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DETERMINATION THE INFLUENCE OF THE SYNTHETIC ANTIOXIDANTS MIXTURE ON THE OXIDATIVE STABILITY OF SUNFLOWER OIL

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The object of the study is the process of sunflower oil oxidation under conditions of increased temperature.

Sunflower oil is one of the most common oils and is used in the chemical, food and other industries. The main type of oil spoilage is oxidation, which is accelerated under the influence of radiation, elevated temperatures, long-term storage with oxygen access. Oxidation products prevent the effective use of oil in chemical reactions and technological processes. An important task is to develop and improve methods for increasing the oxidative stability of sunflower oil using antioxidants.

The oxidation process of refined deodorized frozen sunflower oil according to DSTU 4492 (CAS Number 8001-21-6) was studied by the method of differential scanning calorimetry. The simultaneous effect of synthetic antioxidants (tert-butylhydroquinone, butylhydroxyanisole, butylhydroxytoluene) in different ratios on the oil induction period at a temperature of 110 °C was determined. The total concentration of the antioxidant mixture in each experiment was 0.02 %. The initial oil induction period is 270.61 min. Rational ratios of antioxidants were determined: tert-butylhydroquinone: butylhydroxyanisole: butylhydroxytoluene (16.67:66.67:16.67) %; tert-butylhydroquinone: butylhydroxyanisole: butylhydroxytoluene (33.33:33.33:33.33) %. The corresponding oil induction periods were 382.56 min. and 385.87 min.

The effect of citric acid (0.005 %) and defoamer (polydimethylsiloxane, 0.0002 %)) on the induction period of oil with the addition of antioxidant mixtures was determined. The corresponding oil induction periods were 420.78 min. and 430.25 min.

The results of the study make it possible to increase the oxidative stability of sunflower oil, which will contribute to the effective use of oil in various areas

Keywords: oxidative stability, synthetic antioxidants, sunflower oil, induction period, triglyceride hydroperoxides

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1. Introduction

Sunflower oil is one of the most common oils. The world production of sunflower oil in the 2023/2024 marketing year amounted to 21.8 million tons, vegetable oil as a whole – 223.03 million tons. The oil content of sunflower can be more than 50 %. Sunflower oil, along with other liquid vegetable oils, is widely used in the chemical, food, paint, and cosmetic industries, metallurgy, etc. [1].

Sunflower oil refers to linoleic-oleic oils and contains the following triglycerides: trisaturated (0.3 %), disaturated (3.1 %), monosaturated (26.6 %), triunsaturated (70.2 %). In the fatty acid composition of the oil, unsaturated linoleic acid has the highest content (up to 74.0 %). The high content of unsaturated acids causes the low oxidative stability of the oil [2].

Oxidative spoilage worsens oil properties, requiring increased consumption of oil and reagents in production processes. For example, the oil undergoing a transesterification reaction should have a peroxide value of no more than 0.25 ½ O mmol/kg. This is 40 times lower than the standard limit for sunflower oil [3].

Oxidation of oil glycerides occurs by a chain free radical mechanism. The primary oxidation products are peroxides and hydroperoxides, secondary – aldehydes, ketones, alcohols, etc. The oxidative stability of oils depends on the fatty acid composition, accompanying substances, temperature, light, radiation, etc. [4].

In order to increase oxidative stability, antioxidants of various nature are added to oils. Synthetic antioxidants are obtained from petroleum-based products. Such antioxidants are economical, easy to use, effective, and dissolve well in oils and fats. The permitted content of these antioxidants in edible oils and fats is 200 mg/kg. If the permissible limit is exceeded, synthetic antioxidants are harmful to human health (for example, they can cause liver damage). Among synthetic antioxidants, propyl gallate (n-propyl ester of 3, 4, 5-trioxybenzoic acid), phenolic compounds: butylhydroxyanisole, butylhydroxytoluene, tert-butylhydroquinone [5] are widely used.

