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ASSESSMENT OF THE MINIMUM SHELF LIFE OF SUNFLOWER OIL BY DIFFERENTIAL SCANNING CALORIMETRY

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Abstract. Sunflower oil is one of the leading vegetable fats and occupies a key position in global production and consumption. The high content of polyunsaturated fatty acids in conventional sunflower oil results in low oxidative stability, limiting its minimum shelf life. An alternative is high-oleic sunflower oil, whose fatty acid composition consists of more than 75% oleic acid, providing enhanced resistance to oxidation. However, oxidative changes during storage remain relevant even for high-oleic sunflower oil. This study investigated the oxidative stability of high-oleic refined deodorized sunflower oil and determined its minimum shelf life using differential scanning calorimetry. The evaluation of oxidation processes was performed using a kinetic approach based on the induction period, calculated from thermograms recorded at three temperatures with 10 ºC intervals, using TA Universal Analysis software. To describe the dynamics of oil quality changes depending on temperature and time, Arrhenius kinetic equations were applied. The rate constants of oxidation for the studied oil were determined at 383, 393, and 403 K. From the ln k versus 1/T dependence, the activation energy (100.93 kJ·mol^{-1}) and the pre-exponential factor were estimated. The ln k/T versus 1/T dependence was used to determine thermodynamic parameters: enthalpy (97.61 kJ·mol^{-1}), entropy (-13.27 J·(K·mol)$^{-1}$), and Gibbs free energy. Compared with conventional sunflower oil, the Gibbs free energy of high-oleic oil is higher (101.43–101.56 vs. 93.73–94.15 kJ·mol^{-1}), confirming its thermodynamic resistance to oxidation. It has been demonstrated that an increase in temperature from 288 to 298 K accelerates oxidative processes and shortens the predicted shelf life of the studied oil from 940 to 429 days. These results confirm the feasibility of using differential scanning calorimetry combined with kinetic analysis for the rapid prediction of fat shelf life.

Keywords: sunflower oil, differential scanning calorimetry, oxidation, rate constant, kinetics, shelf life.

Introduction. Formulation of the problem

Sunflower oil is one of the leading edible vegetable fats and ranks among the top in global production and consumption [1]. It is characterized by a high content of linoleic acid (up to 74%) and tocopherols, which determine its nutritional value for humans. However, the large proportion of polyunsaturated fatty acids reduces its resistance to oxidative processes, thereby limiting its minimum shelf life and its use in technologies involving high-temperature treatment. To improve oxidative stability, high-oleic sunflower varieties were developed by U.S. breeders in the late 1970s. The oil obtained from these cultivars contains an increased proportion of oleic acid (up to 90%). Such a modification of the fatty acid profile ensures greater oxidative stability, making high-oleic sunflower oil suitable both for long-term storage and for applications in the food industry, particularly in the production of frying fats. Over the past decade, global sunflower oil production, including the high-oleic segment, has shown steady growth [2]. The leading producers are countries of the Black Sea region, in particular Ukraine, which accounts for a significant share of world exports. Each year, Ukraine exports about 5–6 million tons of sunflower oil to more than 120 countries, making this product an important contributor to the state budget. However, in the 2024/25 marketing year, export

volumes decreased to 4.73 million tons, which is 24% lower than in the previous season (6.2 million tons) and represents the lowest figure in the last three years. At the same time, compared with the previous season, exports to key markets increased: to India by 44%, to Spain by 11%, and to Italy by 28%.

