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STUDY OF THE DYNAMICS OF OXIDATION OF VEGETABLE OILS TO PROLONG THE STORAGE

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Abstract

Aim. To investigate the oxidation processes of edible vegetable oils: unrefined flaxseed oil, refined high-oleic sunflower oil, and refined traditional sunflower oil. The purpose of the study was to examine and analyze the dynamics of oxidation processes in vegetable oils and their impact on the shelf life of food products containing these oils. Methods. The oxidation of oils was analyzed using the peroxide number indicator, which showed that the ratio of the average rates of peroxide compound accumulation in unrefined flaxseed oil, refined traditional sunflower oil, and refined high-oleic sunflower oil was 54 : 43 : 1, indicating a proportional relationship with their degree of unsaturation. The primary oxidation products formed in the oil are unstable, leading to the formation of new radical compounds and more stable secondary oxidation products. The study included the determination of carbonyl compounds, characterized by the anisidine number. Results. The research revealed an important feature of unrefined flaxseed oil oxidation: the anisidine number increased more rapidly compared to refined traditional and high-oleic sunflower oils. This indicates the relative instability of unrefined flaxseed oil hydroperoxides, which undergo destruction to form carbonyl and other secondary compounds. Due to its high content of polyunsaturated fatty acids, unrefined flaxseed oil is vulnerable to oxidation and mixing it with refined high-oleic sunflower oil can enhance the oxidative stability of food products. Conclusions. The results highlight the importance of considering the dynamics of oxidation processes when selecting vegetable oils for food products and suggest that mixing different types of oils can improve their oxidative stability and the overall stability of food products.

*Keywords***:** vegetable oil; peroxide number; anisidine number; oxidation; oxidation products.

ДОСЛІДЖЕННЯ ДИНАМІКИ ОКИСЛЕННЯ РОСЛИННИХ ОЛІЙ ДЛЯ ПРОДОВЖЕННЯ ЗБЕРІГАННЯ

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Анотація

Мета. Дослідити процеси окислення харчових рослинних олій: нерафінованої лляної олії, рафінованої високоолеїнової соняшникової олії та рафінованої традиційної соняшникової олії. Завданням дослідження було вивчення та аналіз динаміки процесів окислення в рослинних оліях та їх вплив на термін зберігання харчових продуктів, що містять ці олії. Методи. Окиснення олій аналізували за допомогою показника пероксидного числа, який показав, що співвідношення середніх швидкостей накопичення пероксидних сполук у нерафінованій лляній олії, рафінованій традиційній соняшниковій олії та рафінованій високоолеїновій соняшниковій олії становило 54 : 43 : 1, що свідчить про пропорційний зв'язок зі ступенем їх ненасиченості. Первинні продукти окислення, що утворюються в олії, є нестабільними, що призводить до утворення нових радикальних сполук та більш стабільних вторинних продуктів окислення. Дослідження включало визначення карбонільних сполук, що характеризуються анізидиновим числом. Результати. Дослідження виявило важливу особливість окислення нерафінованої лляної олії: анізидинове число збільшувалося швидше порівняно з рафінованими традиційними та високоолеїновими соняшниковими оліями. Це свідчить про відносну нестабільність гідропероксидів нерафінованої лляної олії, які руйнуються з утворенням карбонільних та інших вторинних сполук. Через високий вміст поліненасичених жирних кислот нерафінована лляна олія вразлива до окислення, і змішування її з рафінованою високоолеїновою соняшниковою олією може підвищити окислювальну стабільність харчових продуктів. Висновки. Отримані результати підкреслюють важливість врахування динаміки процесів окислення при виборі рослинних олій для харчових продуктів та свідчать про те, що змішування різних типів олій може покращити їх окислювальну стабільність та загальну стабільність харчових продуктів.

*Ключові слова***:** рослинна олія; пероксидне число; анізидинове число; окислення; продукти окислення.

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Introduction

Vegetable oils and fats occupy an important place in human nutrition, they are used both directly in food and in the preparation of many food products and culinary dishes [1–3]. Oils are a valuable source of high-calorie triglycerides and essential fatty acids, phospholipids, carotenoids, natural antioxidants and other physiologically active substances, presented in different qualitative and quantitative ratios depending on the type of oil and production technology [4–5]. Vegetable fats are also used as a base for cosmetics and are part of creams, massage oils and other skin care products [6].

In recent years, interest in the problem of controlling the process of fat oxidation has increased, since the activation of free radical oxidation and the so-called peroxidation syndrome are at the root of many diseases and have a direct connection with the aging process, among the causes of which the importance of the nutritional factor is the least studied [7–8].

The study of oxidation processes of vegetable oils is of key importance in determining ways to minimize them and developing adequate methods and criteria for quality control, storage conditions and setting shelf life of products [9–11].