An alternative to synthetic antioxidants is natural antioxidants obtained from vegetable raw materials by extraction. Using these substances in food products has the following advantages: safety, increased biological value of products, potential benefits for the human body. The most common natural antioxidants are simple phenols, phenolic acids, terpenoids, carotenoids, vitamins, etc. The use of natural antioxidants is safer and more environmentally friendly in foods, but these substances have low stability. During heat treatment (usually at temperatures above 90 °C), decomposition and loss of antioxidant substances occur. The problem is also the introduction of these antioxidants into the food product. Usually, natural antioxidants are extracted with ethanol to obtain an extract, which is sparingly soluble in oil or fat. Evaporation of the extract produces a concentrate containing suspended particles insoluble in oils. When using water as an extractant, the problem of introducing the extract into oil or fat is even more acute. For effective oxidative stabilization, the antioxidant must be evenly distributed in the oil or fat, and the presence of moisture in the oil causes hydrolytic spoilage. For some technological processes (for example, transesterification), the presence of moisture or alcohol in the reactor is unacceptable, as this will lead to the loss of catalysts, the formation of by-products, and a low-quality final product [6].

Using natural antioxidants is more appropriate in emulsion products, in particular, creams, ointments, margarines, etc., under conditions of introduction and use at standard temperature. But to stabilize oils and fats that undergo heating and long-term storage, it is advisable to use synthetic antioxidants.

When used simultaneously, antioxidants can mutually enhance each other's effect, i. e. show a synergistic effect. Synergism is possible for inhibitors of different types (for example, one inhibitor reacts with peroxide radicals, breaking the chains, and the second decomposes the hydroperoxide formed), as well as for the same-type inhibitors. Technological processes that have special requirements for the oxidative stability of fats are the production of modified fats, incomplete acylglycerols, fat derivatives, etc. Also, an important application area of synthetic antioxidants is the production of deep-frying fat, which is used for heat treatment of products (the temperature can reach 190 °C). These processes are the field of application of synthetic antioxidants, where using antioxidant mixtures with the maximum antioxidant effect is relevant [7].

Thus, an urgent task is to develop and improve methods for increasing the stability of sunflower oil using effective antioxidant systems. Especially important is the oxidative stabilization of oil at elevated temperatures, which will ensure the preservation of oil quality during technological processes and storage.

2. Literature review and problem statement

There are various ways to increase the oxidative stability of sunflower oil, vegetable oils in general and oil-based products, using antioxidants of various nature.

In [8], lipid oxidation in sunflower oil triglycerides at 120 °C in the presence of gallic acid (GA), methyl gallate (MG), combinations of MG/HA (75:25, 50:50 and 25:75) and tert-butylhydroquinone (TBHQ) was investigated. Analysis of kinetic oxidation parameters based on hydroperoxide formation showed the highest effectiveness of TBHQ. The oxidation rate constant of the initial oil was 2.0346 mEq/kg min., oil with TBHQ addition – 0.0267 mEq/kg min. But no simultaneous effect of antioxidants on the oxidative stability of the oil is shown. Also, the gallic acid-based antioxidant, myristyl gallate, was studied in [9] for linseed oil. The shelf life of the oil was extended 4.83 times compared to the control sample at 25 °C. But there is no data on the effectiveness of this method at elevated temperatures.

The work [10] investigated the use of antioxidants D-alpha-tocopherol and ascorbyl palmitate in sunflower oil instead of tert-butylhydroquinone. Samples with 200 ppm ascorbyl palmitate and 100 ppm D-alpha-tocopherol have the highest stability by the Rancimat method. The effectiveness of these antioxidants was similar to that of tert-butylhydroquinone. But the antioxidants studied have a high cost. So, the cost of tert-butylhydroquinone is $ 20/kg, and ascorbyl palmitate – $ 525/kg.

The work [11] shows the effectiveness of using hydroxytyrosyl oleate for oxidative stabilization of olive oil. This substance demonstrates the ability to absorb free radicals, reduce Fe^{3+} and adsorb oxygen. The induction period of olive oil containing hydroxytyrosyloleate was 77.12 hours, which is 1.6, 8.7, 3.0 times more than that of hydroxytyrosol, vitamin E, butylhydroxytoluene, respectively. But there is no data on the effectiveness of this antioxidant at elevated temperatures and when mixed with other antioxidants. After all, antioxidants can exhibit synergistic properties.

