The object of the study is the dependence of the induction period of rapeseed oil on the content of oxidation and hydrolysis products. A feature of the work is determining the approximation dependence of the induction period of accelerated oxidation of refined rapeseed oil on the content of primary oxidation products and free fatty acids. This is useful when predicting the shelf life of refined rapeseed oil. It was determined that both factors negatively affect the oxidation stability of refined rapeseed oil. An increase in the peroxide value decreases the induction period of model oil samples by 32.8512 units for each additional mmol ½ O/kg. In turn, increasing the acid value of oil samples reduces the induction period by 19.8424 units for each additional mg KOH/g. Different oxidation dynamics of model samples of refined rapeseed oil with tocopherol were revealed, depending on the concentration of primary oxidation and hydrolysis products. The obtained data are explained by the fact that the primary lipid oxidation products are unstable and quickly decompose to form free radicals. These radicals initiate further lipid oxidation, resulting in reduced oil quality. In addition, free fatty acids are more reactive than triglycerides and are more easily oxidized. A feature of the obtained results is the possibility of modeling processes that affect the oxidation stability of refined rapeseed oil. From a practical point of view, the research results allow initiating measures to maintain the safety of oil-containing food products based on refined rapeseed oil. An applied aspect of using the scientific results is the possibility of rationalizing the storage conditions of refined rapeseed oil to maximize its shelf life and increase competitiveness

Keywords: *refined rapeseed oil, primary oxidation products, free fatty acids, accelerated oxidation*

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IDENTIFICATION OF THE OXIDATION AND HYDROLYSIS PRODUCTS CONTENT INFLUENCE ON THE RAPESEED OIL OXIDATION INDUCTION PERIOD

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1. Introduction

Integration of complex technological processes can significantly increase the sustainability and efficiency of industrial production [1, 2]. This approach can be applied to the stability study of edible oils, which opens up new opportunities for improving product quality by controlling and reducing the content of oxidation and hydrolysis products.

Vegetable oils are complex multicomponent systems, which, depending on the type, differ in the composition of fatty acids, phospholipids, carotenoids, natural antioxidants and other physiologically active compounds. The biological effectiveness and nutritional value of vegetable oils depend on the composition, conditions and terms of storage.

Under the influence of a number of complex chemical transformations during oxidation in fats and oils, there is an accumulation of specific breakdown products of triacylglycerols – free fatty acids, peroxides, hydroperoxides, carbonyl compounds – aldehydes and ketones, fatty alcohols, oxypolymers [3, 4]. These compounds, in addition to the bitter taste and smell, can cause a decrease in the smoke formation temperature, foaming of frying oils, breakdown of vitamins, as well as possible toxic effects and even destructive changes in the digestive tract [5]. Oxidative spoilage of fats and oils in the initial stages is not identified organoleptically, but leads to changes in the composition of raw materials [3, 6]. The formation of peroxides is enhanced by the presence of compounds with pro-oxidant activity, temperature effects, UV radiation, etc. [7]. With insufficient content of antioxidants in lipid systems, the intensity of free radical oxidation and its destructive effect increases. The content of lipid peroxides and hydroperoxides is the most important hygienic characteristic of the quality of oils and lipid-containing products. The content of primary and secondary oxidation products of vegetable oils is determined according to quality standards [8, 9].

Rapeseed oil is a fairly common product, it has properties that cause it to oxidize rather quickly and deteriorate over time [10, 11]. Analysis of the influence of various factors on the stability of this oil will help optimize its storage and use conditions. Therefore, research aimed at identifying the influence of the content of oxidation and hydrolysis products on the oxidation induction period of rapeseed oil will allow predicting the shelf life of the specified oil and products based on it, optimizing a number of production processes. Scientific research aimed at identifying patterns of influence of the content of oil oxidation and hydrolysis products on technological processes is relevant. The results of such research are necessary for production due to the need to predict the shelf life of such products, improve rapeseed oil refining technologies using non-traditional methods to preserve valuable biologically active compounds.