Regardless of the type of sunflower oil, the issues related to oxidative changes during storage and thermal processing remain relevant, as they affect the safety, quality, and nutritional value of the product. Various methods are used to assess the quality and stability of oils, for example, the Active Oxygen Method (AOCS Cd 12-57 *Fat Stability, Active Oxygen Method*). This method measures the time (in hours) required for a fat or oil sample to reach a specified peroxide value under defined test conditions. The duration of this period is considered an indicator of oxidative stability. However, this method is poorly reproducible, labor-intensive, and requires toxic reagents. In November 1993, the AOCS Technical Committee on Commercial Fats and Oils Analysis declared it obsolete and recommended, as an alternative, the instrumental method AOCS Cd 12b-92, *Oil Stability Index*. This method, implemented using the *Rancimat* instrument (*Metrohm, Switzerland*), is currently the most widely applied. It is based on determining the induction period (IP) by monitoring the conductivity of water, into which volatile organic acids formed during oil oxidation are transferred. The longer the IP, the higher the oxidative stability of the oil. The method makes it possible to determine the time until the onset of intensive oxidation, which is an important indicator of the minimum shelf life of the oil. A modern alternative to *Rancimat* is the *Oxitest* instrument (*Velp, Italy*), which makes it possible to study both liquid and solid samples with a fat content of at least 2–4% without prior sample preparation. It determines the consumption of oxygen by reaction-active components under elevated temperature (up to 110 ºC) and oxygen pressure (up to 0.8 MPa). In 2016, the AOCS approved the analytical procedure Cd 12c-16 *Accelerated Oxidation Test for the Determination of the Oxidation Stability of Foods, Oils, and Fats Using the Oxitest Oxidation Test Reactor* and included it in the *Official Methods and Recommended Practices of the AOCS* (7th edition) [3]. The use of *Oxitest* for assessing oil stability and minimum shelf life has been confirmed in studies [4, 5]. A popular method for evaluating the oxidative stability of oils and fats is differential scanning calorimetry (DSC). The DSC method has been actively investigated and compared with the *Rancimat* method in many scientific studies [6–9]. Research shows that it allows the determination of the onset temperature of oxidation and the heat released during this process. Experiments can be carried out under dynamic conditions (linear increase in temperature) or isothermally (constant temperature). The oxidation environment (oxygen or air) may be maintained at atmospheric or elevated pressure. Most often, dynamic DSC with a heating rate of 2–20 ºC/min is applied [10]. The DSC method is characterized by speed and simplicity of implementation, does not require preliminary sample treatment, needs only a minimal amount of material, and provides rapid results [11]. However, at present, it is not included in the official AOCS methods for assessing oxidative stability or determining the predicted minimum shelf life of oils.

Thus, instrumental methods of accelerated oxidation, such as *Rancimat* and *Oxitest*, are actively used to assess oxidative stability and to predict the minimum shelf life of oil. At the same time, differential scanning calorimetry can be considered a promising tool for predicting the minimum shelf life of oil, as it makes it possible to study oxidation processes under controlled conditions and is characterized by high reproducibility of results.

Analysis of recent research and publications

The minimum shelf life of a food product is defined as the date until which the product retains its properties under proper storage conditions. In Ukraine, this period is regulated by the Law of Ukraine “On Consumer Rights Protection”, the Law of Ukraine “On the Quality and Safety of Food Products and Food Raw Materials”, the Civil Code of Ukraine, and other regulatory legal acts governing specific product categories. The manufacturer establishes the shelf life based on product stability testing and the availability of relevant regulatory documents and indicates it on the product packaging. Traditional real-time shelf-life testing involves storing the product under normal conditions throughout the expected shelf life to determine optimal quality. This process can take from several months to several years. Moreover, such tests are usually conducted at only one temperature or storage condition, which does not provide a complete understanding of the product’s behavior in different environments. An alternative is *Accelerated Shelf Life Testing* (ASLT) – a scientific method that allows modeling the product’s aging process under controlled conditions. ASLT is most often implemented using a kinetic modeling approach, which includes: selecting kinetic factors to accelerate the degradation process; studying the course of deterioration under conditions that ensure sufficiently rapid changes; extrapolating the results to real storage conditions; and using the extrapolated data to predict the minimum shelf life [12, 13]. Thus, the ASLT method allows for a significant reduction in the time required to determine the minimum shelf life – from months or even years to much shorter periods. The most commonly used accelerating factor is temperature, while humidity and light can also be employed. The most recognized relationship between temperature and the rate of product quality deterioration is described by the Arrhenius equation [14]. Traditional instrumental methods, such as *Rancimat* and *Oxitest*, are used to predict the minimum shelf life of oils. However, the use of differential

scanning calorimetry may represent a promising approach.