In [3], the effect of synthetic antioxidants (0.15 wt %) on biodiesel fuel obtained by methanolysis of sunflower oil was studied. Poly (1,2-dihydro-2,2,4-trimethylquinoline) (Orox PK), tetrakis [methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)] methane (Anox 20) and tris (nonylphenyl) phosite (Naugard P), tert-butylhydroquinone, propyl gallate and pyrogallol were tested. Tert-butylhydroquinone, propyl gallate, and pyrogallol and their 2:1 mixtures with Orox PK provided an induction period of more than 8 h. This value corresponds to the standard value for biodiesel according to the European standard EN 14214. But there is no data on the effectiveness of these antioxidants for sunflower oil.

In [12], the influence of tert-butylhydroquinone on the properties of biodiesel fuel during oxidation was investigated. At an antioxidant dosage of 450 ppm, a standard fuel induction period (8 h) was observed. But the effect of this antioxidant in combination with other antioxidants and possible synergistic action have not been investigated.

The work [13] found the synergistic effect of butylhydroxyanisole (100 mg/kg) with butylhydroxytoluene, tert-butylhydroquinone and propyl gallate (100 mg/kg). In tests on pork fat, the mutual increase in antioxidant action was between 4.54 % and 18.03 %. But these patterns are not shown for liquid oils, which are less stable to oxidation.

The work [14] investigated the effectiveness of synthetic antioxidants (pyrogallol, propyl gallate, butylhydroxytoluene, tert-butylhydroquinone) in the amount of 204 ppm for oxidative stabilization of biodiesel fuel based on methyl esters of fatty acids. The best result was shown by pyrogallol. But the simultaneous action of antioxidants, the relationship between antioxidant ratios and the oxidative stability of the product is not shown.

Antioxidants of vegetable origin are also used for the oxidative stabilization of oils and fats. For example, in [15] the antioxidant effect of green tea extract (200, 400 and 800 ppm) and tert-butylhydroquinone (75 ppm) was compared in relation to sunflower oil at 25 °C and 60 °C. The antioxidants were similar in effectiveness. But the concentrations of green tea extract were much higher than that of tert-butylhydroquinone, and no effect of the extracts at higher temperatures was shown.

The work [16] compared the effectiveness of butylhydroxytoluene and rosemary essential oil for the antioxidative stabilization of sunflower oil. Butylhydroxytoluene proved to be more effective. The disadvantage of the work is the lack of data on using these antioxidants at elevated temperatures.

The work [9] compared the antioxidant activity of turmeric alcoholic extract and synthetic antioxidants butylhydroxylanisole, butylhydroxytoluene, propyl gallate in relation to biodiesel fuel. The antioxidants are identical in effectiveness and can increase the product stability by more than 4.5 times. But no simultaneous action of antioxidants and possible synergistic effect have been found.

The work [17] gives results on the oxidative stabilization of rapeseed oil using a mixture of tocopherols and synthetic antioxidants (butylhydroxyanisole, butylhydroxytoluene). Adding the antioxidant mixture made it possible to increase the oil induction period by 1.4 times. But it would also be appropriate to consider other synthetic antioxidants, in particular, tert-butylhydroquinone. The cost of tert-butylhydroquinone ($ 20 kg) is lower than that of tocopherols ($ 30/kg).

Thus, it is necessary to study the effect of antioxidant mixtures on the oxidative stability of sunflower oil and determine the possible synergistic action of antioxidants for maximum oil stabilization. Existing studies [3, 8–17] present various methods of oxidative stabilization of oils, fats and products based on them using antioxidants of various nature. But it remains an unresolved issue to determine the simultaneous effect of synthetic antioxidants on the oxidative stability of sunflower oil at elevated temperature and develop a rational composition of the antioxidant mixture.