2. Literature review and problem statement

There are numerous studies [12–14] describing the dependence of the stability of oils of different purification degrees on the content of natural fat-soluble antioxidants. In particular, the dependence of the oxidative stability of cold-pressed sunflower oil on the tocopherol content was investigated in [12]. Antioxidant concentrations were measured in model samples of fresh oils, as well as oils oxidized for 6 and 30 days. Oxidation was carried out in a drying cabinet at a temperature of 50 °C, in an air atmosphere. It was found that the initial concentration of tocopherols was high – $(1.4...2.2)\cdot10^{-3}$ mol/kg. At the end of the oxidation period of the model samples, the tocopherol concentration tends to zero. The study [13] determined the dependence of the photooxidative stability of red palm oil on the content of tocols, β-carotene and chlorophyll. The presence of tocols and β-carotene together revealed protective effects for the photooxidative stability of the oil. The presence of chlorophyll increased the rate of photooxidation at high light intensity. The interaction between tocols and β-carotene contributed to the photooxidative stability of the lipid system. The study [14] evaluated the effectiveness of adding propolis extract in improving the oxidative stability of sunflower oil compared to synthetic hydroxytoluene. Propolis was confirmed to have a protective effect on the thermal oxidation of triglycerides in oils. It is worth noting that in [12–14], the effective concentrations and features of the synergistic interaction of fat-soluble antioxidants during oxidation inhibition of oil triglycerides were not determined.

The works [15, 16] substantiate rational concentrations and ratios of fat-soluble antioxidants for effective inhibition of oxidative spoilage of lipids of various oils. For example, the study [15] found that using natural antioxidants affects the oxidative stability of peanut-flax blends, namely the organoleptic properties, acid and peroxide values of oil samples. Oil extracts of sage and black currant leaves, garlic and rosehip were used as antioxidants in the study. It is proved that the introduction of 5 % experimental oil extracts increases the oxidative stability of the peanut-flax blend by 1.2–1.7 times. In [16], the dependence of the oxidation induction period of refined sunflower oil on the content of chlorophyll and β-carotene was investigated. It was determined that chlorophyll *A* has practically no pro-oxidant effect if its content is up to 0.05 g/l. The chlorophyll *A* content at the level of 0.10 g/l leads to a decrease in the induction period by 14 %; 0.30 g/l – by 48 %. The β-carotene content at the level of 0.10 g/l leads to an increase in the induction period by 35 %; 0.30 g/l – by 54 %. The content of 0.10 g/l β-carotene and 0.05 g/l chlorophyll *A* in the oil system leads to a reduction in the induction period of accelerated oxidation by 8.4 % compared to an oil solution of 0.10 g/l beta-carotene without chlorophyll *A*. The obtained data are explained by a compensatory effect of the antioxidant beta-carotene on the pro-oxidant effect of chlorophyll *A* in the oil solution. But the dependence of lipid oxidative stability on the features of temperature treatment during extraction or processing remains uncertain.

Answers to this question are somewhat given in [17, 18]. In [17], the dependence of the oxidative stability of palm oil on the carotene content under simulated refining conditions was determined. The protective role of carotenoids in preventing oxidative spoilage of oil during heat treatment has been proven, as evidenced by the relationship between the content of oxidation products and the concentration of carotenoids after refining. The work [18] investigated the thermal stability of olive oil with and without adding natural (extracts of immortelle, milk thistle, smokehouse tree) and synthetic antioxidants (propyl gallate, butylhydroxyanisole, and butylhydroxytoluene). It was determined that elevated temperature has a significant effect on changes in the oxidative stability of oil samples, especially when it comes to the content of free fatty acids and primary oxidation products, as these indicators increase. Smokehouse tree extract (from natural antioxidants) and propyl gallate (from synthetic antioxidants) have been proven to be effective antioxidants. But the question remains how the oxidative stability of lipids is affected by the fatty acid composition of oils.

To some extent, the aspects of this question are disclosed in [19–21]. So, the work [19] investigated the dependence of the oxidative stability of rice bran oil on the fatty acid composition and the content of specific antioxidants. It was