A significant number of studies in the scientific literature focus on the use of differential scanning calorimetry for investigating the oxidative stability of oils, determining antioxidant activity, detecting adulteration, and analyzing the kinetics of oxidation processes. Indeed, DSC is a versatile tool for assessing the oxidative stability of oils in both isothermal and non-isothermal modes [15]. The isothermal mode allows for the determination of the oxidation induction period, making it particularly useful for measuring oil resistance to oxidation at a specific temperature. For instance, in [16], the oxidative stability of oils obtained by pressing pre-roasted oilseeds, as well as berry and fruit kernels, was studied at 140 ºC under a constant oxygen flow of 20 ml/min. Due to the high measurement speed and the absence of toxic chemicals, the authors recommend DSC for industrial analysis of oil stability. The non-isothermal mode enables the determination of the onset temperature of oxidation. The study [17] investigated the oxidation kinetics of a soybean oil and milk fat blend using DSC at different heating rates (2.5, 5.0, 7.5, 10.0, and 12.5 ºC/min). The main kinetic parameters were calculated using the Arrhenius equation according to the Ozawa–Flynn–Wall method. In [18], researchers assessed the oxidative stability of camelina seed oils obtained by different extraction methods using DSC. The non-isothermal oxidation kinetics of these oils were studied at various heating rates (2.5, 5, 10, and 15 ºC/min).

In [19], the results of a comparative study on the oxidative stability of various oils using differential scanning calorimetry and the *Rancimat* apparatus are presented. The application of these two approaches allowed for the assessment of the stability of buriti pulp oil (*Mauritia flexuosa Mart*), rubber seed oil (*Hevea brasiliensis*), and passion fruit oil (*Passiflora edulis*). Similar results are reported in [10], where the oxidation processes of four olive oil samples were compared: under dynamic conditions in a DSC cell at atmospheric pressure and under isothermal conditions using the *Rancimat* apparatus. DSC experiments were carried out in an oxygen flow atmosphere using various linearly programmed heating rates in the range of 4–20 ºC/min. From the obtained DSC exotherms, extrapolated onset temperatures of the reactions were determined, which were used to assess the thermo-oxidative stability of the samples. Using the Ozawa–Flynn–Wall method and the Arrhenius equation, the activation energies (Ea), pre-exponential factors (A), and reaction rate constants (k) for oil oxidation under DSC conditions were calculated. Oxidation induction periods measured by the Rancimat method were conducted in an air atmosphere at temperatures ranging from 100 to 140 ºC in 10 ºC increments. Using an Arrhenius-type correlation between the reciprocal induction periods and the absolute measurement temperatures, Ea, A, and k for oil oxidation under *Rancimat* conditions were calculated. The main kinetic parameters obtained by both methods demonstrated qualitative agreement and allowed for the evaluation of oxidative stability of oils at elevated temperatures. Thus, *Rancimat* measurements confirmed that DSC can be recommended as a suitable method for assessing oil oxidative stability. Compared to *Rancimat*, DSC provides significantly shorter analysis times, requires smaller sample amounts, and, due to its simplicity and speed, can be applied in routine quality control of oils and fats. Although *Rancimat* remains the primary instrumental method widely used in the food and cosmetic industries, the results of [10, 19] indicate the potential of implementing DSC in oil stability monitoring practice.

In [15], the deterioration of three cold-pressed oils (linseed, camelina, and hemp) was studied over six months of storage under conditions approximating supermarket shelves. Changes were assessed using traditional chemical methods as well as the instrumental differential scanning calorimetry method. The novelty of the study was that DSC parameters obtained from isothermal and non-isothermal measurements corresponded to the chemical indicators throughout the oils' shelf life.

In [20], it was shown that olive oil analysis can be conducted using differential scanning calorimetry as an alternative method for evaluating its quality and stability, as well as for determining the effect of heating on the oil's properties. The authors of [15, 20] concluded that DSC is an effective, fast, accurate, and environmentally safe method for assessing the oxidative stability of oils.