3. The aim and objectives of the study

The aim of the study is to increase the oxidative stability of sunflower oil using mixtures of synthetic antioxidants: tert-butylhydroquinone, butylhydroxyanisole and butylhydroxytoluene. This will make it possible to increase the stability of sunflower oil during use and storage, and contribute to the rational use of oil, chemical reagents, catalysts, and consumables in various technological processes.

To achieve the aim, the following objectives were accomplished:

– to determine the influence of the ratio of synthetic antioxidants in the mixture on the induction period of sunflower oil and find the ratio under which the oxidative stability of the oil is maximum;

– to investigate the effect of adding citric acid and defoamer (polydimethylsiloxane) on the induction period of sunflower oil with the addition of the developed rational mixtures of antioxidants.

4. Materials and methods

4. 1. The object and hypothesis of the study

The object of the study is the process of sunflower oil oxidation under conditions of increased temperature. The main hypothesis of the study is that changing the ratio of synthetic antioxidants affects the synergistic effect of antioxidants. The study suggests that the simultaneous use of several antioxidants is more effective than each individual antioxidant. A simplification was adopted that the degree of purification of the initial sunflower oil does not affect the results of determining the effect of antioxidant ratios on the induction period of sunflower oil.

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

The following reagents and materials were used:

– refined deodorized frozen sunflower oil according to DSTU 4492 (CAS Number 8001-21-6);

– tert-butylhydroquinone, purity 99.0 % (CAS Number 1948-33-0);

– butylhydroxyanisole, purity 98.0 % (CAS Number 25013-16-5);

– butylhydroxytoluene, purity 99.0 % (CAS Number 128-37-0);

– citric acid, purity 99.5 % (CAS Number 5949-29-1);

– polydimethylsiloxane, purity 99.0 % (CAS Number 63148-62-9).

The equipment used in the study is the DSC differential scanning calorimetry device, model Q20 (USA).

4. 3. Method of studying the physico-chemical indicators of sunflower oil

The quality indicators of sunflower oil were investigated by standard methods for the analysis of oils and fats. The mass fraction of moisture and volatile substances was determined according to ISO 662:2016. The acid and peroxide values were tested according to international standards ISO 660:2020 and ISO 3960:2017, respectively. The content of triglyceride hydroperoxides in the oil was determined by the method of high-performance liquid chromatography (HPLC) according to AOCS Ce 5c-93.

4. 4. Method of determining the induction period of sunflower oil

The induction period of sunflower oil at a temperature of 110 °C in experiments according to the experimental plan was determined by the method of differential scanning calorimetry (DSC). Measurements were made under the ISO 11357-1:2016 standard. During the study, the difference in heat flows between the experimental and reference samples is measured. The time of the oxidation process, during which a sharp decrease in the difference in heat flows was recorded, characterizes the induction period. This value reflects oxidative stability and correlates with the shelf life of oils and fats. Induction periods were calculated using TA Universal Analysis software.

4. 5. Experiment planning and mathematical processing of results

To determine the rational composition of the mixture of synthetic antioxidants, a third-order Scheffe's simplex lattice design for a three-component mixture was chosen. Each experiment was repeated twice. Mathematical processing of the obtained results was performed using the Stat Soft Statistica v6.0 software package (USA). The selected methods make it possible to consider the simultaneous effect of antioxidants on the oxidative stability of the experimental oil and determine the rational ratios of antioxidants.

In the Stat Soft Statistica v6.0 package (USA), calculations were performed in the "3 Factor mixture design" module. The following tabs were used: Coeffs (calculated equation coefficients, standard error); "Observed, Predicted, and Residual Values" (estimated values of oil induction periods in each experiment); "ANOVA" (analysis of variance) [17].

5. Results of the study on increasing sunflower oil oxidative stability using mixtures of synthetic antioxidants

5. 1. Determining the effect of antioxidant ratios on the induction period of sunflower oil

Refined deodorized frozen sunflower oil according to DSTU 4492 (CAS Number 8001-21-6) was used. The determined quality indicators of the experimental sample of sunflower oil and standard values of quality indicators in accordance with DSTU 4492 are presented in Table 1.

