The object of the research is the process of oxidation of linseed oil at elevated temperature. Linseed oil is a valuable raw material for the chemical, food, cosmetic and other industries. The use of linseed oil is complicated by intensive oxidation processes associated with a high content of unsaturated fatty acids. Therefore, an important task is to develop and improve methods of oxidative stabilization of linseed oil.

The oxidation process of unrefined linseed oil (CAS Number 8001-26-1) at a temperature of 110 °C in its original form and with the addition of antioxidants was studied. The effect of antioxidant concentrations (tocopherol, butylhydroxyanisole and butylhydroxytoluene) in the mixture on the induction period of linseed oil was found. The induction period was determined by differential scanning calorimetry. The total concentration of the mixture of antioxidants in each experiment was 0.02 %. The induction period of the initial oil was 155.31 min. Rational ratios of antioxidants in the mixture were found: tocopherol: butylhydroxyanisole (50:50) %; tocopherol: butylhydroxytoluene (50:50) %; tocopherol: butylhydroxyanisole: butylhydroxytoluene (33.33:33.33:33.33) %; at the same time, the oil induction periods are 295.7 min., 290.1 min. and 290.2 min., respectively.

The quality indicators of the initial linseed oil and with the addition of the determined rational ratios of antioxidants after 2 hours of aging at a temperature of 110 °C were determined. The peroxide values of the samples were 8.5, 3.2, 3.6, 3.7 1/2 0 mmol/kg, respectively. The research results make it possible to introduce antioxidants in the production of linseed oil in rational concentrations. This will help increase the production of linseed oil resistant to oxidation at elevated temperatures, which will provide various industries with high-quality raw materials.

Keywords: linseed oil, free-radical process, oxidative stability, induction period, oxidation inhibitor
The peculiarity of the linseed oil composition is the high content of polyunsaturated fatty acids – (65.5–71.1) %. For sunflower oil, this indicator is (54.8–58.1) % [8]. This causes low oxidative stability and limits the use of linseed oil during heat treatment. In some cases, particularly, in the production of paint and varnish coatings, the increased ability of linseed oil to oxidize and polymerize is important [9, 10]. But for many directions, the appropriate quality of oil without oxidative degradation products is necessary, since oil acts as a reagent for obtaining products of a given composition [11, 12].

2. Literature review and problem statement

There are various ways to increase the oxidative stability of linseed oil, which involve the use of various antioxidants, as well as special conditions of storage and use of the oil. Thus, in [18], an oxygen-absorbing film based on the catalytic system with palladium was used to prevent the oxidation of lipids in linseed oil. Linseed oil was packaged in the normal or modified (with 2 % oxygen by volume) atmosphere with or without the catalytic system and stored at 45 °C for 6 months. During storage, peroxide and anisidine values were determined. The use of such a system significantly reduced lipid oxidation in linseed oil. However, there are no data on the effect of temperatures above 45 °C on oil storage under these conditions.

The method of oxidative stabilization of linseed oil is the use of antioxidants from vegetable raw materials. The authors [19] showed an increase in the oxidative stability of linseed oil using rice protein hydrolyzate obtained by the alcalase method. This was revealed by the reduction of the peroxide value by (95–96) %. The disadvantage is the complexity of the technology and protein instability at elevated temperatures. This was revealed by the reduction of linseed oil and use of the oil significantly intensifies the processes of oxidative deterioration.

3. The aim and objectives of the study

The aim of the study is to determine the rational concentrations of antioxidants (tocopherol, butylhydroxyanisole and butylhydroxytoluene) in the mixture for oxidative stabilization of linseed oil. This will make it possible to obtain linseed oil with increased oxidative stability for various industries, as well as predict the induction period of linseed oil depending on the concentration of introduced antioxidants.

To achieve the aim, the following objectives were accomplished:

- to find the dependence of the induction period of linseed oil on the concentration of antioxidants in the mixture and determine the ratio of antioxidants under which the oxidative stability of the oil is maximum;
- to determine the effect of antioxidant mixtures in rational ratios on the quality indicators of linseed oil at elevated temperature.

4. Materials and methods of research

4.1. The object and hypothesis of the research

The object of the research is the process of linseed oil oxidation at elevated temperature. The main hypothesis of...
the research is that the concentrations of individual antioxidants affect the oxidative stability of linseed oil. The study suggests that the combined use of antioxidants has the greatest effect on increasing the induction period of linseed oil. A simplification is adopted that the initial physicochemical parameters of the oil do not affect the dependence of the oil induction period on the concentration of antioxidants. Standard research methods were applied.

4.2. Examined materials and equipment used in the experiment

The following reagents and materials were used (CAS Number is a unique numerical identifier assigned to chemicals for a consistent method of identification by the Chemical Abstracts Service):
- unrefined linseed oil (CAS Number 8001-26-1);
- butylhydroxyanisole, purity 98.0 % (CAS Number 25013-16-5);
- butylhydroxytoluene, purity 99.0 % (CAS Number 128-37-0);
- α-tocopherol (CAS Number 1406-18-4).

