UDC 665.1
DOI: 10.15587/1729-4061.2020.209000

DETERMINATION OF THE INFLUENCE OF NATURAL ANTIOXIDANT CONCENTRATIONS ON THE SHELF LIFE OF SUNFLOWER OIL

N. Sytnik
PhD*
E-mail: ntlsytnik@gmail.com
E. Kunitsa
PhD
Department of Innovative Food and Restaurant Technologies
Kharkiv Institute of Trade and Economics of Kyiv National University of Trade and Economics
O. Yarosha lane, 8, Kharkiv, Ukraine, 61045
V. Mazaeva
PhD*
A. Chernukha
PhD**
O. Bezuglov
PhD, Associate Professor**
O. Bogatov
PhD, Associate Professor
Department of Metrology and Life Safety
Kharkiv National Automobile and Highway University
Yaroslava Mudroho str., 25, Kharkiv, Ukraine, 61002
D. Beliuchenko
Lecturer**
E-mail: mr.funt1984@i.ua
A. Maksymov
Lecturer**
M. Popov
PhD***
I. Novik
PhD, Associate Professor***
*Department of Studies of Technology for Processing Oils and Fats
Ukrainian Research Institute of Oils and Fats of National Academy of Agrarian Sciences of Ukraine
Dziuby ave., 2a, Kharkiv, Ukraine, 61019
**Department of Fire Tactics and Rescue Operations
National University of Civil Defence of Ukraine
Chernyshevska str., 94, Kharkiv, Ukraine, 61023
***Department of Innovative Entrepreneurship Management and International Economic Relations
National Technical University «Kharkiv Polytechnic Institute»
Kyrpychova str., 2, Kharkiv, Ukraine, 61002

The influence of natural antioxidants from different types of vegetable raw materials on the processes of oxidative and hydrolytic spoilage of sunflower oil during storage is studied. Plant antioxidants are more environmentally friendly and safer than synthetic ones.

Green tea leaves and oak bark were used as vegetable raw materials. Water-ethanol extracts from vegetable raw materials were added to oil samples in experimental concentrations. The samples were stored in the laboratory conditions at the temperature of (20±2) °C. The study was performed for 5 months. The values of the acid and peroxide numbers were determined.

The most effective blend of antioxidants showed the increase in the acid number from 0.12 to 0.20 mg KOH/g (concentration of green tea extract – 0.05 %, without the addition of oak bark extract).

According to the values of the peroxide number, the most effective blends of antioxidants were the experiment points with the following green tea extract:oak bark extract ratio: (0.05:0.05) %, (0.025:0.025) %,(0.025:0.05) %, (0.05:0.025) %.

To determine the induction period of oil and, accordingly, its shelf life under experimental conditions, the values of the peroxide numbers were used. It is rational to use extractives from oak bark and green tea under the following conditions: the concentration of each of the antioxidant extracts in terms of dry matter – (0.025 0.04) %. The maximum induction period is 100 days.

The efficiency of natural antioxidants in terms of the concentration of oak bark and green tea extracts is 0.05 and 0.025 %, respectively, was compared to the effectiveness of the corresponding concentration of one of the synthetic antioxidants – butylhydroxyanisole. When using butylhydroxyanisole, the induction period of oil was 65 days, and when using natural antioxidants – 74 days

Keywords: oil, antioxidant, oxidative spoilage, hydrolytic spoilage, induction period, economic substantiation

Received date 02.04.2020
Accepted date 17.07.2020
Published date 26.08.2020

1. Introduction

Oils and fats are one of the most important components of food, cosmetics and hygiene products, chemical and pharmaceutical products, etc. In addition, the use of oils and fats on their own is widespread in both food and non-food purposes.

An acute problem associated with the obtaining, processing and use of oils is various types of spoilage, which lead to a negative change in the technological characteristics of oils, as well as to the harmful effects on the human body in the case of consumption of spoiled oil [1, 2].

In general, oils and fats are the main factor determining the stability of the oil-containing product during storage. Therefore, important tasks during production are the selection of high-quality oils and fats, study of changes during their storage and the impact of stabilizers and antioxidants.

Various synthetic antioxidants are widely used in the production of oil-containing products, but from a hygienic point of view, it is advisable to use natural compounds derived from plants, which are biologically valuable products and do not cause toxic effects on the human body. Among the substances included in plant raw materials, tocopherols, sesamol, carotenoids, phosphatides, chlorophyll, phenolic compounds, etc. have the antioxidant effect. Plant antioxidants can not only protect the fatty product from oxidation, but also preserve the biological value of the product.

Plant products, as well as medicinal herbs, contain a number of antioxidant components that can prevent or delay oxidative processes [3]. For example, valuable natural sources of antioxidant compounds are oak bark, rowan, coltsfoot, mint, thyme, chamomile and more.

Thus, the study of plant raw materials to obtain effective natural antioxidants for oils is an actual scientific task.