The authors of [6] investigated the oxidative stability of cold-pressed camelina (*Camelina oil*). The aim of the study was to compare the oxidative stability of camelina oil samples and to evaluate the kinetic parameters of their oxidation using DSC and *Rancimat* methods. The analysis was conducted under isothermal conditions at temperature ranges of 90–130 ºC for DSC and 80–120 ºC for *Rancimat*. Based on the results, the time to reach the maximum oxidation peak and the induction period were compared, and the activation energy, pre-exponential factors, and rate constants were calculated using the Arrhenius equation and transition state theory. A high correlation between the results obtained by DSC and *Rancimat* (R^2>0.98) was demonstrated, allowing DSC to be recommended as a promising and objective method for assessing the oxidative stability of the oil.

In summary, differential scanning calorimetry can be considered a versatile and promising tool, widely used for studying the oxidative stability of oils, assessing antioxidant activity, and investigating the kinetics of oxidation processes. However, to date, there are no systematic studies dedicated to the direct determination of the minimum shelf life of oils, particularly high-oleic sunflower oil, using this method. Considering the importance of predicting the preservation of oils' quality and safety characteristics,

conducting such studies is highly relevant. The development of an effective DSC-based tool for assessing and predicting the shelf life of oils, especially high-oleic sunflower oil, will help prevent errors in determining their compliance with safety and quality requirements, increase the accuracy and efficiency of stability assessment, and contribute to the implementation of more reliable quality control systems in the food industry.

The purpose of this work is to::

– study the oxidative stability of refined, deodorized high-oleic sunflower oil at 383, 393, and 403 K using differential scanning calorimetry;

– determine the kinetic characteristics of the oxidation reaction of the studied oil;

– establish an equation that adequately describes the kinetic patterns of the oxidation process;

– calculate the thermodynamic parameters of the oxidation reaction;

– predict the minimum shelf life of refined, deodorized high-oleic sunflower oil.

Materials and methods.

The following materials were used for the study: refined, deodorized high-oleic sunflower oil in accordance with DSTU 9127:2021 "High-Oleic Sunflower Oil. Technical Specifications".

High-oleic sunflower oil, like other fats and oils, is susceptible to lipid oxidation, which leads to the deterioration of its chemical and sensory properties during storage. This directly affects the minimum shelf life of the product and represents a significant issue for both producers and consumers. The evaluation of oxidation processes can be performed using a kinetic–thermodynamic approach based on induction period data determined at three different temperatures with 10 ºC intervals. To describe the dynamics of oil quality changes depending on time and temperature, as in [5], it is appropriate to use the Arrhenius kinetic equation, which in logarithmic form is expressed as follows:

$$\ln k = \ln A - (\frac{E_a}{R \cdot T}), \quad (1)$$

where k – rate constant or the inverse value of oxidation induction time, h^{-1}; A – pre-exponential factor, h^{-1}; Ea – activation energy, J/mol; R – universal gas constant (8.314510 $J \cdot (K \cdot mol)^{-1}$); T – temperature, K.

This approach allows for a comprehensive assessment of the impact of oxidation processes on oil stability during storage and provides a rationale for determining its minimum shelf life.

To determine the induction periods, a DSC Q20 instrument was used, which enables accelerated assessment of the oxidative stability of oils and fats. The method is based on measuring the difference in heat flow between the tested sample and an inert reference, allowing detection of thermal effects associated with physicochemical processes or oxidation reactions. Measurements were conducted according to ISO 11357-6:2018. The induction period, reflecting the sample's oxidative stability, was determined from the heat flow versus time curve, which exhibits an S-shaped form. Its value was established graphically: tangents were drawn to the curve sections before and after the inflection point, and their intersection was projected onto the time axis. Calculations were performed using *TA Universal Analysis* software. Based on the determined IP values, reaction rate constants, k, were calculated as the inverse of the induction period duration. This approach assumes that lipid oxidation in an environment of excess oxygen or air, typical for the DSC method, can be described as an exothermic process, approximately modeled as a first-order reaction [21, 22].

The detailed methodology for calculating the kinetic and thermodynamic parameters of the oil oxidation reaction, namely: the rate constants within the selected temperature range; the pre-exponential factor; the activation energy; enthalpy, ΔH; entropy, ΔS; Gibbs free energy, ΔG; the temperature acceleration coefficient, Q_{10}; and the predicted shelf life at different temperatures, is presented in [5].

For data processing, mathematical methods within the *Microsoft Excel* software environment were applied.

