The object of the research is the oxidation process of rapeseed oil. Rapeseed oil is used for technical purposes, in the chemical and food industries, in particular, in the production of ecological fuel. Vegetable oils are subjected to oxidative deterioration processes, which are intensified under the conditions of access to oxygen, elevated temperatures, etc. Oxidation products worsen the technological properties and complicate the use of oils in chemical reactions. An important task is to improve the technology of oxidative stabilization of rapeseed oil, which is of great industrial importance.

The oxidation process of refined deodorized rapeseed oil according to DSTU 8175 (CAS Number 120962-03-0) at a temperature of 110 °C was studied by the method of differential scanning calorimetry. The influence of different ratios of antioxidants (tocopherol, butylhydroxyanisole and butylhydroxytoluene) in the mixture on the oil induction period was determined. The total concentration of the antioxidant mixture in each experiment was 0.02%. The induction period of the initial oil is 408.48 min. The ratio of the components of the antioxidant mixture were determined: tocopherol: butylhydroxyanisole (73:23) %; tocopherol: butylhydroxyanisole: butylhydroxytoluene (66.67:16.67:16.67) %. The corresponding oil induction periods were 579.75 min. and 561.55 min.

The physico-chemical indicators of rapeseed oil after 12 months of storage at a temperature of (20 ± 2) °C in its original form and with the addition of the developed antioxidant mixtures were determined. The peroxide value of the oil was 12.5, 4.39, 6.45 ½ O mmol/kg, respectively.

The research results allow improving the technology of oxidative stabilization of rapeseed oil at elevated and standard temperatures. This will help to extend the oil shelf life, more efficiently and rationally use the oil in various areas.

Keywords: rapeseed oil, free radical oxidation process, induction period, oxidative stabilization technology

1. Introduction

Rapeseed oil is widely used in the chemical, food, paint, and cosmetic industries, metallurgy, and biofuel production. The use of biofuel reduces the release of harmful substances in exhaust gases by (25–50) % [1].

Rapeseed oil contains the following triglycerides: tri-saturated (0.4 %), disaturated (3.4 %), monosaturat-
ed (20.2 %), triunsaturated (75.9 %). Fatty acids important for oxidative stability (linoleic, linolenic) are located mainly in position 2 of triglycerides. This determines a higher stability of rapeseed oil compared to other vegetable oils [2]. Oxidation products worsen the technological properties of oils, increase oil losses, consumption of catalysts and reagents during production processes, etc. [3]. Thus, during the production of biodiesel fuel, the transesterification reaction is used. The oil peroxide value of 1.0 % Ìmol/kg causes deactivation of the sodium methoxide catalyst in the amount of 0.054 kg/t of oil [4]. Oxidation processes in the obtained fuel lead to negative changes: increase in viscosity, deterioration of lubricating properties, etc. [5].

Oxidation of oil glycerides occurs by a radical-chain mechanism with the formation of unstable peroxy radicals, which quickly transform into more stable peroxide compounds. Oxidative processes are influenced by the fatty acid composition of triglycerides, the content of natural antioxidants and related substances, temperature, radiation, access to air oxygen, and antioxidants adding [6]. Tocopherols, ascobic acid, propyl gallate, phenolic compounds (butylhydroxyanisole, butylhydroxytoluene, tert-butylhydroquinone), etc. are used as antioxidants. Phenolic antioxidants are used at elevated temperatures. Propyl gallate loses its effectiveness at a melting point of 148 °C [7]. The most effective are butylhydroxyanisole and butylhydroxytoluene, which are well soluble in oils and fats and are effective at elevated temperatures.

Therefore, an urgent task is to improve the technology of increasing the oxidative stability of rapeseed oil, which is a valuable component in the production of various types of products. At the same time, the oxidative stabilization of the oil is important both at elevated temperatures and under standard storage conditions.

2. Literature review and problem statement

Various methods of oxidative stabilization of rapeseed oil and products based on it are known, as well as methods for studying the antioxidants effectiveness.

The effect of high frying temperatures (140, 160, 180 °C) on the effectiveness of antioxidants (tocopherols, phenolic compounds, canolol, and phytosterols) in rapeseed oil was investigated in [8]. But the effect of antioxidant concentrations on oil stability is not shown.