2. Literature review and problem statement

All foods consist of primary biomaterials, which inevitably decompose and spoil over time. Deterioration of products cannot be prevented, but it is possible to slow down the spoilage process, which requires the correct selection of recipes, methods of processing, packaging, storage and transportation of products.

Fat spoilage can be caused by the accumulation of free fatty acids, peroxides, as well as rancidity and salinization [2]. Each of these types of food spoilage from a chemical point of view is characterized by the predominant accumulation of substances belonging to a certain group of chemical compounds.

Triacylglycerols (TAGs) of fats are labile components and undergo various transformations, the main of which are hydrolysis and oxidation. As a result of these reactions, the chemical composition changes, organoleptic characteristics worsen, nutritional and biological value of fat decreases. The mechanism of chemical and biochemical reactions of TAG transformation is complex, including the formation of both labile intermediates with high reactivity and stable end products – carbonyl compounds. The depth and rate of these processes depend on the chemical composition of stored products, enzyme activity, presence of microorganisms, contact with air oxygen, use of antioxidants, inert environment, technological parameters of raw material processing and storage [4].

Compounds such as fatty alcohols and oxypolymers can be formed in fats. In addition to the bitter taste and smell, these substances can cause the decomposition of vitamins, lowering the temperature of smoke formation, foaming of oils and fats subjected to heat treatment. One of the most important indicators of oil oxidation is the peroxide number, which characterizes the content of peroxides and hydroperoxides in the oil [4].

Therefore, oils and fats, as well as products containing them, require the introduction of special substances with antioxidant action.

Natural (tocopherols, tocotrienols) and synthetic (propyl gallate, butylhydroxyanisole, butylhydroxytoluene, tert-butylhydroquinone) antioxidants are used to inhibit spoilage processes. Synthetic antioxidants are used in strictly regulated concentrations because they are substances that are dangerous to human health.

Recently, more and more attention of researchers has been attracted by antioxidant substances extracted from plant raw materials, in particular, various parts of trees, flowers, medicinal herbs, etc. For example, the antioxidant and antimicrobial effects of oregano extract in the production of meat products were researched in [5]. It was found that this plant extract contributes to a significant extension of the shelf life while maintaining a high quality of beef products. But in the study, it would be useful to separate how the oregano extract affects the peroxidation of the fatty phase of the product, as well as to conduct studies with different antioxidant concentrations.

Currently, a promising type of raw material for extracting antioxidants are tea leaves.

Thus, the authors [6] presented the results of the study of the antioxidant properties of infusions of medicinal herbs, teas, wines, balms, beer. Evaluation of antioxidant capacity was performed by coulometric titration with electrogenerated bromine compounds. It was found that samples of green tea have the highest indicators of antioxidant activity. It was also shown that plant biopolymers – lignins have high antioxidant properties in comparison with known synthetic antioxidant preparations. However, there are no results on the specific use of green tea as an antioxidant for oils and fats, it is not shown how the physical and chemical indicators of oil oxidation change during the use of such an antioxidant.

The production of phenolic compounds, which have a pronounced antioxidant effect, from fresh and old tea leaves was studied in [7]. Phenolic profiles of old and young tea leaves were compared using ultra-high-performance liquid chromatography combined with hybrid quadrupole Orbitrap mass spectrometry (UHPLC-Q-Orbitrap-MS). It was found that the phenolic composition of old tea leaves has an antioxidant effect similar to the new ones, which makes it possible to use old tea leaves and tea production waste as raw material. This indicates that green tea leaves can be a cost-effective source of valuable antioxidants. But the study does not show how antioxidant substances from tea leaves affect the processes of oxidative and hydrolytic spoilage of oils, and shows only the phenolic composition of tea leaf samples. Phenolic compounds are known to have antioxidant activity, but a number of studies should be performed to confirm their effectiveness during oil storage and to determine how much the oil shelf life increases when using tea leaf extracts.

In addition, wood residues such as bark are an attractive source of natural antioxidants.

The efficiency of extraction of total polyphenols and flavonoids from oak bark was evaluated in [8]. The total amount of phenols extracted with water and aqueous ethanol solution with a concentration of 60 % was within (55.4–60.4) and (71.0–79.3) mg of gallic acid/g of bark, respectively, and the total content of flavonoids in these extracts was determined within (35.1–38.0) and (72.0–78.4) mg of catechin/g of bark. Aqueous-ethanol extracts showed higher activity against free radicals than a common synthetic antioxidant – butylhydroxytoluene. The study is very valuable in terms of the chemical composition and properties of antioxidants extracted from oak bark, but there are no data on the use of these substances in oils, fats and fat-containing systems.