found that the oxidation stability shown by the oil is mostly due to a well-balanced composition of fatty acids and specific antioxidants. The presence of γ-oryzanol and its synergistic activity with tocols were proved to be the main factors that cause high oil stability. It was determined that the content of other minor components (sterols, phenolic compounds, squalene, etc.) in rice bran oil also slows down the oxidation of triglycerides. A high concentration of free fatty acids was found to negatively affect oil oxidation and quality. It was revealed that the content of metals does not correlate with the oxidative stability of the oil, although these compounds act as pro-oxidants. The study [20] determined the dependence of the oxidative stability of cold-pressed camelina, sunflower, and canola oils on the fatty acid composition and β-carotene content. Correlation analysis of the results showed that in addition to the fatty acid profile and unsaturation level, it is advisable to take into account the content of natural antioxidants to determine the oxidative stability of the above oils. In turn, the work [21] presents the results of studies on the effect of the fatty acid composition, tocopherol isomer composition on the oxidative stability of acai oil during auto- and photooxidation. It was shown that an increase in the content of a-linolenic fatty acid in oil samples plays a negative role in oxidation stability in the presence and absence of ultraviolet radiation. The content of tocopherols has a positive effect on increasing the induction period during oxidation under light. But the question remains how the oxidative stability of lipids is affected by the content of minor accompanying substances – oxidation and hydrolysis products. In addition, it is of interest to study the oxidative stability of nutritionally valuable oils with a high content of oxidation-labile ω-3 fatty acids, in particular, rapeseed.

Thus, there is not enough scientific data on the dependence of the oxidative stability of oils on the content of oxidation and hydrolysis products in them. In particular, no data were found on the effect of primary oxidation products (peroxides and hydroperoxides), as well as hydrolysis products (free fatty acids) on the oxidation stability of refined rapeseed oil. Thus, it is advisable to identify the influence of the content of oxidation and hydrolysis products on the induction period of accelerated oxidation of rapeseed oil. This development will make it possible to rationalize a number of oil and fat production processes, as well as determine the dependence of the storage duration of oil-containing products based on rapeseed oil on production processes and storage conditions.

3. The aim and objectives of the study

The aim of the study is to identify the influence of the content of oxidation and hydrolysis products on the oxidation induction period of rapeseed oil. This will make it possible to predict the shelf life of the specified oil and products based on it. The data obtained will also be useful for improving rapeseed oil refining technologies using non-traditional methods to preserve biologically active compounds.

To achieve the aim, the following objectives should be accomplished:

– to determine the quality indicators of refined rapeseed oil;

– to build a regression equation for determining the dependence of the induction period of accelerated oxidation of refined rapeseed oil on the values of oxidation indicators;

– to determine the effect of an antioxidant on the dynamics of accelerated oxidation of refined rapeseed oil with different contents of oxidation and hydrolysis products.

4. Materials and methods

4. 1. Object and hypothesis of the study

The object of the study is the induction period of accelerated oxidation of refined rapeseed oil containing different concentrations of peroxides and hydroperoxides, as well as free fatty acids.

The main hypothesis of the study is the existence of an inversely proportional relationship between the oxidation induction period of refined rapeseed oil and the content of the specified compounds, which are products of oxidation and hydrolysis of triglycerides having a pro-oxidant effect on the free radical oxidation process.

The following assumptions were made in the study:

– the oxidation induction period of refined rapeseed oil under recommended storage conditions is directly proportional to the oxidation induction period under accelerated conditions.

– the content of secondary oxidation products (aldehydes, ketones and other low molecular weight substances) in model samples of refined rapeseed oil is directly proportional to the content of primary oxidation products (peroxides and hydroperoxides) in the range of peroxide values of 0.260...10.30 mmol ½O/kg.

The recommended storage conditions for refined rapeseed oil are considered to be storage in the temperature range of 0...+5 °C [22] in the absence of sunlight. Accelerated oxidation conditions are oxidation at a temperature of +110 °C with free oxygen access.

The following simplifications were adopted in the study:

– the content of primary oxidation products in the composition of refined rapeseed oil is determined without taking into account other secondary oxidation products;

– samples of refined rapeseed oil from different manufacturers and different batches have similar composition and quality indicators, which affect the stability to oxidative spoilage. Composition and quality indicators are analytical values (peroxide, acid, anisidine), fatty acid composition, moisture content and volatile substances. This simplification should prove the regularity of the repeatability of the oxidation and hydrolysis products content influence on the oxidation stability of refined rapeseed oil samples.

4. 2. Materials and equipment used in the experiment

The following materials were used during the research:

– samples of refined, bleached and deodorized rapeseed oil with a low content of erucic acid (produced in Ukraine), according to DSTU 8175/CAS 8002-13-9;

– a mixture of tocopherols in sunflower oil (concentration 50 %), according to CAS 16698-35-4. The ratio of tocopherol isomers in the mixture: α-tocopherol – 20–22 %; β-tocopherol 8–10 %; g-tocopherol 68–72 %.