Experimental part

The following were used in the work: unrefined linseed oil, refined traditional sunflower oil, and refined high-oleic sunflower oil of industrial production [12–14].

Experiments on the study of oxidation kinetics and to establish temperature dependence were carried out as follows: 10 cm^3 samples of oils placed in transparent glasses without lids with a volume of 20 cm^3 were oxidized in the dark at temperatures (20±2), 60, 80, 120 °C, free access of air oxygen and the ratio of the surface area of contact with air to the volume of oil 0.45 cm^{-1} [15–17].

Experiments on oxidation of mixtures of unrefined linseed oil and refined high-oleic sunflower oil were carried out in buxes at 80 °C, free access of air oxygen and the ratio of the surface area of contact with air to the volume of oil 2.5 cm^{-1}, sample weight 6 g [18].

Methods of analysis: peroxide number – DSTU 4570; anisidine number – DSTU ISO 6885; compounds with conjugate bonds (dienes and trienes) – AOCS, Official Methods, cd. 5-91, Reaptoval, 1997; polar substances: accelerated version of the JUPAC 2.505 method; fatty acid composition – gas-liquid chromatography of methyl esters of fatty acids - DSTU ISO 5508 [19].

The antiradical method modified by us DPPH: 5 ml of 0.1 mM DPPH solution in isooctane was mixed with 3 μL of essential oil sample (or with 3 μL of 10 %, 1 % solution in isooctane) and after exposure for 24 hours in the dark, the absorption of the mixture was measured at λ = 520 nm on the SF-26 spectrophotometer [20].

Results and their discussion

To assess the effect of the fatty acid composition of vegetable oils on their oxystability and to identify oxidation patterns, experiments were carried out on model deep oxidation of small volumes of oil (10 cm^3) with the measurement of the main chemical parameters (Peroxide Value (PV), Anisidine value (AV), concentration of tocopherols and compounds with conjugated double bonds).

Vegetable oils, as a natural product, are a complex mixture of substances belonging to different classes of compounds. In the process of their oxidation, many sequential and parallel reactions take place, in which both macro- and microcomponents are involved.

The kinetics of oxidation of vegetable oils according to the studied indicators was characterized by the average oxidation rate for the storage period (V_{avg}) according to the studied indicators, calculated by the formula:

$$V_{avg} = \frac{C_{end} - C_{beginning}}{t_{exp}},$$

where: $C_{beginning}$ – the value of the indicator in the sample received for oxidation; C_{end} – the value of the indicator at the end of the experiment; t_{exp} – the duration of the experiment, hour.

The study of oxidation processes was carried out on the following types of vegetable oils: linseed, sunflower high-oleic and traditional, which refers respectively to oils of linolenic, linoleic and oleic groups, the fatty acid composition of which is given in Table 1.

During the experiment at a temperature of 22 °C, the pH of linseed oil increased from 1.9 to 240 (126.3 times), traditional sunflower oil – from 6.9 to 184 (26.7 times), high-oleic sunflower oil – from 1.0 to 5.3 mmol act. O/kg (5.3 times). The average growth rates of P.V. for the same time were 0.054, 0.043 and 0.001 mmol act. O/kg·h, respectively.

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Table 1

Fatty acid composition of the samples studied

Essential fatty acids		Content, % of the sum of fatty acids		
		Linseed oil	Traditional Sunflower oil	Sunflower High Oleic Oil
Palmitic	C16:0	5.1	6.1	3.6
Stearic	C18:0	3.0	3.9	3.1
Oleic	C18:1	17.5	25.6	89.1
Linoleum	C18:2	24.5	63.0	2.5
Linolena	C18:3	49.9	1.4	1.7
Sum		100.0	100.0	100.0

The value of traditional sunflower oil slowly increased during storage. On the graph of the growth of P.V. linseed oil, an induction period equal to 4 weeks is expressed (Fig. 1). The graph of changes in the P.V. of sunflower high-oleic oil is an abscissa parallel to the axis, since its value changed little during the experiment.

At the initial stage of oxidation, the growth rate and value of traditional sunflower oil were higher than those of linseed oil (Figs. 2 and 3). After the end of the induction period, the rate of accumulation of peroxides in linseed oil increased dramatically, and after 6 weeks of storage, it exceeded the rate of accumulation of peroxides in traditional sunflower oil. At the point corresponding to 11 weeks of oxidation of oils, the values of the P.V. of these two oils equalized, after which the P.V. of flaxseed oil was higher by the end of the experiment.