The authors [9] evaluated the total content of polyphenols, content of heavy metals and antioxidant capacity of oak bark (*Quercus robur L.*) and pine bark (*Pinus sylvestris L.*). Identification and quantification of flavonoids and phenolic acids were performed by chromatographic analysis. Phenol extraction efficiency was higher in oak bark than in pine bark. The metal content in the crude bark of the experimental raw material and its extracts decreased in the order: Zn>Cu>Cr>Pb>Ni>Cd. The obtained extracts were found to inhibit free radical reactions and can be used as additives in food and cosmetic products, as well as for wood preservation. Based on the results of the study, only the assumption is made that the extracted substances can be additives to different types of products, but there is no experimental confirmation of how the rate of oil spoilage decreases individually and in fat-containing products.

Also of great scientific and practical interest are eucalyptus leaves in terms of obtaining antioxidant substances.

The pronounced antioxidant and antibacterial action of eucalyptus leaf extracts has been experimentally confirmed. Eucalyptus leaves contain substances such as cineole and eucalypton, which are able to inhibit free radical processes [10–12]. However, there are no data on the use of eucalyptus leaf extracts as antioxidants for oils and oil-containing products, the effect of these antioxidants on the indicators of peroxide and acid numbers, which reflect the degree of product spoilage and the presence of harmful substances.

Thus, at present, the directions related to the development of antioxidant systems to extend the shelf life, ensure safety and preserve the properties of various types of food and non-food products are very relevant. But there is not enough data that would reflect the real impact of such antioxidants directly on the quality of oils during storage, without the use of elevated temperatures, special devices, and during the simulation of the actual process of oil storage.

The rational conditions for obtaining water-ethanol extracts from oak bark, green tea leaves and eucalyptus leaves were determined in [13]. Sunflower oil was used as a model substance and an accelerated oxidation method – the method of active oxygen – at the temperature of 110 °C. The work contains important information on the rational conditions for obtaining antioxidants. However, there are no data on the effectiveness of such antioxidants under the actual storage conditions of the oil, as well as on the effect of different concentrations of antioxidants on the rate of oxidative and hydrolytic processes in the oil. It is shown that the most effective were extracts of green tea leaves and oak bark.

Thus, research on the impact of effective antioxidants from oak bark and green tea on physical and chemical indicators and shelf life of oil during storage is an important direction. This will allow improving the quality, safety and preserving the functional properties of oils and oil-containing products.

3. The aim and objectives of the study

The aim of the study was to determine the dependence of physical and chemical indicators and shelf life of sunflower oil during storage on the concentration of natural antioxidants. This will allow to use natural antioxidants of plant origin effectively and efficiently, significantly increase the shelf life of sunflower oil by slowing down the formation of harmful oxidation products, reduce the cost of oil.

To achieve the aim, the following objectives were set:

– to experimentally determine the effect of different concentrations of natural antioxidants (water-ethanol extracts of oak bark and green tea leaves) on the value of the acid number of sunflower oil during storage;

– to experimentally determine the effect of different concentrations of natural antioxidants on the value of the peroxide number of sunflower oil during storage;

– to investigate the dependence of the shelf life of sunflower oil on the concentration of antioxidants and to determine rational concentrations of natural antioxidants;

– to determine the economic feasibility of using the rational composition of natural antioxidants.

4. Materials and methods to study the dependence of physical and chemical indicators of oil on the concentration of antioxidants

4. 1. Examined materials and equipment used in the experiment

The following reagents and materials were used in this study:

– oak bark, green tea leaves according to acting normative documentation;

– refined deodorized winterized sunflower oil, grade P, according to DSTU 4492:2017;

– rectified ethyl alcohol, according to DSTU 4221:2003;

– distilled water, according to acting normative documentation;

– potassium iodide, grade “pure chemical”, according to acting normative documentation;

– soluble starch, according to acting normative documentation;

– sodium thiosulfate, according to acting normative documentation;

– acetic acid, according to acting normative documentation;

– chloroform, according to acting normative documentation;

– potassium hydroxide, grade “clean for analysis”, according to acting normative documentation;

– phenolphthalein, according to acting normative documentation.

4. 2. Procedure for determining the indicators of oxidative and hydrolytic spoilage of oil during storage

Oxidative spoilage of oil during storage is evaluated by the peroxide number, which is determined by standard methods according to DSTU 4570: 2006.

Hydrolytic spoilage of oil during storage is evaluated by the acid number, which is determined by standard methods according to DSTU 4350: 2004.

4. 3. Planning of experimental research and processing of results

In order to plan our study and process the results obtained, a full first-order factorial experiment was applied; the calculation was performed in the Microsoft Office Excel 2003 (USA) and Stat Soft Statistica v6.0 (USA) software packages. The experiments were repeated twice.

5. Results of studying the relationship between the concentration of antioxidants, physical and chemical indicators and shelf life of oil

5. 1. Studying the effect of antioxidant concentration on changes in the acid number of sunflower oil during storage

The influence of the concentration of green tea and oak bark extracts on the stability of the oil was determined, for which a mixture of antioxidant extracts with the concentrations of components listed in Table 1 was introduced into the initial oil.