4. 3. Method of determining the physico-chemical parameters and composition indicators of oil samples

Organoleptic indicators of refined rapeseed oil samples were determined according to DSTU 2575. Color value – according to DSTU 4568; peroxide, anisidine and acid values – according to DSTU ISO 3960, DSTU ISO 6885 and

DSTU ISO 660, respectively. The mass fraction of moisture and volatile substances in the oil samples was determined according to DSTU 4603. Fatty acid methyl esters of the refined rapeseed oil samples were obtained according to DSTU ISO 5509. The fatty acid composition of the oil samples was determined according to DSTU ISO 5508 on a Shimadzu chromatograph (Japan).

4. 4. Method of obtaining model samples of refined rapeseed oil with different contents of oxidation and hydrolysis products

Model samples of refined rapeseed oil with different contents of oxidation and hydrolysis products are obtained as follows. The raw material is selected – high-quality refined rapeseed oil having a minimum content of oxidation and hydrolysis products. To obtain samples with different contents of primary oxidation products (peroxides, hydroperoxides), thermal oxidation with free oxygen access is used. To obtain samples with different free fatty acid contents, an appropriate amount of oleic fatty acid is added to the oil samples. After these manipulations, the content of peroxides, hydroperoxides and free fatty acids is measured by standard analysis methods according to regulatory documentation. The concentration of peroxides, hydroperoxides and free fatty acids can be adjusted by adding the raw material – refined rapeseed oil with a minimum content of oxidation and hydrolysis products. After reaching the specified composition of the model oil sample, it is stabilized and stored under conditions that prevent further oxidation and hydrolysis.

4. 5. Method of determining the induction period of accelerated oxidation using differential scanning calorimetry

Determination of the induction period of model samples of refined rapeseed oil was carried out at a temperature of +110 °C using differential scanning calorimetry according to [23]. The essence of the method is to determine the period during which oxidation is inhibited if the model samples are kept in an isothermal mode at a given temperature in an oxygen atmosphere. The oxidation induction period is considered to be an estimate of the oxidative stability of the model oil samples being tested.

The sample is weighed (about 10 mg) into a clean, dry crucible. The crucible with the sample and the reference crucible are loaded at ambient temperature. Before carrying out the heating cycle, the device is purged with an inert gas for 5 minutes. The sample and the reference material are heated to 110 °C with purging at a constant rate in an inert gas environment. When the set temperature is reached, oxygen is supplied instead of an inert gas at a constant flow rate. The sample is exposed at a constant temperature, the oxidation reaction of the lipid component is displayed on the thermal curve of the monitor. The induction period is identified as the time between the beginning of oxygen supply to the measuring cell and the beginning of the actual oxidation reaction, which is characterized by a sharp increase in the heat released. This can be observed using the heat flow-temperature curve.

4. 6. Research planning and results processing

A two-factor experiment was used in the study to determine the effect of the–peroxide and acid values on the induction period of accelerated oxidation of refined rapeseed oil. Each experiment was repeated three times. Processing of the data obtained and construction of a graphical dependency were performed using the Microsoft Stat Soft Statistica v 6.0 package (USA). The significance of individual coefficients of the regression equation (1) was carried out using the Student's test by testing the hypothesis that the corresponding parameter of the equation is equal to zero. The calculated absolute value of the Student's test when evaluating individual regression coefficients was compared with its critical table value at a significance level p=0.05. To assess the quality of the regression equation (1) and the completeness of the influence of the selected factors, the coefficient of determination R^2 was defined. The obtained value of R^2=0.93 allows us to draw a conclusion about the effect, greater than 93 %, of variations in the peroxide and acid values on variations in the induction period of accelerated oxidation of refined rapeseed oil. To determine the significance of the regression model, the Fisher's test was calculated, based on the assumption that the equation is not statistically significant.

5. Results of studies on the influence of the content of oxidation and hydrolysis products on the oxidation induction period of rapeseed oil

5. 1. Determination of quality indicators of refined rapeseed oil

The quality indicators of the original sample of refined rapeseed oil were studied. The results of the study are shown in Table 1.