The authors [9] investigated the influence of 2,4,6-tris-isopropylbenzoic acid hydrazide, benzoic acid hydrazide, 2,2'-methylenbis(6-tert-butyl-4-methyl-phenol) increased the ether induction period from 3.7 h to 21.2 h in the Rancimat test. The disadvantage of the study is the lack of data on the effect of antioxidants on the stability of the oil during long-term storage.

In [10], the effect of adding marjoram essential oil and butylhydroxyanisole on the inhibition of rapeseed oil oxidation at 40 °C was analyzed. However, the effect of antioxidant concentrations on oil oxidation parameters is not shown.

The authors [11] investigated the antioxidant effect of octyl esters of sinapic, ferulic and caffeic acids on the stability of rapeseed oil in the concentration range from 0.005 to 0.9 %. Enriched rapeseed oils showed an increase in the induction period (up to 12.5 h) compared to the original oil (3.9 h). But the simultaneous action of antioxidants is not shown.

In [12], the effect of vinyl derivatives of ferulic and sinapic acids on the content of terpenoids (sterols, tocols, carotenoids, squalene) at the end of the induction period during the accelerated oxidation of rapeseed and linseed oils was investigated. The use of 4-vinylsyringol or 4-vinylguayacol increased the content of sterols and carotenoids (2 times) and squalene (4 times). The obtained data will help to increase the stability of oils, but the influence of the investigated compounds on changes in the physicochemical parameters of oils during storage is not shown.

The work [13] shows the influence of phenolic compounds (phenylacetic and ferulic) acids on the delay in the oxidation of rapeseed oil. The optimal concentration of antioxidants was 1.04 %. The disadvantage of the work is the lack of results regarding the effects of antioxidants during long-term oil storage.

Antioxidants of plant origin are also used. The work [15] investigated the antioxidant properties of grape tea extracts (Ampelopsis grossedentata) and the inhibition of rapeseed oil oxidation. But no correlation was shown between the concentration of antioxidants, the induction period and oxidation indicators of oil. The paper [16] presents data on the influence of polyphenolic extracts and fractions of Canadian mountain ash (Sorbus aucuparia) on the oxidation of rapeseed oil. At the end of 7-day storage, the peroxide value of the oil was reduced to 42 % in the presence of the extracts. But there is no data on the influence of antioxidant concentrations on oil oxidation indicators.

In [17], the effect of adding marjoram essential oil and butylhydroxyanisole on the inhibition of rapeseed oil oxidation at 40 °C was analyzed. However, the effect of antioxidant concentrations on oil oxidation parameters is not shown.

The authors [18] presented data on the influence of high-oleic rapeseed oil production methods on the content of endogenous antioxidants in the oil and its stability. The method involving microwave pretreatment and hexane extraction resulted in the highest levels of tocopherols (688.4 mg/kg), polyphenols (1007.76 mg/kg), and phytosterols (1810.6 mg/kg). But there is no data on the effect of these antioxidants on the stability of the oil during storage.

The work [19] investigated the interaction of canolol and α-tocopherol with reverse micelles obtained from phospholipid (1,2-disoleyl-sn-glycero-3-phosphocholine) in rapeseed oil. Canolol can enter the structure of phospholipid reverse micelles and accumulate in oil at the oil/water interface, which is important for emulsion products. But there is no data on the effectiveness of the method at elevated temperatures.

In [20], the oxidation kinetics of olive, rapeseed, and rice bran oils in the presence of γ-orzanol at 60 °C were investigated. The inhibitory mechanism of γ-orzanol attacks unstable hydroperoxides, causing the formation of water and reverse micelles. The maximum increase in the critical concentration of micelles was observed in rapeseed oil (by 34.4 %). But the effect of the antioxidant on the oxidation indicators of the oils is not shown.
The work [21] investigated the effectiveness of using tocopherol, butylhydroxyanisole, and butylhydroxytoluene for the oxidative stabilization of linseed oil. Linseed oil is one of the least stable oils due to the high content of unsaturated fatty acids. The use of the mixture of antioxidants made it possible to increase the oil induction period from 153.31 min. to 295.7 min. at a temperature of 110 °C. But there is no data on the effectiveness of antioxidants at standard temperature during long-term storage.