Aqueous-ethanol extracts were obtained under the following conditions:

– vegetable raw material-solvent ratio: 1:10;

– volume fraction of ethyl alcohol in the extractant: for oak bark 30%, for green tea 50%;

– extraction temperature: for oak bark 50 °C, for green tea 60 °C.

To conduct the experiment and obtain a mathematical model that relates the shelf life and concentration of antioxidants, a full factorial experiment was used: the number of factors – 2, the number of experiments – 9, the number of levels – 3. The matrix of experiment planning is given in Table 1. The upper level (+1) is 0.05 %, the lower level (–1) is 0 %, the range of variation is 0.025 % (concentrations of antioxidant extracts in terms of dry matter).

Table 1

Experimental concentrations of antioxidant extracts

Experiment number	Concentration of antioxidant extracts in oil,% (in terms of dry matter)	
	Oak bark	Green tea
1	0.05	0.05
2	0	0
3	0.025	0.025
4	0.05	0
5	0	0.05
6	0.025	0.05
7	0.025	0
8	0.05	0.025
9	0	0.025

Thus, the minimum total content of antioxidant extracts in the oil is 0.025 %, the maximum – 0.1 % (in terms of dry matter).

The stability of the oil in the presence of antioxidant extracts was investigated in comparison with the oil without the addition of antioxidants (experiment 2 in Table 1).

All oil samples were stored in the laboratory conditions at the temperature of (20±2) °C, in a dark glass container. The study was performed for 5 months.

For each sample (No. 1–9 in Table 1), the values of acid numbers were studied for 5 months. In order to determine the standard deviation when determining the acid numbers for point 1 (1 month), six parallel determinations were performed. The mean value of the acid number was 0.15 mg KOH/g, the standard deviation was 0.01 mg KOH/g.

The results of the study of acid numbers for 9 samples are shown in Fig. 1. As evidenced by Fig. 1, for each experimental month, the values of the acid numbers of 9 samples differ by a value exceeding the standard deviation.

In this case, for certain samples, the value of the acid number at certain intervals of storage time is constant. Thus, for sample 1, the acid number is equal to 0.15 mg KOH/g for 1 and 2 months, and 0.16 mg KOH/g for 2.5 and 3 months.

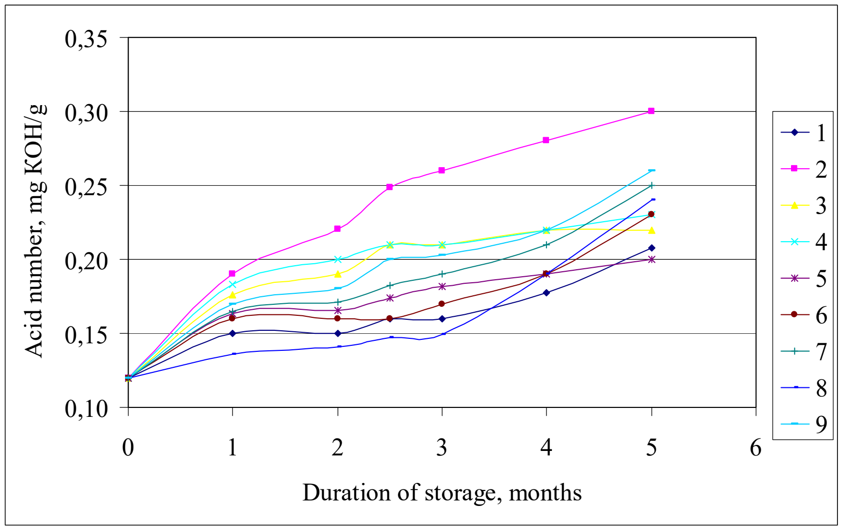

Fig. 1. Dependence of the acid number of oil samples on shelf life

From Fig. 1, it is found that all samples of oil with the addition of plant antioxidants generally show lower values of acid numbers during storage compared to the sample without the addition of antioxidants. The values of the acid number of samples increase slightly over time, within (0.12–0.30) mg KOH/g, while the highest value in the study (0.30 mg KOH/g) does not reach the limit according to DSTU 4492:2017 (for refined deodorized winterized sunflower oil, grade P – not more than 0.50 mg KOH/g). Thus, despite the fact that the values of the acid numbers of the samples differ by a value greater than the standard deviation, the increase in the acid number is not significant in determining the rational conditions for using antioxidant extracts.

5. 2. Studying the effect of antioxidant concentration on changes in the peroxide number of sunflower oil during storage

During the study period, along with the values of the acid numbers, the values of the peroxide number of the oil were determined.

For each sample (No. 1–9 in Table 1), the values of peroxide numbers were studied for 5 months. In order to determine the standard deviation when determining the peroxide numbers for point 1 (1 month), six parallel determinations were performed. The mean value of the peroxide value was 2.47 ½ O mmol/kg, the standard deviation was 0.05 ½ O mmol/kg. The results of the determinations are shown in Fig. 2.