Table 1

Organoleptic and physicochemical indicators of the original sample of refined rapeseed oil

Indicator	Value	Indicators according to regulatory documentation
Transparency	Transparent	
Taste and smell	Taste of depersonalized oil	
Color value, mg of iodine	4.0±0.2	not more than 10
Peroxide value, mmol ½O/kg	0.260±0.012	not more than 5.0
Anisidine value, c.u.	1.80±0.01	not standardized
Acid value, mg KOH/g	0.140±0.005	not more than 0.4
Mass fraction of moisture and volatile substances, %	0.0120±0.0004	not more than 0.15

According to the experimental results (Table 1), by organoleptic and physicochemical indicators, the studied sample of refined rapeseed oil meets the requirements established in the regulatory documentation – DSTU 8175 (*CAS* 8002-13-9).

The fatty acid composition of the original sample of refined rapeseed oil was determined. The obtained data are shown in Table 2.

According to the experimental results, the fatty acid composition of refined rapeseed oil meets the requirements of DSTU 8175 (*CAS* 8002-13-9).

Table 2

Fatty acid composition of the original sample of refined rapeseed oil

Fatty acid	Rapeseed oil sample	Indicators according to regulatory documentation
$C_{14:0}$ (myristic)	0.055±0.001	0.05...0.07
$C_{16:0}$ (palmitic)	4.450±0.089	4.4...5.4
$C_{16:1}$ (palmitoleic)	0.235±0.005	0.2...0.3
$C_{18:0}$ (stearic)	1.960±0.039	1.7...2.1
$C_{18:1}$ (oleic)	51.660±1.033	49.0...63.5
$C_{18:2}$ (linoleic)	34.110±0.682	19.5...36.5
$C_{18:3}$ (linolenic)	5.750±0.115	4.6...8.3
$C_{20:0}$ (arachidic)	0.500±0.010	0.4...0.6
$C_{20:1}$ (gondoic)	0.965±0.019	0.8...1.1
$C_{22:0}$ (behenic)	0.300±0.006	0.3...0.4
$C_{22:1}$ (erucic)	0.0150±0.0003	0.00...0.15
Total	100.00	100

5. 2. Determination of the regression equation of the dependence of the rapeseed oil oxidation induction period on the values of oxidation indicators

The two-factor dependence of the rapeseed oil induction period on the content of primary oxidation products and hydrolysis products was studied. The obtained approximation dependence of the induction period of accelerated oxidation of refined rapeseed oil (*IP*, min) on the peroxide value (*PV*, mmol ½O/kg) and the acid value (*AV*, mg KOH/g) is presented using equation (1):

$$IP(PV, AV)=204.5519-32.8512\cdot PV-19.8424\cdot AV+1.5477\cdot PV^2+1.2938\cdot PV\cdot AV+1.9171\cdot AV^2. \quad (1)$$

It is worth noting that the given approximation dependence has a high level of adequacy, as evidenced by the coefficient of determination R^2 exceeding 93 %. The approximation dependence describes the induction period of accelerated oxidation of refined rapeseed oil samples in the intervals of the peroxide value of 0.260...10.30 mmol ½O/kg and acid value – 0.14...2.60 mg KOH/g. Exceeding these ranges can lead to inaccurate predictions, so when predicting shelf life, it is important to ensure that the *PV* and *AV* values fall within these limits. The graph of the obtained dependence (1) is shown in Fig. 1.

An increase in the content of primary oxidation products in model samples of refined rapeseed oil leads to a decrease in the induction period of accelerated oxidation compared to the control sample. As a control sample, refined rapeseed oil with minimum peroxide and acid values (0.26 mmol ½O/kg and 0.14 mg KOH/g, respectively) was selected. As shown by the research results (Fig. 1, dependence (1)), an increase in the peroxide value reduces the induction period of model oil samples by 32.8512 units for each additional mmol ½O/kg. In turn, increasing the acid value of oil samples reduces the induction period by 19.8424 units for each additional mg KOH/g. This indicates that both factors negatively affect the stability of refined rapeseed oil, i.e. an increase in their values reduces the induction period, which means an acceleration of the oxidative spoilage process.

Given the experimental results (dependence (1) and Fig. 1), it is of interest to determine the effect of natural antioxidants on the induction period of accelerated oxidation of refined rapeseed oil of different oxidation degrees.