Thus, it is necessary to determine the effect of antioxidant concentrations on the oxidative stability of rapeseed oil. The existing studies [8–21] provide various methods of increasing the oxidative stability of rapeseed oil and products based on it. But the research of simultaneous action and rational ratios of antioxidants for effective oxidative stabilization of rapeseed oil at elevated temperatures and standard storage temperature remains an unsolved issue. Therefore, an urgent task is to improve the technology of oxidative stabilization of rapeseed oil by developing a rational composition of an antioxidant mixture.

3. The aim and objectives of the study

The aim of the study is to improve the technology of oxidative stabilization of rapeseed oil using a mixture of antioxidants (tocopherol, butylhydroxyanisole and butylhydroxytoluene). This will make it possible to increase the stability of rapeseed oil at standard and elevated temperatures, which will contribute to more efficient use of oil in various industries and the production of higher quality products.

To achieve the aim, the following objectives were accomplished:

- to find the dependence of the induction period of rapeseed oil on various ratios of the components of the antioxidant mixture and determine the ratios at which the maximum oxidative stabilization of rapeseed oil is achieved;
- to investigate the influence of antioxidant mixtures with rational ratios of components on the physical and chemical indicators of rapeseed oil under standard storage conditions.

4. Materials and methods of research

4.1. The object and hypothesis of the research

The object of the research is the process of rapeseed oil oxidation at elevated and standard temperatures. The main hypothesis of the research is that different ratios of antioxidants in the mixture affect the oxidation processes in rapeseed oil. The study suggested that the simultaneous use of several antioxidants in the mixture is more effective than the use of each antioxidant separately. It is a simplification that the initial indicators of rapeseed oil oxidation do not affect the results of the study of the oil induction period at different antioxidant ratios.

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 Reference Service for Chemical Substances):

- refined deodorized rapeseed oil according to DSTU 8175 (CAS Number 120962-03-0);
- butylhydroxyanisole, purity 98.0 % (CAS Number 25013-16-5);
- butylhydroxytoluene, purity 99.0 % (CAS Number 128-37-0);
- tocopherol (CAS Number 1406-18-4).

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

4.3. Method of studying the quality indicators of rapeseed oil

The physico-chemical indicators of rapeseed oil are determined according to the following standard methods of analysis of oils and fats.

The mass fraction of moisture and volatile substances is determined according to ISO 662:2016. Method A is applied, which is used for liquid and solid fats and oils (with different acid values). About 20 g of the sample is weighed in a porcelain or glass cup pre-weighed together with a thermometer. The cup with the sample is heated, adjusting the temperature increase to 90 °C at a rate of 10 °C/min. The heating rate is reduced, observing the rate of bubble formation at the bottom of the cup, and the temperature is raised to (103±2) °C (not higher than 105 °C). Stirring is continued until the release of bubbles stops. Heating to (103±2) °C is repeated several times, cooling after each heating to 95 °C. The cup with the thermometer is left in the desiccator to cool the sample to room temperature and weigh. This operation is repeated until the difference between the results of two consecutive weighings does not exceed 2 mg.

The acid and peroxide values are determined according to the international standards ISO 660:2020 and ISO 3960:2017, respectively.

4.4. Method of determining the induction period of rapeseed oil

To determine the induction period of rapeseed oil, the method of differential scanning calorimetry (DSC) according to ISO 11357-1:2016 at a temperature of 110 °C was used. The DSC method is based on measuring the difference in heat fluxes coming from the test sample and the control sample for comparison. During the course of processes related to the release or absorption of heat (chemical reactions, phase transitions, etc.) in the sample, deviations from the monotonic dependence of the signal on time are observed on the DSC curves. The oxidation process is characterized by a slow and then sharp decrease in the difference in heat fluxes over time. This allows the induction period to be measured. The DSC method is a reliable and operational method for measuring the degree of oxidation of oils and fats.

4.5. Planning of experimental studies and processing of data obtained

Scheffe's three-factor simplex lattice design was used. Data processing was performed in the Stat Soft Statistica v6.0 package environment (USA). Each experiment was repeated twice. Scheffe's simplex lattice designs provide a graphical visualization of results in the form of “composition – property” diagrams, which allow you to analyze the simultaneous influence of 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. The following tabs are used: Coeffs (calculation of equation coefficients, standard error, 95% confidence interval); “Observed, Predicted, and Residual Values” (determination of calculated values of the response function); “ANOVA” (analysis of variance).