So, the experimental sample of sunflower oil corresponds to DSTU 4492.

The effect of antioxidant ratios in the mixture (tert-butylhydroquinone, butylhydroxyanisole, butylhydroxytoluene) on the induction period of sunflower oil at a temperature of 110 °C was studied. The concentration of the antioxidant mixture in all experiments was 0.02 %. The initial oil induction period is 270.61 min. As factors of variation, the concentration of each of the antioxidants in the mixture was considered:

– x_1 – concentration of tert-butylhydroquinone: from 0 to 100 %;

– x_2 – concentration of butylhydroxyanisole: from 0 to 100 %;

– x_3 – concentration of butylhydroxytoluene: from 0 to 100 %.

Table 1

Physico-chemical indicators of sunflower oil

Indicator	Value	
	Studied oil	According to DSTU 4492
Mass fraction of moisture and volatile substances, %	0.02	0.10
Acid value, mg KOH/g	0.16	0.5
Peroxide value, ½ O mmol/kg	0.35	10.0

As a response function (y), the induction period of sunflower oil at a temperature of 110 °C, min. is accepted. The coefficients of the regression equation were calculated, and the significance of the coefficients was determined by the p-criterion (p>0.05), which reflects a 95 % confidence probability. The calculated value of the induction period in each experiment and the coefficient of determination (0.999) were determined. Table 2 shows the experiment planning matrix, experimental (y_e) and calculated (y_c) values of the oil induction period.

The dependence of the induction period of sunflower oil (y) on the concentration of each antioxidant in the mixture, in natural variables, is as follows:

$$y=3.160\cdot x_1+3.436\cdot x_2+3.081\cdot x_3+ +0.019\cdot x_1\cdot x_2+0.018\cdot x_1\cdot x_3+0.020\cdot x_2\cdot x_3. \quad (1)$$

A graphical dependence of the induction period of sunflower oil on the concentration of each antioxidant in the mixture was plotted (Fig. 1).

From equation (1), Table 2 and Fig. 1, it was found that butylhydroxyanisole is the most effective when using antioxidants individually. With the simultaneous use of antioxidants, their effectiveness in mixtures was in all cases higher than with the separate use of each of the antioxidants, i.e. a synergistic effect was found. The oxidative stability of sunflower oil is most effectively increased by the following antioxidant mixtures: tert-butylhydroquinone: butylhydroxyanisole: butylhydroxytoluene (16.67:66.67:16.67) %; tert-butylhydroquinone: butylhydroxyanisole: butylhydroxytoluene (33.33:33.33:33.33) %. The corresponding sunflower oil induction periods were 382.56 min. and 385.87 min. Thus, using these antioxidant mixtures is rational.

Table 2

Experiment planning matrix, experimental (y_e) and calculated (y_c) values of the response function

Experiment No.	Factors of variation			Induction period, min. (y_e)	Induction period, min. (y_c)
	Concentration of tert-butylhydroquinone, %	Concentration of butylhydroxyanisole, %	Concentration of butylhydroxytoluene, %		
1	100.00	0	0	316.12	315.98
2	0	100.00	0	343.34	343.58
3	0	0	100.00	308.25	308.09
4	50.00	50.00	0	376.31	376.93
5	50.00	0	50.00	356.37	356.59
6	0	50.00	50.00	375.64	376.24
7	66.67	16.67	16.67	365.68	365.63
8	16.67	66.67	16.67	382.56	381.37
9	16.67	16.67	66.67	362.76	362.77
10	33.33	33.33	33.33	385.87	385.71