Analyzing the data of Fig. 2, it was found that for each experimental month the values of the acid numbers of 9 samples differ by a value exceeding the standard deviation. In addition, for all samples in all experimental months there is an increase in peroxide numbers by a value that significantly exceeds the standard deviation.

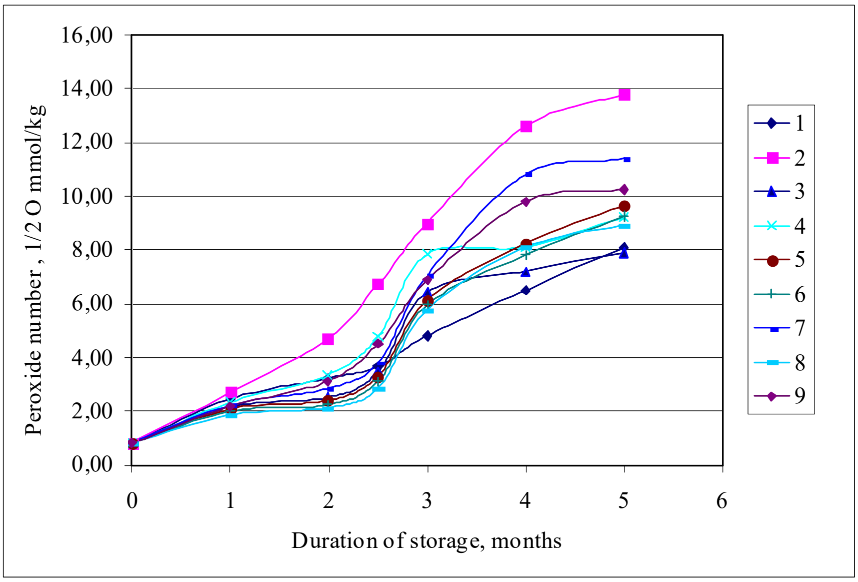

Fig. 2. Dependence of the peroxide number of oil samples on shelf life

The values of the peroxide number increase significantly, with varying intensity. The sample without the addition of antioxidants (2) has the highest peroxide value at the end of the study period. Thus, for points 2, 7, 9, at the end of the study, the values of peroxide numbers are observed above standard (according to DSTU 4492:2017 for refined deodorized winterized sunflower oil, grade P – no more than 10 ½ O mmol/kg).

Thus, the conducted studies demonstrate the effect of antioxidants on the most important indicators of oil spoilage – acid and peroxide number. Due to the significant increase in peroxide numbers, the value of this indicator is taken to further determine the induction periods of samples that reflect the actual shelf life of the oil.

5. 3. Studying the dependence of the shelf life of sunflower oil on the concentration of antioxidants

To determine the relationship between the concentrations of antioxidants and the shelf life of the experimental oil, the values of the induction periods for each experiment are determined, which are presented in Table 2. Induction periods reflect the shelf life of experimental samples.

Table 2

Value of experimental induction periods

Experiment number	Induction period, days
1	100
2	45
3	72
4	70
5	70
6	72
7	65
8	74
9	60

Therefore, the induction periods are maximum for points 1, 3, 6, 8.

As a result of processing experimental data in the environment of the Statistica 8 package (StatSoft, Inc.), a mathematical model was obtained that reflects the dependence of the induction period of sunflower oil on the concentrations of antioxidant extracts in terms of dry matter. The upper level of variation of the input variables (+1) is 0.05 %, the lower level (–1) is 0 %, the interval of variation is 0.025 % (concentration of antioxidant extracts in terms of dry matter).

In normalized form, the regression relationship has the form:

$$y = 69.78 + 11.5 \cdot x_1 + 10.33 \cdot x_2. \quad (1)$$

In real variables:

$$y = 47.95 + 460 \cdot x_1 + 413.2 \cdot x_2, \quad (2)$$

where *V* – value of the induction period, days, *x* – the concentration of oak bark extract, %, in terms of dry matter, *y* – the concentration of green tea extract, %, in terms of dry matter.

The adequacy of the obtained model was checked using Fisher's criterion (Table 3).

Table 3

Results of checking the adequacy of the model

Value	*SS*	*df*	*MS*	*F*	*p*
(1) Oak bark L	793.500	1	793.5000	19.88814	0.004285
(2) Green tea L	640.667	1	640.6667	16.05755	0.007061
Error	239.389	6	39.8981	–	–
General SS	1673.556	8	–	–	–

In Table 3: *SS* – sum of squares; *df* – degree of freedom; *MS* – mean square value; *p* – level of significance; *F* – Fisher's criterion. The value of the coefficient of determination R^2=0.85696.

Thus, the absence of loss of consistency (significance level p>0.05) and the value of the coefficient of determination, close to one, allow us to conclude that the obtained model adequately describes the response function.

Fig. 3 shows the projection of the response surface, which is the dependence of the induction period of oil with concentrations of antioxidant extracts in % in terms of dry matter.

Analysis of the obtained data revealed that it is rational to use extractives from oak bark and green tea leaves under the following conditions: the concentration of each of the antioxidant extracts in terms of dry matter (0.025–0.04) %. In this range, there is the zone of rational values.