5. Results of determining rational antioxidant ratios for oxidative stabilization of rapeseed oil

5.1. Determination of the dependence of the induction period of rapeseed oil on the ratio of the antioxidant mixture components

Refined deodorized rapeseed oil according to DSTU 8175 (CAS Number 120962-03-0) was used. The obtained physico-chemical indicators of the experimental oil and the limit values of the corresponding indicators according to DSTU 8175 are given in Table 1.

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>0.05 0.15</td>
</tr>
<tr>
<td>Acid value, mg KOH/g</td>
<td>0.12 0.4</td>
</tr>
<tr>
<td>Peroxide value, % O mmol/kg</td>
<td>0.95 10.0</td>
</tr>
</tbody>
</table>

Thus, the experimental sample of oil meets the requirements of DSTU 8175.

The influence of the ratios of the antioxidant mixture components (tocopherol, butylhydroxyanisole and butylhydroxytoluene) on the induction period of rapeseed oil at a temperature of 110 °C was determined. The total concentration of the antioxidant mixture in each experiment was 0.02 %. The induction period characterizes resistance to oxidation and correlates with the shelf life of oils and fats. The initial oil induction period was 408.48 min. The concentrations of the components in the antioxidant mixture were studied as factors of variation:

\[ y = 5.902x_1 + 5.647x_2 + 4.86x_3 - 0.003x_1x_2 - 0.003x_1x_3 - 0.006x_2x_3. \] (1)

The graphical dependence of the induction period of rapeseed oil on the concentrations of antioxidants in the mixture is presented in Fig. 1.

![Fig. 1. Dependence of the induction period of rapeseed oil on the concentration of components in the antioxidant mixture](image)

Table 2

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Factors of variation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration of tocopherol, %</td>
</tr>
<tr>
<td>1</td>
<td>100.00</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>50.00</td>
</tr>
<tr>
<td>5</td>
<td>50.00</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>66.67</td>
</tr>
<tr>
<td>8</td>
<td>16.67</td>
</tr>
<tr>
<td>9</td>
<td>16.67</td>
</tr>
<tr>
<td>10</td>
<td>33.33</td>
</tr>
</tbody>
</table>
Analyzing equation (1), Table 2 and Fig. 1, tocopherol and butylhydroxyanisole have been found to be the most effective antioxidants for rapeseed oil. Pure tocopherol showed the greatest antioxidant effect. But butylhydroxyanisole and butylhydroxytoluene are also effective antioxidants, which cost less than tocopherol. The cost of tocopherol reaches $23/kg, and butylhydroxyanisole and butylhydroxytoluene – $18 and $15, respectively [7]. It is also advisable to use these antioxidants in mixtures that provide maximum values of the oil induction period. The longest induction period is observed when using mixtures of antioxidants: tocopherol: butylhydroxyanisole (75:25) %; tocopherol: butylhydroxytoluene: butylhydroxytoluene (66.67:16.67:16.67) %. The corresponding oil induction periods were 579.75 min. and 561.55 min. Therefore, these antioxidant mixtures are rational.

5.2. Study of the effect of antioxidant mixtures on the physical and chemical indicators of rapeseed oil under standard storage conditions

The physico-chemical indicators of rapeseed oil after 12 months of storage in its original form and with the addition of the developed antioxidant mixtures were determined. The oil samples were stored in standard laboratory conditions: temperature (20±2) °C, air humidity no more than 70 %, in a non-hermetic darkened glass container. The results of changes in the physico-chemical indicators of the oil with and without the addition of antioxidants are shown in Table 3.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Value of oil indicators after storage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial oil</td>
</tr>
<tr>
<td>Mass fraction of moisture and volatile substances, %</td>
<td>0.06</td>
</tr>
<tr>
<td>Acid value, mg KOH/g</td>
<td>0.19</td>
</tr>
<tr>
<td>Peroxide value, % O mmol/kg</td>
<td>12.5</td>
</tr>
</tbody>
</table>

Thus, the peroxide values of oil stored with antioxidant mixtures are much lower and correspond to standard values at the end of storage. The acid value in oil with antioxidants is also lower.

6. Discussion of the results of determining rational ratios of the antioxidant mixture components to increase the stability of rapeseed oil

The use of antioxidant mixtures in the technology of increasing the oxidative stability of rapeseed oil at elevated and standard temperatures was studied. According to equation (1), Table 2 and Fig. 1, rational ratios of antioxidants were determined: tocopherol: butylhydroxyanisole (75:25) %; tocopherol: butylhydroxyanisole: butylhydroxytoluene (66.67:16.67:16.67) %. Oil induction periods were 579.75 min. and 561.55 min., respectively. The initial oil induction period was 408.48 min.