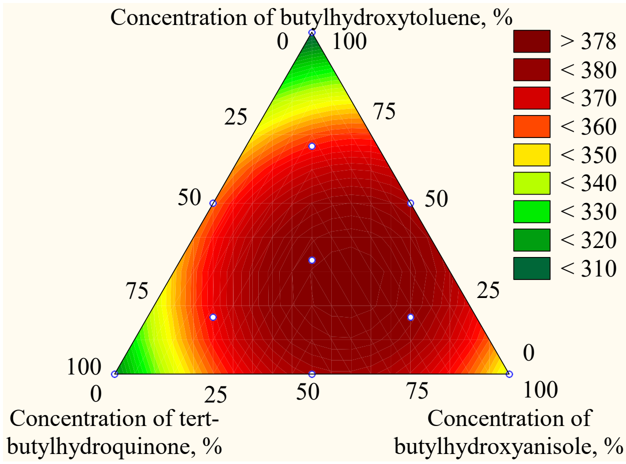


Fig. 1. Dependence of the induction period of sunflower oil on the concentration of components in the antioxidant mixture

The synergistic effect of the antioxidant mixture was confirmed by the study of the increase in the peroxide value of oil as a result of heating. Oil samples with the addition of butylhydroxyanisole and a mixture of tert-butylhydroquinone: butylhydroxyanisole: butylhydroxytoluene (33.33:33.33:33.33) % after exposure in an oven at 110 °C for 6 hours were studied. The content of triglyceride hydroperoxides in these aged samples was determined by the method of high-performance liquid chromatography. Table 3 shows the results of the study.

Table 3

Results of determining the peroxide value and hydroperoxides content in the oil after aging at 110 °C

Sample	Peroxide value, ½ O mmol/kg	Content of triglyceride hydroperoxides, %
Oil with the addition of butylhydroxyanisole	7.8	1.94
Oil with the addition of antioxidant mixture	5.1	0.88

Thus, the synergistic effect of antioxidants in the mixture was experimentally confirmed. The content of oxidation products in the case of using the antioxidant mixture turned out to be lower than when one, the most effective, antioxidant was added.

5. 2. Study of the influence of citric acid and defoamer (polydimethylsiloxane) on the induction period of sunflower oil

The effect of citric acid and defoamer (polydimethylsiloxane) on the induction period of sunflower oil with the addition of the developed rational mixtures of antioxidants at a temperature of 110 °C was investigated by the DSC method.

The induction period of the initial sunflower oil with the addition of different concentrations of citric acid and defoamer without adding antioxidants was previously investigated to determine the optimal concentration of these additives. The initial induction period of the oil without additives and antioxidants is 270.61 min. Table 4 shows the corresponding results of the study.

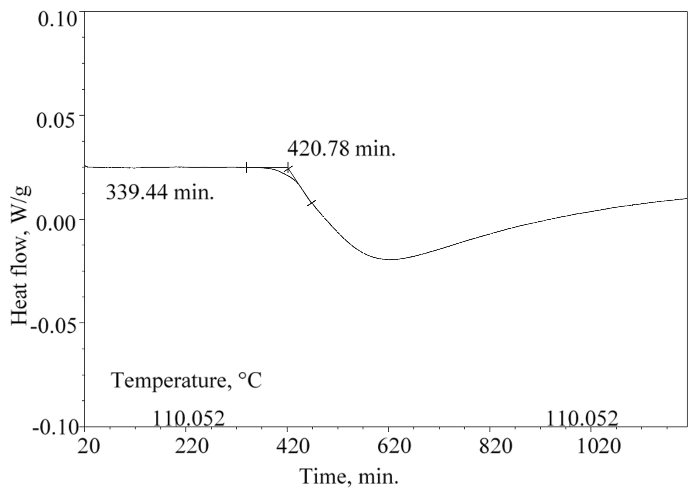
Table 4

Results of the study of the induction period of the initial sunflower oil with the addition of different concentrations of citric acid and defoamer