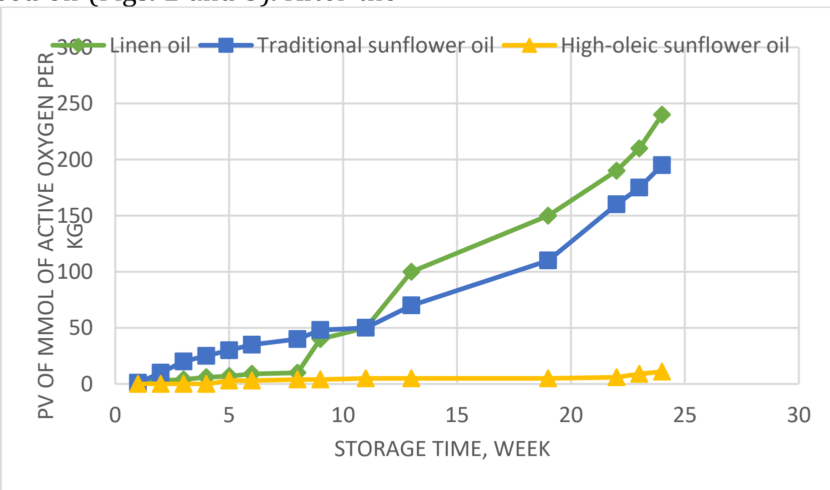

Fig. 1. Change in peroxide value during storage of oils at 22 °C

As follows from the results of Fig. 2, the rate of accumulation of peroxides was uneven over time and went through a series of maxima and minima during storage.

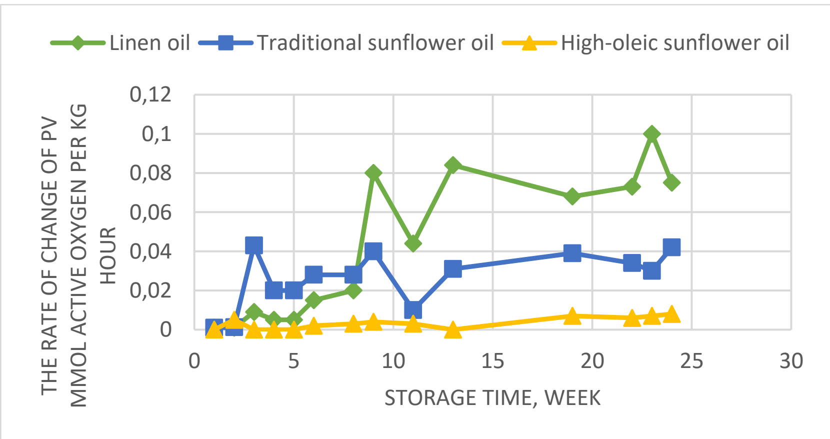

Fig. 2. Rate of change in peroxide value during storage of oils at 22 °C

The presence of a peak at the beginning of oxidation is a consequence of the free radical nature of self-oxidation of oils. In sunflower high-oleic oil, similar peaks were not noted, possibly since against the background of low obtained values of P.V., the amplitude of fluctuations of the

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indicator did not exceed the margin of error in its determination. The presence of a peak at the beginning of oxidation is a consequence of the free radical nature of self-oxidation of oils. In sunflower high-oleic oil, similar peaks were not noted, possibly since against the background of low obtained values of P.V., the amplitude of fluctuations of the indicator did not exceed the margin of error in its determination.

The analysis of the kinetics of oxidation of oils by the P.V. index showed that during the experiment, the ratio of average rates of accumulation of peroxide compounds in linseed, traditional sunflower and sunflower high-oleic oil was 54 : 43 : 1. This ratio was determined based on the following experimental data: for linseed oil, the average rate of peroxide accumulation was 0.054 mmol act. O/kg·h; for traditional sunflower oil, it was 0.043 mmol act. O/kg·h; and for high-oleic sunflower oil, it was 0.001 mmol act. O/kg·h. These results confirm the proportionality of the oxidation process to the degree of unsaturation of the oils.

Since the primary lipid oxidation products formed are unstable, so peroxides easily decompose to form new radical compounds and more stable secondary oxidation products. Of the numerous oxygen-containing substances formed during oxidation, in this work, carbonyl compounds characterized by the value of the anisidine number (A.V.) were determined.