Results of the research and their discussion

To predict the minimum shelf life of refined, deodorized high-oleic sunflower oil under storage conditions at temperatures of 288, 293, and 298 K, the induction period of the oil was first determined using differential scanning calorimetry. The study was conducted in the temperature range of 383–403 K with a step of 10 K. Analysis of the obtained thermograms using the *TA Universal Analysis* software allowed automatic generation of S-shaped oxidation kinetics curves. For each curve, the inflection point between the pre-exothermic and exothermic regions was determined by the tangent method and projected onto the time axis to establish the induction period values. Based on these data, the rate constants of the oxidation reaction were calculated as the reciprocals of the induction periods. The summarized results are presented in Table 1.

Table 1 – Kinetic parameters of the oxidation reaction of refined, deodorized high-oleic sunflower oil

Temperature, K	Induction period, h	Rate constant, h^{-1}
383	13.33	0.075019
393	5.38	0.185874
403	2.77	0.361011

Analysis of the data (Table 1) shows that an increase in temperature leads to higher reaction rate constants and a corresponding decrease in the induction period. The obtained values are in good agreement with previously published results obtained using the DSC method [23–26], confirming the reproducibility and reliability of the results.

The kinetic parameters presented in Table 1 allowed for the construction of an Arrhenius plot (ln k versus 1/T), shown in Figure 1. The slope of the linear relationship served as the basis for calculating the activation energy, while the intercept with the ordinate axis enabled the determination of the pre-exponential factor. The R^2 value above 0.99 confirms the high quality of the approximation and the reliability of the obtained data.

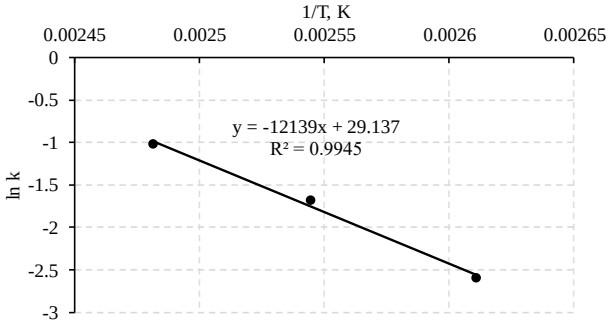

Fig. 1. Dependence of the logarithm of the reaction rate constant on the reciprocal temperature in Arrhenius plot coordinates

The dependence shown in Fig. 1 allows for the calculation of the reaction rate constant over a wider temperature range. Based on the graphical data and Equation (1), the kinetic equation of the oxidation process of the studied oil in logarithmic form was formulated:

$$\ln k = 29.137 - (\frac{12139}{T}), \quad (2)$$

After mathematical transformation, Equation (2) is presented in the form of an exponential dependence:

$$k = 4.5086 \cdot 10^{12} \cdot e^{\left[-\frac{100929}{RT}\right]}, \quad (3)$$

According to Equation (3), the pre-exponential factor and activation energy were determined. The obtained activation energy value (100.93 kJ·mol⁻¹) is consistent with literature data, which range from 79 to 104 kJ·mol⁻¹ [27]. Activation energy is one of the key indicators characterizing the oxidative stability of oils. For conventional sunflower oil, it is lower compared to high-oleic sunflower oil, due to the significant content of polyunsaturated fatty acids (primarily linoleic acid), which have increased reactivity toward radical processes. In contrast, high-oleic sunflower oil contains a much higher proportion of oleic acid and significantly fewer polyunsaturated compounds, which enhances its oxidative stability. Accordingly, the activation energy of oxidation processes in high-oleic oil is higher than in conventional sunflower oil, confirming its greater thermal stability and longer shelf life [28, 29]. In study [5], the authors determined the activation energy for conventional sunflower oil as 84.99 kJ·mol⁻¹. Following the approach in [5], regression analysis of the dependence ln(k/T) versus 1/T (Fig. 2) allowed the calculation of enthalpy and entropy, as well as the Gibbs free energy of the reaction.