The equipment used in the work is a differential scanning calorimeter (model Q20).

4.3. Methods of studying the quality indicators of linseed oil

Physicochemical indicators were determined using generally accepted methods presented in international documentation on the analysis of oils and fats. The mass fraction of moisture and volatile substances is determined by the standard method intended for animal or vegetable fats and oils according to ISO 662:2016. Method A is used, which is applied for liquid and solid fats and oils (with different acid values). Acid value and peroxide value are determined according to the international standards ISO 660:2020 and ISO 3960:2017, respectively.

4.4. Methods of determining the induction period of linseed oil

The induction period of linseed oil was investigated by differential scanning calorimetry (DSC) in the isothermal mode at a temperature of 110 °C in accordance with ISO 11357-1:2016. Research by the DSC method is carried out using a differential scanning calorimeter. The device has two measuring cells: one is intended for the test sample, in the other (comparison cell) an empty crucible is placed. The dependence of the heat flow difference between these two cells on time is measured. During the course of heat release or absorption processes (chemical reactions, phase transitions, etc.) in the sample, deviations from the monotonic change of the signal dependence on time (anomalies) are observed on the DSC curves. Thus, the oxidation process is characterized by a slow, and then a sharp decrease in the difference in the heat fluxes of the cells over time. The time of a sharp decrease in the signal value is determined. This is the time during which the slow phase of the chemical oxidation reaction (induction period) took place. The DSC method is a reliable and efficient method for measuring the degree of oxidation of oils and fats.

4.5. Planning of experimental studies and processing of the data obtained

Scheffe’s three-factor simplex lattice design was used to plan research and calculate mathematical dependence. Data processing was performed in the environment of the Stat Soft Statistica v.6.0 package (USA). Each experiment was repeated twice. Scheffe’s simplex lattice designs provide a graphical visualization of the results in the form of “composition-property” diagrams, which allow you to efficiently determine the rational concentrations of the three components and analyze the simultaneous effect of the components on the response function. Thus, the use of Scheffe’s design meets the objectives of the study. In the Statistica package, calculations were made using the “3 Factor mixture design” module, which uses the following tabs:
- “Coefs” (calculation of equation coefficients, standard error, 95 % confidence interval);
- “Observed, Predicted, and Residual Values” (determination of estimated values of the response function);
- “ANOVA” (analysis of variance).

5. Results of determining rational concentrations of antioxidants for oxidative stabilization of linseed oil

5.1. Determining the dependence of the induction period of linseed oil on the concentration of antioxidants in the mixture

Unrefined linseed oil was used in the study. The determined quality indicators of the oil are presented in Table 1.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass fraction of moisture and volatile substances, %</td>
<td>0.2</td>
</tr>
<tr>
<td>Acid value, mg KOH/g</td>
<td>1.6</td>
</tr>
<tr>
<td>Peroxide value, % O mmol/kg</td>
<td>2.3</td>
</tr>
</tbody>
</table>

According to the international standard for vegetable oils (CODEX STAN 210-1999), oils must have a mass fraction of moisture and volatile substances of no more than 0.2 %, acid value of no more than 4.0 mg KOH/g, peroxide value of no more than 10.0 % O mmol/kg. Therefore, the indicators of linseed oil correspond to the standard values.

The influence of antioxidant concentrations in the mixture on the induction period of linseed oil at a temperature of 110 °C was determined. The induction period is a slow phase of the chemical oxidation reaction, after which a rapid chain process begins. This parameter characterizes resistance to oxidation and reflects the shelf life of oils and fats. The induction period of the initial oil was 155.31 min. The following factors were studied:
- \( x_1 \) – concentration of tocopherol: (0–100) %;
- \( x_2 \) – concentration of butylhydroxyanisole: (0–100) %;
- \( x_3 \) – concentration of butylhydroxytoluene: (0–100) %.

The total concentration of the antioxidant mixture in each experiment was 0.02 % by mass of oil. The response function (\( g \)) is the induction period of linseed oil, determined in the isothermal mode at a temperature of 110 °C by the DSC method, min. In the package Stat Soft Statistica v.6.0 (USA), the coefficients of the regression equation, the significance of the coefficients according to the \( p \)-criterion (\( p>0.05 \), which represents a 95 % confidence probability, are determined. The estimated values of the induction period in each experiment and the coefficient of determination (0.986) were determined. Table 2 shows the experimen-
The method of increasing the oxidative stability of linseed oil at elevated temperature using synthetic antioxidants was investigated. According to equation (1), Table 2 and Fig. 1, rational ratios of antioxidants were determined: tocopherol: butylhydroxyanisole (50:50)%; tocopherol: butylhydroxytoluene (50:50)%; tocopherol: butylhydroxyanisole: butylhydroxytoluene (33:33:33:33:33)%. The obtained data are shown in Table 3.