Oil oxidation occurs as a chain free-radical process, the speed and intensity of which depend on temperature, radiation, and the presence of oxidation initiators or inhibitors. Phenolic antioxidants – oxidation inhibitors (in particular, butylhydroxyanisole and butylhydroxytoluene) are able to quickly react with peroxide radicals with chain breakage. Oxidized oils make it difficult to use in production and deteriorate the quality of finished products.

According to Table 2, the most effective antioxidants are tocopherol and butylhydroxyanisole. The greatest induction period of oil is observed when using mixtures of antioxidants: tocopherol: butylhydroxyanisole (75:25) %; tocopherol: butylhydroxyanisole: butylhydroxytoluene (66.67:16.67:16.67) %. The addition of the developed antioxidant mixtures made it possible to increase the oil induction period by 1.4, 1.37 times, respectively.

The effect of the developed antioxidant mixtures on the physico-chemical indicators of rapeseed oil after 12 months of storage under standard laboratory conditions was studied: temperature (20±2) °C, air humidity no more than 70 %.

The peroxide values of oil stored with the addition of the developed antioxidant mixtures were 2.7 and 1.9 times lower compared to oil stored without antioxidants (Table 3). The result is explained by the effect of applied antioxidants – oxidation inhibitors, which cause chain breakage in reactions with peroxide radicals.

The obtained results make it possible to effectively increase the oxidative stability of rapeseed oil, which is used in various technological processes. In particular, the oxidative stability of rapeseed oil is important in the technology of obtaining an alternative ecological fuel based on fatty acid methyl esters. At the same time, the transesterification reaction is used, the implementation of which requires low peroxide value and oxidation resistance of the initial oil. The use of oxidized oil leads to oil losses, increased consumption of reagents, etc.

The works [8–21] provide data on various methods of oxidative stabilization of rapeseed oil and products based on it. Thus, in [11], octyl esters of sinapic, ferulic, and caffeic acids were used for the oxidative stabilization of rapeseed oil. According to [15], inhibition of oxidation processes in rapeseed oil using grape tea extracts (Amelopsis grossedentata) was investigated. Antioxidants of various nature are used to increase the oxidative stability of rapeseed oil, which is used in this work. But the influence of antioxidant concentrations, antioxidant ratios in the mixture on the oxidative stability of rapeseed oil at elevated and standard temperatures remains an unsolved issue. This task is solved in this work.

The limitation of using the results is the temperatures at which the oil was tested. When the oil is stored at higher temperatures than those used in the study, the effectiveness of antioxidants may be reduced, and it is necessary to introduce more antioxidants.

The disadvantage of the work is the study of the induction period of rapeseed oil at only one elevated temperature (110 °C). It is advisable to study the effectiveness of antioxidants and the oxidative stability of rapeseed oil at higher temperatures.
A promising area of work is the study of other types of antioxidants, as well as other additives (defoamers, citric acid for binding metals, etc.) on the oxidative stability of rapeseed oil at different temperatures. This will allow more efficient use of rapeseed oil for various industrial purposes.

7. Conclusions

1. The dependence of the induction period of rapeseed oil on various ratios of the components of the antioxidant mixture was determined. The following mixtures of antioxidants are rational for use in the technology of oxidative stabilization of rapeseed oil: tocopherol: butylhydroxyanisole (75:25) %; tocopherol: butylhydroxyanirole: butylhydroxytoluene (66.67:16.67:16.67) %. The corresponding oil induction periods were 579.75 min. and 561.55 min. The induction period of the initial oil is 408.48 min. the addition of the developed antioxidant mixtures made it possible to increase the oil induction period by 1.4 and 1.37 times, respectively.

2. The influence of the developed antioxidant mixtures on the physico-chemical indicators of rapeseed oil under standard storage conditions: temperature (20±2) °C, air humidity no more than 70 % was studied. The peroxide values of the oil stored with the addition of antioxidant mixtures were 2.7 and 1.9 times lower compared to the oil stored without antioxidants.

Conflict of interest

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

Financing

The study was conducted without financial support.

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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