At the next stage, from the equation describing the graphical dependence in Fig. 3, k_0 and log IP_0 were determined. The obtained parameters made it possible to establish the minimum shelf life and the induction period (IP) of high-oleic refined deodorized sunflower oil at temperatures of 288, 293, and 298 K, as well as to calculate the temperature acceleration coefficient of the oxidation reaction. The calculation results are presented in Table 2.

In Fig. 3, within the studied temperature range, a clear linear relationship between the logarithm of the induction period and temperature was observed, confirming the preservation of a single oxidation mechanism even under elevated temperature conditions. This indicates the appropriateness of using the DSC method, which is based on measuring the difference in heat flow between the sample (in this case, oil) and an inert reference during controlled heating, as a reliable tool for the accelerated assessment of the minimum shelf life of oils.

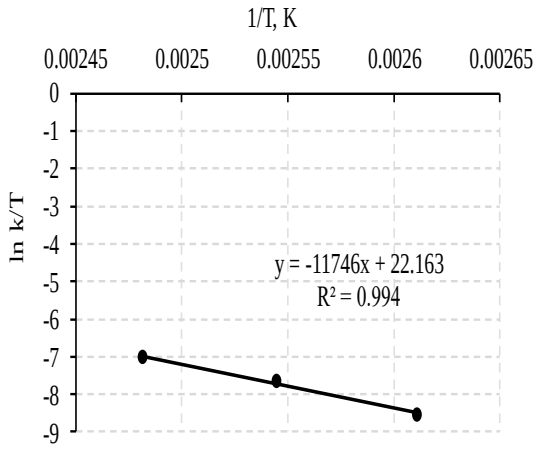

Fig. 2. Dependence of ln(*k*/*T*) on the inverse temperature in the coordinates of the Eyring equation

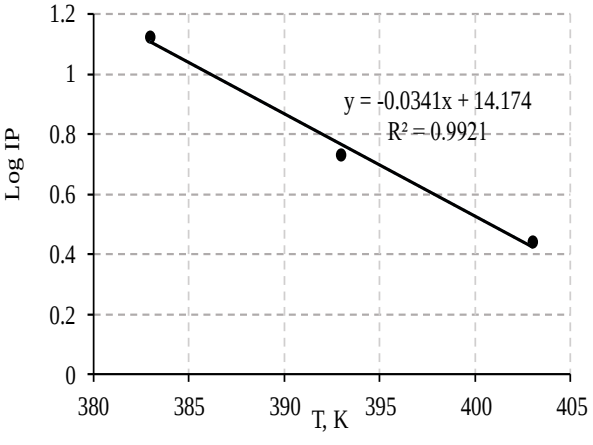

Fig. 3. Dynamics of the change in the logarithm of the oil oxidation induction period depending on temperature

Table 2 – Kinetic and thermodynamic parameters of the oxidation reaction of refined deodorized high-oleic sunflower oil

Tempe-rature, K	Rate constant, h^{-1}	A	Activation energy, $kJ \cdot mol^{-1}$	Activation enthalpy, $kJ \cdot mol^{-1}$	Activation entropy, $J \cdot (K \cdot mol)^{-1}$	Gibbs energy, kJ·mol	Shelf life, days	Q_{10}
288	$2.233 \cdot 10^{-6}$	$4.51 \cdot 10^{12}$	100.93	97.61	-13.27	101.431	940	2.19
293	$4.584 \cdot 10^{-6}$					101.498	635	
298	$9.185 \cdot 10^{-6}$					101.564	429	