The effectiveness of natural antioxidants at point 8 (concentration of oak bark and green tea extracts, 0.05 and 0.025 %, respectively) compared to the effectiveness of the corresponding concentration of one of the synthetic antioxidants – butylhydroxyanisole. The total concentration of the two extracts used in terms of dry matter corresponded to the concentration of butylhydroxyanisole in sunflower oil (0.075 %).

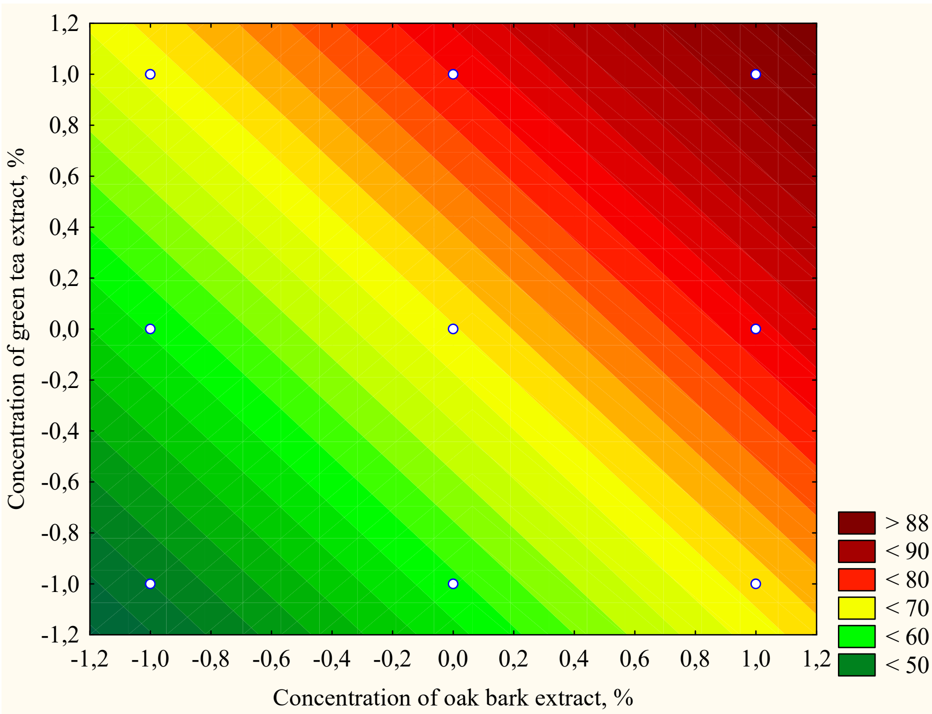

Fig. 3. Dependence of the induction period (days) on the concentration of antioxidant extracts, % in terms of dry matter (projection of the response surface)

In this case, the induction period of oil, which corresponds to the shelf life and is determined by the change in peroxide numbers, was 65 days, and when using natural antioxidants –74 days. Thus, the use of natural antioxidants is more effective in inhibiting the oxidative spoilage of oils.

5. 4. Economic feasibility of using natural antioxidants in oils

Economic effect ($E_{cost\ reduct}$) lies in the reduction of production cost, comparing the use of natural antioxidants (oak bark extract, green tea extract) with synthetic (butylhydroxyanisole) in production conditions, which can be calculated by the following formula:

$$E_{cost\ reduct} = (P_{synt} \cdot G_{synt} - P_{nat} \cdot G_{nat}) \cdot V_{pr},$$

where P_{synt}; P_{nat} – the price of synthetic and natural antioxidants, $/kg; G_{synt}; G_{nat} – specific consumption of synthetic and natural antioxidants, kg/t, V_{pr} – volume of sunflower oil, t.

The results of calculations of the economic feasibility of using different types of antioxidants are given in Table 4.

Table 4

Economic evaluation of using different types of antioxidants

Indicator	Butylhydroxyanisole	Oak bark extract	Green tea extract
Price of antioxidant, $/kg	33.70	5.60	4.40
Specific consumption of antioxidant, kg/t (in terms of dry matter)	0.75	0.5	0.25
Volume of sunflower oil, t	1.000		
Economic effect, $	–	20.80	22.50

According to the calculations, we can conclude that when saturating 1 ton of sunflower oil with natural antioxidants, the cost reduction is:

– using oak bark extract – 20.80 $;

– using green tea extract – 22.50 $.

Therefore, this will significantly reduce the cost of production and, accordingly, increase the financial results, which indicates the economic feasibility of their use in enterprises that produce any oil-containing products.