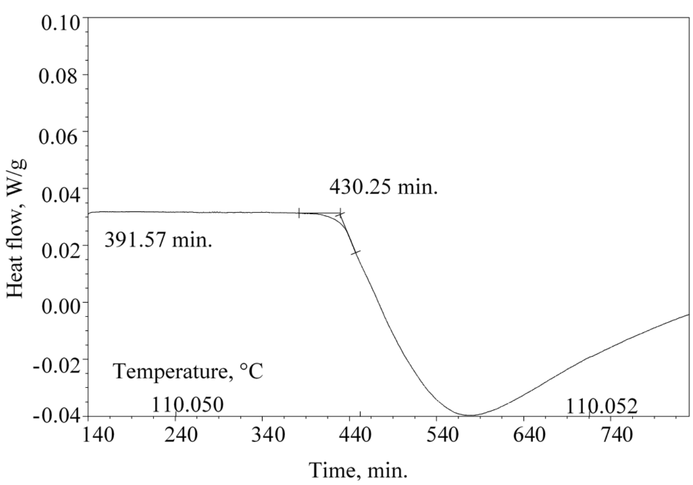
Additive	Concentration, %					
Citric acid	0.003	0.005	0.007	–	–	–
Defoamer	–	–	–	0.0002	0.0006	0.001
Oil induction period, min	274.46	279.15	280.23	277.56	278.92	280.59

The addition of citric acid in an amount greater than 0.005 % and defoamer in an amount greater than 0.0002 % practically does not increase the induction period. So, these amounts of the substances are optimal and applied to sunflower oil together with the developed rational mixtures of antioxidants.

The results of studying the induction period of oil with the developed antioxidant mixtures, with the addition of 0.005 % citric acid and 0.0002 % defoamer are presented in DSC-grams (Fig. 2).



a



b

Fig. 2. DSC-grams of the oxidation process of oil samples with the addition of citric acid, defoamer and developed antioxidant mixtures: *a* – tert-butylhydroquinone: butylhydroxyanisole: butylhydroxytoluene (16.67:66.67:16.67) %; *b* – tert-butylhydroquinone: butylhydroxyanisole: butylhydroxytoluene (33.33:33.33:33.33) %

Therefore, the corresponding induction periods were 420.78 min and 430.25 min. This indicates an additional increase in the oxidative stability of sunflower oil with the simultaneous addition of antioxidants, citric acid and defoamer.

6. Discussion of the results of increasing the oxidative stability of sunflower oil using antioxidants

The influence of mixtures of synthetic antioxidants on the oxidative stability of sunflower oil at a temperature of 110 °C was investigated. Based on equation (1), Table 2 and Fig. 1, rational ratios of antioxidants in the mixture were determined: tert-butylhydroquinone: butylhydroxyanisole: butylhydroxytoluene (16.67:66.67:16.67) %; tert-butylhydroquinone: butylhydroxyanisole: butylhydroxytoluene (33.33:33.33:33.33) %. The oil induction periods were 382.56 min. and 385.87 min., respectively. The initial oil induction period is 270.61 min. Therefore, when these antioxidant mixtures were added, the induction period of the oil increased by 1.41 and 1.43 times, respectively.

Oil oxidation occurs by a chain free radical mechanism. The antioxidants tert-butylhydroquinone, butylhydroxyanisole, butylhydroxytoluene react with peroxide radicals with chain breakage. This explains the inhibitory ability of the antioxidants used and the increased induction period of sunflower oil.

According to Table 2, the most effective antioxidant in individual form is butylhydroxyanisole. With the simultaneous use of antioxidants, a synergistic effect was revealed – mutual strengthening of the antioxidants action. Synergism was confirmed by studies of the increase in the peroxide value and the content of triglyceride hydroperoxides in the oil after exposure to 110 °C for 6 hours. In the oil sample with the addition of butylhydroxyanisole, the peroxide value was 7.8 ½ O mmol/kg, the content of hydroperoxides was 1.94 %. In the sample with adding the mixture of tert-butylhydroquinone: butylhydroxyanisole: butylhydroxytoluene (33.33:33.33:33.33) %, these indicators were 5.1 ½ O mmol/kg and 0.88 %, respectively.

The effect of citric acid (0.005 %) and defoamer (polydimethylsiloxane, 0.0002 %) on the induction period of sunflower oil with the addition of the developed rational mixtures of antioxidants was determined. The corresponding oil induction periods with the addition of these components simultaneously with antioxidants were 420.78 min. and 430.25 min. This effect is due to the fact that citric acid binds metals present in the oil. Metals are oxidation catalysts. Polydimethylsiloxane increases the smoke formation temperature of oil, slows down polymerization processes, performs a barrier function, protecting the oil surface from air exposure. This protective effect is explained by the presence of a monomolecular layer of polydimethylsiloxane on the oil surface in contact with air, which slows down oxidative polymerization. This leads to an increase in the oil induction period.