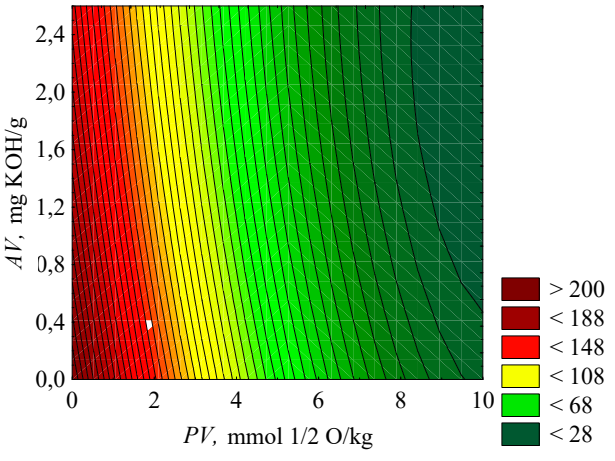

Fig. 1. Dependence of the induction period of accelerated oxidation of refined rapeseed oil (*IP*, min) on the peroxide value (*PV*, mmol ½O/kg) and acid value (*AV*, mg KOH/g)

5. 3. Determination of the antioxidant effect on the oxidation of rapeseed oil with different contents of oxidation products

One-factor dependences of the peroxide value during the accelerated oxidation of refined rapeseed oil with different contents of primary oxidation and hydrolysis products in the presence of a natural antioxidant – a mixture of natural tocopherols (0.05 %) were studied. Approximation dependences of the accumulation dynamics of peroxides and hydroperoxides of model samples of tocopherol-stabilized refined rapeseed oil ($PV_1(\tau)$–$PV_4(\tau)$) on the time of accelerated oxidation (τ) with different initial parameters:

$$PV_1(\tau)=0.0055\cdot\tau^3-0.0917\cdot\tau^2+0.6009\cdot\tau-0.535; \quad (2)$$

$$PV_2(\tau)=0.1877\cdot\tau^2-0.2365\cdot\tau+3.6046; \quad (3)$$

$$PV_3(\tau)=2.405\cdot\tau+4.6; \quad (4)$$

$$PV_4(\tau)=4.52\cdot\tau+5.56. \quad (5)$$

Graphical expressions of the obtained dependences (2)–(5) are presented in Fig. 2.

It is worth noting that the given approximation dependences (2)–(5) have a high level of adequacy, as evidenced by the coefficients of determination R^2, exceeding 96 %, 98 %, 99 %, and 100 %, respectively. Dependences (2)–(5) describe the induction periods of accelerated oxidation of refined rapeseed oil, stabilized with a mixture of natural tocopherols, in the ranges of the peroxide value of 0.260...10.08 mmol ½O/kg and acid value – 0.14...2.60 mg KOH/g.

Dependence (2) is cubic, indicating complex nonlinear dynamics of peroxide accumulation over time. At the initial oxidation stages, the peroxide value may increase with acceleration, which later slows down and then accelerates again. Dependence (3) is quadratic, indicating that the accumulation of peroxides may initially slow down, but will accelerate over time. A positive coefficient before τ^2 indicates a positive acceleration of the oxidation process. Dependence (4) is linear, demonstrating the constant accumulation of peroxides

over time. This indicates a stable oxidation rate without significant changes in the process. In turn, dependence (5) is also linear, but with a higher coefficient before the variable τ, indicating a faster accumulation of peroxides compared to dependence (4). This indicates a more intense process of oxidative destruction of the sample.

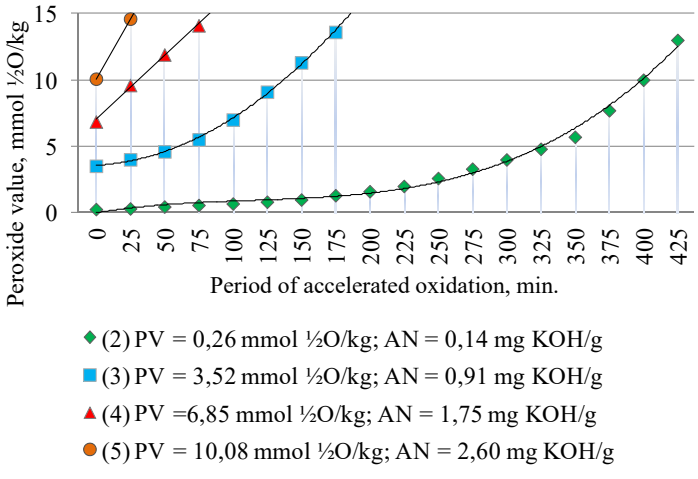

Fig. 2. Dependence of the peroxide value of refined rapeseed oil with different contents of primary oxidation and hydrolysis products during accelerated oxidation in the presence of a mixture of natural tocopherols (0.05 %)

6. Discussion of the results of the analysis of the oxidation and hydrolysis products influence on rapeseed oil oxidation

The dependence of the influence of oxidation and hydrolysis products content on the oxidation induction period of refined rapeseed oil was investigated. The results of the conducted research, namely the approximation dependence (1), make it possible to predict the oxidation stability of refined rapeseed oil with different analytical values.