6. Discussion of the results of studying the dependence of sunflower oil shelf life on antioxidants concentration

As a result of the research, the effect of different concentrations of natural antioxidants (water-ethanol extracts from oak bark and green tea leaves) on changes in physical and chemical indicators and shelf life of sunflower oil in general is determined. The main causes of spoilage of oils, fats, and, accordingly, oil-containing products, are oxidation and hydrolysis. These processes can be evaluated by the corresponding physical and chemical indicators of the oil – peroxide and acid numbers. These characteristics reflect the accumulation of oxidation products and free fatty acids in the oil. Therefore, during the study, oil samples with different concentrations of antioxidants were stored at the temperature of (20±2) °C, i. e. this allowed estimating the shelf life of samples in real conditions of consumption and using many types of food, cosmetics, pharmaceuticals and the like.

The effect of antioxidant concentration on the growth of the acid number of oil was determined. The values of the acid number in the experimental conditions increased slightly. All samples with the addition of extracts showed a lower growth rate of this indicator than the sample without the addition of extracts. The lowest growth rate is observed for point 5 in terms of the experiment (Table 1). The acid number increased from 0.12 to 0.20 mg KOH/g (concentration of green tea extract – 0.05 %, without the addition of oak bark extract). In general, this indicator increased insignificantly, but the addition of extracts inhibited the formation of free fatty acids.

The dependence of the growth rate of the peroxide number of the oil on the antioxidant concentration was also determined. The lowest growth rate of the peroxide number was shown by the following points of the experiment with the following green tea extract:oak bark extract ratio: 1 – (0.05:0.05) %, 3 – (0.025:0.025) %, 6 – (0.025:0.05) %, 8 – (0.05:0.025) %. That is, in this case, the most effective are mixtures with extracts of both plants.

These effects of reducing the rate of hydrolytic and oxidative spoilage are explained by the presence of active compounds, in particular, phenolic, which have an antioxidant, preservative, antibacterial action.

The peroxide number is associated with the induction period of oil, which corresponds to the actual shelf life. It is rational to use extractives from oak bark and green tea leaves under the following conditions: the concentration of each of the antioxidant extracts in terms of dry matter (0.025–0.04) %. The maximum induction period was 100 days.

Studies have shown a clear dependence of the rate of oxidative and hydrolytic spoilage of oil on the concentrations of plant antioxidants. The samples were stored under normal conditions, without the use of elevated temperature, radiation, oxidation initiators or other effects on the experimental samples.

This work differs from existing scientific research on the antioxidant properties of plants in that it shows the direct effect of different concentrations of antioxidants on the physicochemical parameters and shelf life of sunflower oil under normal storage conditions. Sunflower oil is a common vegetable oil that is widely used both individually and in various fats, as well as many foods.

In addition, it was shown that using oak bark and green tea extracts reduces the cost of oil by $ 20.80 and $ 22.50, respectively.

Thus, the results of the study are important for various industries that use oils and fats.

The plant antioxidants considered in this study can be used to extend the shelf life of oils at concentrations of each of the antioxidants up to 0.05 % inclusive (in terms of dry matter). Therefore, the maximum total concentration of antioxidant extracts in the oil in terms of dry matter can be 0.1 %.

When obtaining antioxidant extracts from the considered vegetable raw materials, the recommended extraction parameters should be taken into account (vegetable raw material-solvent ratio: 1:10; volume fraction of ethyl alcohol in the extractant: for oak bark 30 %, for green tea 50 %; extraction temperature: for oak bark 50 °C, for green tea 60 °C). As the extraction temperature increases, the biologically active substances contained in the plants are able to break down and, consequently, lose their properties.

An aqueous-ethanolic solution was used as an extractant, since the active substances from plants are well soluble in polar solvents. This fact complicates using such water-ethanol extracts in oils and fats. To add the active substances extracted from the plants, the obtained extracts must be added into the oil, after which the oil or fat must be vacuum dried. But this disadvantage is eliminated when using antioxidants in fat emulsion products (margarine, mayonnaise, etc.). In this case, there is no need for additional processing of the product after adding the extracts.

7. Conclusions

1. As a result of experimental studies, the nature of changes in the acid number of sunflower oil from the experimental concentrations of antioxidant extracts from oak bark and green tea leaves was determined. It was found that during storage in the study conditions, the acid number increased slightly. The value of this indicator for the oil sample without the addition of antioxidants increased from 0.12 to 0.30 mg KOH/g. All samples with the addition of extracts showed a lower growth rate of this indicator. The most effective extract was green tea extract with a concentration of 0.05 % in terms of dry matter, without the addition of oak bark extract.

2. The influence of experimental concentrations of antioxidant extracts on the growth rate of the peroxide number of sunflower oil is determined. The sample without the addition of antioxidants has the highest value of the peroxide number at the end of the study period (this indicator changed from 0.82 to 13.80 ½ O mmol/kg). The most effective reduction of the peroxide value was shown by the following points of the experiment with the following green tea extract:oak bark extract ratio: 1 – (0.05:0.05) %, 3 – (0.025:0.025) %, 6 – (0.025:0.05) %, 8 – (0.05:0.025) %. For these points, there was an increase in the peroxide number to the following values: 8.10; 7.89; 9.25; 8.92 ½ O mmol/kg, respectively. All these values are lower than the standard value of the peroxide number for sunflower oil (10 ½ O mmol/kg).