The obtained results regarding the rational composition of mixtures of synthetic antioxidants make it possible to effectively increase the oxidative stability of sunflower oil at elevated temperatures. In particular, this is important in the transesterification process, which is used to obtain biodiesel fuel based on methyl esters of fatty acids. Using oil with increased oxidation rates causes loss of oil, reagents, materials, as well as deterioration of product quality.

The works [3, 8–17] present the results of research on increasing the oxidative stability of oils and fats using antioxidants of various nature. The work [16] compared the effectiveness of butylhydroxytoluene and rosemary essential oil for the antioxidative stabilization of sunflower oil. The greater effectiveness of butylhydroxytoluene has been experimentally confirmed. In [13], the synergistic effect of butylhydroxyanisole (100 mg/kg) with butylhydroxytoluene, tert-butylhydroquinone and propyl gallate (100 mg/kg) was determined in tests on pork fat. However, it remains an unresolved issue to determine the simultaneous action of effective synthetic antioxidants on the oxidative stability of sunflower oil at elevated temperatures. Sunflower oil is a common type of vegetable oil, and there is a large amount of scientific research on it. But it is advisable to determine conditions for maximum oxidative stabilization of the oil. In particular, by determining the dependence of the oil induction period on antioxidant ratios, experimental confirmation of the synergistic effect of antioxidants. This issue is solved in the work.

The limitation of using the results of the work is the temperature of the study. At higher temperatures, the effectiveness of antioxidants can be reduced, it is necessary to introduce more antioxidants or vary the ratios and develop other mixtures.

The disadvantage of the work is the study of the effects of citric acid and defoamer only for oil with the addition of rational mixtures of antioxidants. It would also be useful to investigate the effect of these components on the original oil and oil with other antioxidant addition options.

A promising area of work is to study a wider list of antioxidants at higher temperatures. This will expand the possibilities of using sunflower oil for various industrial purposes.

7. Conclusions

1. The effect of antioxidant ratios in the mixture on the induction period of sunflower oil was determined. Rational ratios of antioxidants, under which the oxidative stability of the oil is maximum, are as follows: tert-butylhydroquinone: butylhydroxyanisole: butylhydroxyt-oluene (16.67:66.67:16.67) %; tert-butylhydroquinone: butylhydroxyanisole: butylhydroxytoluene (33.33:33.33:33.33) %. The corresponding oil induction periods were 382.56 min. and 385.87 min. The initial oil induction period is 270.61 min. The addition of the developed antioxidant mixtures increased the induction period of sunflower oil by 1.41 and 1.43 times, respectively. The antioxidants in the mixture show a synergistic effect, which is confirmed by studies of the increase in the peroxide value and the content of triglyceride hydroperoxides in the oil after exposure to 110 °C for 6 hours. In the oil sample with the addition of butylhydroxyanisole, the peroxide value was 7.8 ½ O mmol/kg, the content of hydroperoxides was 1.94 **%**. In the sample with adding the mixture of tert-butylhydroquinone: butylhydroxyanisole: butylhydroxytoluene (33.33:33.33:33.33)%, these indicators were 5.1 ½ O mmol/kg and 0.88 **%**, respectively.

2. The effect of adding citric acid and defoamer (polydimethylsiloxane) on the induction period of sunflower oil with the addition of the developed rational mixtures of

antioxidants was investigated. The optimal concentrations of citric acid (0.005 %) and defoamer (0.0002 %) were determined experimentally. The corresponding oil induction periods were 420.78 min and 430.25 min, indicating the effectiveness of simultaneously using mixtures of antioxidants, citric acid and polydimethylsiloxane.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this study, whether financial, personal, authorship, or otherwise, that could affect the study and its results presented in this paper.

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Data availability

The manuscript has no associated data.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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