According to the results in Table 2, it was established that with an increase in temperature from 288 to 298 K, the rate constant of the reaction rises from $2.233 \cdot 10^{-6}$ to $9.185 \cdot 10^{-6}$ h^{-1}, indicating an acceleration of the oxidation process, although these values are an order of magnitude lower than those for conventional sunflower oil [5]. The activation energy, determined from the temperature dependence in Arrhenius coordinates, was 100.93 $kJ \cdot mol^{-1}$. The activation enthalpy (97.61 $kJ \cdot mol^{-1}$) and activation entropy (–13.27 $J \cdot (mol \cdot K)^{-1}$) were calculated from the ln(k/T) versus 1/T relationship. The positive enthalpy value confirms the endothermic nature of the process. The negative activation entropy for high-oleic sunflower oil indicates a moderate degree of ordering in the transition state compared to conventional sunflower oil (–41.28 $J \cdot (mol \cdot K)^{-1}$), which is explained by the high content of polyunsaturated fatty acids (linoleic, linolenic) in the fatty acid composition of conventional oil that form more reactive radical complexes requiring stricter molecular ordering. In the fatty acid composition of high-oleic sunflower oil, the main component is oleic acid (monounsaturated), which is less reactive; therefore, radical processes proceed more slowly, and the transition state forms with a lower degree of molecular ordering. The combination of a negative activation entropy with a positive enthalpy confirms the non-spontaneous nature of high-oleic sunflower oil oxidation. The calculated Gibbs free energy values were positive and increased from 101.431 to 101.564 $kJ \cdot mol^{-1}$ with a temperature rise from 288 to 298 K, which correlates with a reduction in the oil's minimum shelf life from 940 to 429 days. The temperature acceleration coefficient, Q_{10}, was 2.19, confirming the high sensitivity of the oxidation rate to temperature: an increase of 10 K approximately doubles the reaction rate. Despite the relatively high thermal stability of high-oleic sunflower oil, controlling storage temperature remains necessary to maintain its stability and prolong its minimum shelf life.

Conclusion

1. Until the 1990s, the oxidative stability of oils was traditionally assessed using the Active Oxygen Method (AOCS Cd 12-57 Fat Stability), which is now considered poorly reproducible, labor-intensive, and requiring toxic reagents. As an alternative, since 1993, the instrumental AOCS Cd 12b-92 Oil Stability Index method using the *Rancimat* device has been implemented, and in 2016, the analytical procedure Cd 12c-16 Accelerated Oxidation Test for the Determination of the Oxidation Stability of Foods, Oils, and Fats Using the *Oxitest* Oxidation Test Reactor with the *Oxitest* device was approved. Additionally, differential scanning calorimetry (DSC) is widely used; it is based on measuring the difference in heat flow between the sample (oil) and an inert reference under controlled heating, allowing rapid assessment of fat oxidative stability. For predicting the minimum shelf life of oils, traditional instrumental methods such as *Rancimat* and Oxitest are employed. Differential scanning calorimetry can be considered a promising approach for evaluating the minimum shelf life of oils.

2. Traditional minimum shelf-life testing (real-time) involves storing the product under normal conditions throughout the expected shelf life to assess optimal quality, which may take from several months to several years. An alternative is accelerated shelf-life testing, where temperature is the most common accelerating factor. To describe the dependence of the rate of oil and fat quality deterioration, the Arrhenius equation is most frequently applied. In this study, the oxidation kinetics of oil were evaluated using DSC. From the graphical dependence of ln k on 1/T, the pre-exponential factor ($4.51 \cdot 10^{12}$) and the activation energy (100.93 $kJ \cdot mol^{-1}$) were calculated. The obtained activation energy is higher compared to conventional sunflower oil (84.99 $kJ \cdot mol^{-1}$), which is due to the high content of monounsaturated fatty acids (oleic acid) in the fatty acid profile. Oleic acid exhibits lower reactivity in radical processes compared to polyunsaturated fatty acids, particularly linoleic acid, which is typical for the fatty acid composition of conventional sunflower oil. The linear character of the dependence and the high correlation coefficient (0.9945) confirm the consistency of the experimental data with the Arrhenius model.

3. The proposed kinetic equation of oxidation of high-oleic refined deodorized sunflower oil made it possible to calculate the rate constant *k* at temperatures of 288, 293, and 298 K. It was established that with increasing temperature, the *k* values rise from $2.233 \cdot 10^{-6}$ to $9.185 \cdot 10^{-6}$ h^{-1}, indicating an acceleration of the oxidation process. Based on the dependence of ln(k/T) on 1/T, the activation enthalpy (97.61 $kJ \cdot mol^{-1}$) and activation entropy (–13.27 $J \cdot (K \cdot mol)^{-1}$) were calculated. The positive enthalpy value confirms the endothermic nature of the process, while the negative entropy value for high-oleic oil indicates a moderate degree of ordering in the transition state compared to

conventional sunflower oil (–41.28 J·(K·mol)$^{-1}$). This difference can be explained by the higher content of polyunsaturated fatty acids (linoleic, linolenic) in conventional oil, which form more reactive radical complexes requiring stricter molecular ordering. In high-oleic oil, the predominant component is monounsaturated oleic acid, which results in a slower course of radical processes and the formation of a transition state with a lower degree of molecular ordering.