According to Tables 1, 2, the organoleptic, physico-chemical parameters, as well as the fatty acid composition of the studied raw materials are within the permissible range justified by regulatory documentation. This makes it possible to minimize the influence of other factors on the oil oxidation process, in particular, the content of moisture and volatile substances, secondary oxidation products, etc. In addition, the minimum content of primary oxidation products and free fatty acids in the raw material allows obtaining model samples with a wide content range of the specified minor accompanying substances. The results of the research can be explained by the quality indicators of the raw material, which makes it possible to minimize the influence of external factors and focus on studying specific aspects of oxidation and hydrolysis in conditions as close as possible to actual storage and use conditions of rapeseed oil.

As a result of research, a two-factor dependence of the induction period of accelerated oxidation of refined rapeseed oil on the content of primary oxidation products and hydrolysis products was revealed. The dependence covers a wide range of the peroxide value (0.260...10.30 mmol ½O/kg) and acid value (0.14...2.60 mg KOH/g). The results of the study can be explained by the complex effect of peroxides and free fatty acids on the chemical and physicochemical properties of rapeseed oil, which leads to an acceleration of oxidation processes and a decrease in the induction period. The data obtained (equation (1), Fig. 1) allow us to determine the ranges of peroxides, hydroperoxides and free fatty acids with different levels of pro-oxidant effect on refined rapeseed oil. The effect of increasing the peroxide and acid values on the induction period of model samples of refined rapeseed oil increases with their increase, but at a lower rate (due to positive coefficients in the square terms of dependence (1)). The positive dependence term (+1.2938·*PV*·*AV*) shows that the presence of an interaction between peroxide and acid values somewhat compensates for their negative effect on the induction period, but this effect is relatively small. At low peroxide and acid values, the oil induction period will be the closest to the basic value (204.6 min). In turn, at high values of factors, the induction period decreases significantly, although positive quadratic terms and interactions among factors somewhat mitigate this effect. Thus, control over the peroxide and acid values in refined rapeseed oil is important to ensure its stability and long-term storage. Reducing these analytical values will help prolong the oxidation induction period and prevent rapid oxidation of the oil, which is important to consider when rationalizing oil storage and processing conditions.

Knowing the initial peroxide and acid values of products and using equation (1), it is possible to estimate when the induction period of accelerated oxidation will become critically small, which will allow determining the final date of product consumption. In addition, by analyzing the effect of different storage conditions on changes in peroxide and acid values, rational storage conditions can be developed for refined rapeseed oil that minimize the rate of changes in these indicators, thereby extending the shelf life of products. Using the equation during production processes, it is possible to control and adjust the parameters that affect the peroxide and acid values, ensuring the production of rapeseed oil with high quality indicators and long shelf life.

One-factor approximation dependences of the induction period of accelerated oxidation of refined rapeseed oil stabilized with the same amount of a mixture of natural tocopherols on the peroxide and acid values (2)–(5) were studied. These dependences were modeled for the intervals of the peroxide value of 0.260...10.08 mmol ½O/kg and acid value – 0.14...2.60 mg KOH/g. Dependences (2)–(5) show different oxidation dynamics of model samples of refined rapeseed oil depending on the concentration of primary oxidation and hydrolysis products. The presence of natural tocopherols as antioxidants negatively affects the accumulation rate of peroxides, however, different initial compositions of the oil lead to different kinetic models. The obtained results can be explained by a combination of the specified factors, which interact with each other, affecting the rate and mechanisms of rapeseed oil oxidation. Approximation models (2)–(5) can be used to predict the shelf life of tocopherol-stabilized refined rapeseed oil, taking into account the initial content of oxidation and hydrolysis products. In addition, a preliminary assessment of the feasibility of antioxidant stabilization of refined rapeseed oil samples with different pro-oxidant contents is possible in view of dependences (2)–(5).

