways to Improve Oxidation Resistance of Low Fat Spreads Using Natural Antioxidants in Micellised Form. *Food industry*, 3: 11-14, (2018).

[9] SAVCHENKO O. A., GREK O. V., PETRINA A. B., TOPCHIY O. A., KRASULYA O. O., Technologies of products with modified fat composition: realities and trends. - Monograph - K.: "Komprint", ISBN 978-966-929-915-4, 250 p. (2018).
[10] LORENZO J. M., MUNEKATA E. S., GOMEZ B., BARBA F. J., MORA L., PEREZ-SANTAESCOLASTICA C., TOLDRA F., Bioactive peptides as natural antioxidants in food products. *Trends in Food Science & Technology*, 79: 136-147, (2018).

[11] GREK O. V., KRASULYA O. O., The influence of complex antioxidants on the storage life of dairy products. *Products & Ingredients*, 8(83): 43-44, (2011).

[12] PODKOVKO O. A., RASHEVSKAYA T. A. Research of antioxidant properties of oil paste with cryopowder from table beet. *Food industry*, 3: 81-86, (2015).

[13] DARMAWAN M. A., MUHAMMAD B. Z., HARAHAP A. F., RAMADHAN M. Y., SAHLAN M., SUPRIYADI T., ADB-AZIZD S., GOZAN M. Reduction of the acidity and peroxide numbers of tengkawang butter (Shorea stenoptera) using thermal and acid activated bentonites. *Heliyon*, 6. (12): (2020). doi.org/10.1016/j.heliyon.2020.e05742

[14] DSTU 4445:2005 Spreads and fat blends. General specifications, *State Committee for Technical Eegulation and Consumer Policy*, 25 p. (2006).