3. The dependence of the shelf life of sunflower oil under experimental conditions on the concentration of antioxidants is studied. The shelf life is determined by the induction period of oil samples, which is determined by the change in peroxide numbers. It is found that it is rational to use extractives from oak bark and green tea leaves under the following conditions: the concentration of each of the antioxidant extracts in terms of dry matter (0.025–0.04) %. The maximum induction period was 100 days.

4. The economic feasibility of using natural antioxidants in industrial conditions is substantiated. Reducing the cost of production when saturating 1 ton of sunflower oil with oak bark extract is $ 20.80, green tea extract – $ 22.50.

References

1. Halliwell, B., Gutteridge, J. M. C. (2015). Free radicals in biology and medicine. Oxford: Oxford University Press. doi: http://doi.org/10.1093/acprof:oso/9780198717478.001.0001
2. Pilipenko, T. V., Nilova, L. P., Naumenko, N. V., Mehtiev, V. S. (2011). Topical issues of vegetable oil quality management. Vestnik Yuzhno-Ural'skogo gosudarstvennogo universiteta. Seriya: Ekonomika i menedzhment, 28, 183–188.
3. Adu, O., Fajana, O., Ogunrinola, O., Okonkwo, U., Evuarherhe, P., Elemo, B. (2019). Effect of continuous usage on the natural antioxidants of vegetable oils during deep-fat frying. Scientific African, 5, e00144. doi: https://doi.org/10.1016/j.sciaf.2019.e00144
4. Akoh, C. C., Min, D. B. (Eds.) (2008). Food Lipids. Chemistry, Nutrition, and Biotechnology. CRC Press, 928. doi: https://doi.org/10.1201/9781420046649
5. Oleynikov, V. (2020). Antioxidant and antimicrobial properties of oregano extract (Origani vulgaris herba L.). Foods and Raw Materials, 8 (1), 84–90. doi: https://doi.org/10.21603/2308-4057-2020-1-84-90
6. Lapin, A. A., Borisenkov, M. F., Karmanov, A. P., Berdnik, I. V., Kocheva, L. S., Musin, R. Z., Magdeev, I. M. (2007). Antioksidantnye svoystva produktov rastitel'nogo proishozhdeniya. Himiya rastitel'nogo syr'ya, 2, 79–83. Available at: https://cyberleninka.ru/article/n/antioksidantnye-svoystva-produktov-rastitelnogo-proishozhdeniya

7. Liu, Z., Bruins, M. E., de Bruijn, W. J. C., Vincken, J.-P. (2020). A comparison of the phenolic composition of old and young tea leaves reveals a decrease in flavanols and phenolic acids and an increase in flavonols upon tea leaf maturation. Journal of Food Composition and Analysis, 86, 103385. doi: https://doi.org/10.1016/j.jfca.2019.103385
8. Dróżdż, P., Pyrzynska, K. (2017). Assessment of polyphenol content and antioxidant activity of oak bark extracts. European Journal of Wood and Wood Products, 76 (2), 793–795. doi: https://doi.org/10.1007/s00107-017-1280-x
9. Dróżdż, P., Pyrzynska, K. (2019). Extracts from pine and oak barks: phenolics, minerals and antioxidant potential. International Journal of Environmental Analytical Chemistry, 1–9. doi: https://doi.org/10.1080/03067319.2019.1668381
10. Gullón, B., Muñiz-Mouro, A., Lú-Chau, T. A., Moreira, M. T., Lema, J. M., Eibes, G. (2019). Green approaches for the extraction of antioxidants from eucalyptus leaves. Industrial Crops and Products, 138, 111473. doi: https://doi.org/10.1016/j.indcrop.2019.111473
11. Nasr, A., Zhou, X., Huang, S.-P., Wang, Y., Li, X., Zhu, G.-P. (2018). Comparative effects of some extraction solvents on the antimicrobial activity of Eucalyptus camaldulensis leaf, bud, capsule and seed crude extracts. Natural Product Research, 33 (17), 2560–2565. doi: https://doi.org/10.1080/14786419.2018.1455049
12. Ben Hassine, D., Abderrabba, M., Yvon, Y., Lebrihi, A., Mathieu, F., Couderc, F., Bouajila, J. (2012). Chemical Composition and in Vitro Evaluation of the Antioxidant and Antimicrobial Activities of Eucalyptus gillii Essential Oil and Extracts. Molecules, 17 (8), 9540–9558. doi: https://doi.org/10.3390/molecules17089540
13. Bilous, O., Sytnik, N., Bukhkalo, S., Glukhykh, V., Sabadosh, G., Natarov, V. et. al. (2019). Development of a food antioxidant complex of plant origin. Eastern-European Journal of Enterprise Technologies, 6 (11 (102)), 66–73. doi: https://doi.org/10.15587/1729-4061.2019.186442