4. The Gibbs free energy values during oxidation were positive, confirming the non-spontaneous nature of the reaction. With an increase in temperature from 288 to 298 K, ΔG for high-oleic refined deodorized sunflower oil increased from 101.431 to 101.564 kJ·mol^{-1} and remained higher compared to conventional sunflower oil (from 93.73 to 94.15 kJ·mol^{-1}). This indicates a greater thermodynamic tendency of conventional oil toward oxidation. The more positive the ΔG value, the less spontaneous the degradation process at a given temperature, and therefore, the higher the oil stability.

5. With an increase in temperature from 288 to 298 K, the Gibbs free energy of the oil rises from 101.431 to 101.564 kJ·mol^{-1}, accompanied by a reduction in the calculated storage period from 940 to 429 days. However, these values remain considerably higher compared to conventional sunflower oil (118–57 days). The temperature coefficient Q_{10}, which equaled 2.19, indicates a pronounced sensitivity of the oxidation rate to temperature changes, highlighting the importance of storage condition control to preserve product quality. Thus, differential scanning calorimetry provides a rapid and safe means of assessing the minimum shelf life of oils without the use of hazardous reagents and with the potential for analysis automation.

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ОЦІНЮВАННЯ МІНІМАЛЬНОГО ТЕРМІНУ ПРИДАТНОСТІ СОНЯШНИКОВОЇ ОЛІЇ МЕТОДОМ ДИФЕРЕНЦІЙНОЇ СКАНУЮЧОЇ КАЛОРИМЕТРІЇ

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Анотація. Соняшникова олія належить до провідних рослинних жирів і посідає одне з ключових місць у світовому виробництві та споживанні. Високий вміст поліненасичених жирних кислот у складі класичної соняшникової олії зумовлює низьку стійкість до окиснення, що обмежує її мінімальний термін придатності. Альтернативою є високоолеїнова соняшникова олія, жирнокислотний склад якої на понад 75% складається з олеїнової кислоти, що забезпечує підвищену стійкість до окиснення. Проте проблеми окисних змін під час зберігання залишаються актуальними й для високоолеїнової олії. У статті досліджено окисну стабільність олії соняшникової високоолеїнової рафінованої дезодорованої та визначено її мінімальний термін придатності методом диференційної скануючої калориметрії. Оцінювання процесів окиснення проведено за кінетичним підходом на основі індукційного періоду, розрахованого за термограмами при трьох температурах з інтервалом 10 ºС з використанням програмного забезпечення *TA Universal Analysis.* Для опису динаміки змін якості олії залежно від температури та часу використано кінетичні рівняння Арреніуса. Для досліджуваної олії встановлено константи швидкості окиснення при 383, 393 та 403 К. За залежністю ln k від 1/T оцінено енергію активації (100.93 кДж·моль$^{-1}$) та преекспоненційний множник. Залежність ln k/T від 1/T застосовано для визначення термодинамічних параметрів: ентальпії (97.61 кДж·моль$^{-1}$), ентропії (-13.27 Дж·(К·моль)$^{-1}$) та енергії Гіббса. В порівнянні з класичною соняшниковою олією показник енергії Гіббса високоолеїнової є вищим (101.43-101.56 проти 93.73-94.15 кДж·моль$^{-1}$), що підтверджує термодинамічну стійкість до окиснення останньої. Доведено, що підвищення температури від 288 до 298 К зумовлює прискорення окисних процесів і скорочення прогнозованого терміну придатності досліджуваної олії з 940 до 429 днів. Результати підтверджують доцільність використання диференційної скануючої калориметрії у поєднанні з кінетичним аналізом для швидкого прогнозування терміну придатності жирів.

Ключові слова: соняшникова олія, диференціальна скануюча калориметрія, окислення, константа швидкості, кінетика, термін придатності.

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