Therefore, the peroxide values of oil samples aged with mixtures of antioxidants are significantly lower than those of the initial sample (without antioxidants). The acid values of samples with antioxidants are also lower. The presence of the developed rational mixtures of antioxidants significantly reduces the rate of oxidative deterioration in linseed oil at elevated temperatures.
The peroxide values of oil samples stored with antioxidant mixtures were, respectively, 2.65, 2.36, 2.30 times lower than the peroxide value of the sample without antioxidants (Table 3). This is due to the action of oxidation inhibitors, which cause chain breakage in reactions with peroxide radicals.

The obtained results make it possible to produce linseed oil with increased stability at elevated temperatures and to predict the effect of antioxidants in different concentrations on the induction period of the oil. The results can be used in the production of linseed oil for various industries: chemical, food, pharmaceutical, cosmetic, etc. For example, in the production of cosmetic creams enriched with polyunsaturated fatty acids, it is advisable to use linseed oil. The use of the determined rational concentrations of antioxidants will help to increase the shelf life of the finished product – cream. This will also make it possible to significantly reduce the rate of formation of toxic oxidation products even in the case of elevated temperatures in production (for example, during the dissolution or melting of individual components of the cream).

The works [8, 18–23] present data on various methods of oxidative stabilization of linseed oil using special storage films that absorb oxygen, as well as various types of antioxidants. Thus, the authors [22] showed the effectiveness of ascorbic acid esters. According to [23], oxidative stabilization of linseed oil using tert-butylhydroquinone and butylhydroxytoluene with the addition of garlic extract is appropriate. The main method of increasing the oxidative stability of linseed oil is the addition of various types of antioxidants, which was used in this work. But there is not enough data on the influence of antioxidant concentrations on the oxidative stability (induction period and physicochemical indicators) of linseed oil at elevated temperatures. This task is solved in the work.

The dependence of the induction period of linseed oil on the antioxidant concentrations in the mixture was determined. The greatest increase in the induction period of linseed oil was demonstrated by tocopherol, the least by butylhydroxyanisole. With the simultaneous use of two or three antioxidants, a phenomenon of synergism is observed – mutual strengthening of the antioxidants action. Rational ratios of antioxidants are as follows: tocopherol: butylhydroxyanisole (50:50) %; tocopherol: butylhydroxytoluene (50:50) %; tocopherol: butylhydroxyanisole: butylhydroxytoluene (33.33:33.33:33.33) %. The addition of antioxidants made it possible to increase the oil induction period by 1.9, 1.86, 1.87 times, respectively.

The effect of mixtures of antioxidants in rational proportions on the quality indicators of linseed oil after exposure at a temperature of 110 °C for 2 hours was studied. The peroxide values of oil samples stored with antioxidant mixtures were, respectively, 2.65, 2.36, 2.30 times lower than the peroxide value of the sample without antioxidants (Table 3). This is due to the action of oxidation inhibitors, which cause chain breakage in reactions with peroxide radicals.

According to Table 2, the greatest increase in the induction period of linseed oil was demonstrated by tocopherol, the least by butylhydroxyanisole. With the simultaneous use of two or three antioxidants, a phenomenon of synergism is observed – mutual strengthening of the antioxidants action. Rational ratios of antioxidants are as follows: tocopherol: butylhydroxyanisole (50:50) %; tocopherol: butylhydroxytoluene (50:50) %; tocopherol: butylhydroxyanisole: butylhydroxytoluene (33.33:33.33:33.33) %. The addition of antioxidants made it possible to increase the oil induction period by 1.9, 1.86, 1.87 times, respectively.

7. Conclusions

1. The dependence of the induction period of linseed oil on the antioxidant concentrations in the mixture was determined. The greatest increase in the induction period of linseed oil was demonstrated by tocopherol, the least by butylhydroxyanisole. With the simultaneous use of two or three antioxidants, a phenomenon of synergism is observed – mutual strengthening of the action of antioxidants. Rational ratios of antioxidants were determined: tocopherol: butylhydroxyanisole (50:50) %; tocopherol: butylhydroxytoluene (33.33:33.33:33.33) %. At the same time, the induction periods of linseed oil at a temperature of 110 °C were 293.61 min., 288.82 min. and 291.19 min., respectively. The induction period of the initial linseed oil was 155.31 min. Therefore, the addition of antioxidants made it possible to increase the oil induction period by 1.9, 1.86, 1.87 times, respectively.

2. The quality indicators of linseed oil with the addition of rational ratios of antioxidants after 2 hours of aging at a temperature of 110 °C were determined. The peroxide values of the samples were 8.5, 3.2, 3.6, 3.7 ½ O mmol/kg, respectively. Therefore, the peroxide values of oil samples that were aged with mixtures of antioxidants were, respectively, 2.65, 2.36, 2.30 times lower than the peroxide value of the sample without antioxidants.

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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The study was conducted without financial support.

Data availability

The manuscript has no associated data.
References