The development differs from [12–21], where the effect of the content of minor components with antioxidant activity on oxidative stability is investigated. This limits the range

of factors that affect the oil oxidation rate, in particular, the pro-oxidant effects of a number of minor accompanying oil compounds (peroxides, hydroperoxides and free fatty acids) are not taken into account. Thus, studying the mutual influence of the content of the main prooxidants of vegetable oil triglycerides on the oxidation of the model system of rapeseed oil, where other factors are practically excluded, is interesting from both a scientific and a practical point of view.

The results of the research (Fig. 1, 2; dependences (1)–(5)) allow predicting changes in the oxidation induction period of refined rapeseed oil depending on the peroxide and acid values. They take into account the non-linear effect of these parameters on oil stability, allowing us to assess the impact of different storage and processing conditions on the quality of rapeseed oil and products based on it.

Approximation dependence (1) allows predicting the oxidation stability of refined rapeseed oil based on the analytical values. This makes it possible to estimate its shelf life and take timely measures to extend it. Using the equations obtained in the research allows determining optimal storage conditions that minimize the oxidation rate, thereby extending the shelf life of the oil. In turn, the analysis of one-factor dependences (2)–(5) allows us to determine the feasibility of using antioxidants for different oil samples with different contents of oxidation and hydrolysis products. The results obtained help to understand the chemical processes occurring during storage and processing of refined rapeseed oil and allow developing effective methods for quality control and extension of its shelf life.

Although the approximation dependences (1)–(5) allow predicting the oxidation stability of refined rapeseed oil samples, the models may be limited in accuracy due to the complexity of chemical reactions that occur during oxidation and hydrolysis. They may not fully account for the effects of other minor components, such as phospholipids or metal residues, which may also affect oxidative spoilage. In addition, the approximation dependences obtained may not take into account various types and concentrations of other antioxidants that may be present in commercial samples. Also, the proposed approximation equations do not take into account external factors, such as temperature, humidity, light and oxygen availability, which can significantly affect the oxidation and hydrolysis rate of triacylglycerols.

The drawback of the study is the lack of a detailed analysis of the impact of secondary oxidation products, which can significantly change the stability and organoleptic parameters of refined rapeseed oil. In addition, actual storage and transportation conditions may differ significantly from laboratory conditions, which may affect the accuracy of forecasts.

These aspects indicate the need for additional research to cover a wider range of conditions and factors affecting the stability of refined rapeseed oil, as well as improving existing models for more accurate prediction. The development of the research may be to expand the range of investigated antioxidants, including synthetic and natural compounds, to compare their effectiveness under different conditions. It is also advisable to study the influence of additional factors, such as temperature, humidity and ultraviolet exposure, on the oxidation and hydrolysis processes of refined rapeseed oil. This will help optimize industrial processes and improve the quality of finished products, as well as products based on refined rapeseed oil.

7. Conclusions

1. The organoleptic (transparency, taste, smell) and physico-chemical parameters (color, peroxide, anisidine, acid values, moisture and volatile substances content), as well as the fatty acid composition of the studied sample of refined rapeseed oil were determined. By organoleptic, physicochemical indicators and fatty acid composition, the studied sample of refined rapeseed oil meets the requirements established in the regulatory documentation – DSTU 8175 (CAS 8002-13-9).

2. A regression equation describing the dependence of the induction period of accelerated oxidation of refined rapeseed oil on factors such as oxidation and hydrolysis products was constructed. Both factors negatively affect the stability of refined rapeseed oil. An increase in peroxide value decreases the induction period of model oil samples by 32.8512 units for each additional mmol ½O/kg. In turn, increasing the acid value of oil samples reduces the induction period by 19.8424 units for each additional mg KOH/g.

3. The effect of a mixture of tocopherols on the dynamics of accelerated oxidation of refined rapeseed oil with different contents of oxidation and hydrolysis products was determined. Different oxidation dynamics of model samples of refined rapeseed oil were revealed depending on the concentration of primary oxidation and hydrolysis products. The presence of natural tocopherols as antioxidants negatively affects the accumulation rate of peroxides, however, different initial compositions of the oil lead to different kinetic models of accelerated oxidation.

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.

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Data availability

The manuscript has no associated data.

Use of artificial intelligence tools

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

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