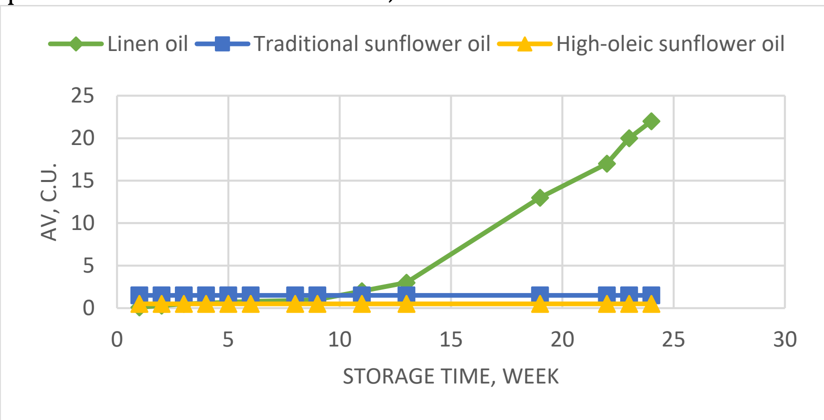

Fig. 3. Change in anisidine value during storage of oils at 22 °C

The kinetics of oxidation of oils according to A.V., graphically presented in Fig. 3, show that the process of oxidation of experimental oils according to this indicator is subject to different patterns than according to the indicator P.V. The values of A.V. traditional sunflower oil and high-oleic sunflower oil practically did not change during storage under experimental conditions. In linseed oil, the A.V. increased from 1.4 to 22.1 c.u. The oxidation kinetics of linseed oil according to the A.V. index, as well as according to the P.V. index, was characterized by an induction period of 4 weeks.

The reactions of the formation of aldehydes and ketones in sunflower oil (traditional and high-oleic) took place at an average rate of 0.0001 c.u./h, and in linseed oil – 0.005 c.u./h, i.e. 50 times faster.

Thus, the studies revealed an important feature of the oxidation of linseed oil, which consists in the outstripping growth of A.V. in comparison with traditional sunflower and high-oleic oils. This fact indicates the relative instability of hydroperoxides of linseed oil, which undergo destruction with the formation of carbonyl and other secondary compounds.

It was found that one of the main secondary oxidation products in linseed oil are E, E-2,4-heptadienal, 3,5-octadiene-2-he and E,E-2,4-decadienal, in sunflower oil – E,E-2,4-decadienal. The values obtained of A.V. for experimental oils indicate that carbonyl oxidation products reduce quality, not only due to the negative impact on the formation of smell and taste. For example, dienals are known for their cytotoxic properties, so for highly unsaturated edible oils, control of the content of secondary oxidation products is especially important.

One of the conditional indicators that consider the influence of the values of P.V. and A.V. at the same time is totox (2P.V. + A.V.). Despite the lack of physical sense, totox is often used as a standard indicator, as it characterizes the dynamics of changes in the oxidative states of the oil. One of the calculated terms of the totox value can be underestimated, for example, the P.V. of sunflower oil that has undergone deep technological processing: adsorption refining and deodorization, but at the same time the value of the A.V. indicator increases significantly. In particular, the World Food Program recommended the use of oils with a totox value of less than 10.

In the oxidation experiments carried out, the value of totox increased in linseed oil from 5 to 501, in traditional sunflower oil – from 5 to 386, in high-oleic sunflower oil – from 2 to 11.

The average rates of change in oxidation indices during autooxidation are shown in Table 2.

Table 2

Average rates of change in oxidation indicators

Name of indicators	Average change rates (V_{avg}) for oils		
	Linseed	Traditional sunflower	Sunflower high-oleic
Peroxide value	0.054	0.043	0.001
Anisidine value	0.005	0.0001	0.0001
TOTOX, hours	0.113	0.086	0002
Pairing with paired double bonds:			
Diena	0.00080	0.00047	0.000012
Triena	0.00007	0.000014	0.000006
Tocopherols	0.016	0.011	0.004

Experiments were conducted at temperatures of (20±2) °C, 60°C, 80 °C, 120 °C, with free access to air oxygen. Oil samples of 10 cm^3 were placed in transparent glasses without lids. Measurements were taken every 4 weeks over a period of 24 weeks.

Measurement Results:

- Linseed oil: the average rate of peroxide compound accumulation was 0.054 mmol act. O/kg·h.
- Traditional sunflower oil: the average rate of peroxide compound accumulation was 0.043 mmol act. O/kg·h.
- High-oleic sunflower oil: the average rate of peroxide compound accumulation was 0.001 mmol act. O/kg·h.

These values were used to determine the average rates of change in oxidation indicators for each type of oil. For example, the average rate of peroxide compound accumulation for linseed oil was 0.054 mmol act. O/kg·h, for traditional sunflower oil – 0.043 mmol act. O/kg·h, and for high-oleic sunflower oil – 0.001 mmol act. O/kg·h.

The results presented in Table 2 allow us to conclude that the oxidation of vegetable oils at room temperature is accompanied by the transition of double bonds to the conjugate state and a decrease in the concentration of tocopherols (Fig. 4) at a rate proportional to the degree of unsaturation of oils.

The results obtained showed that the process of auto-oxidation of vegetable oils obeys different patterns depending on their biochemical composition.

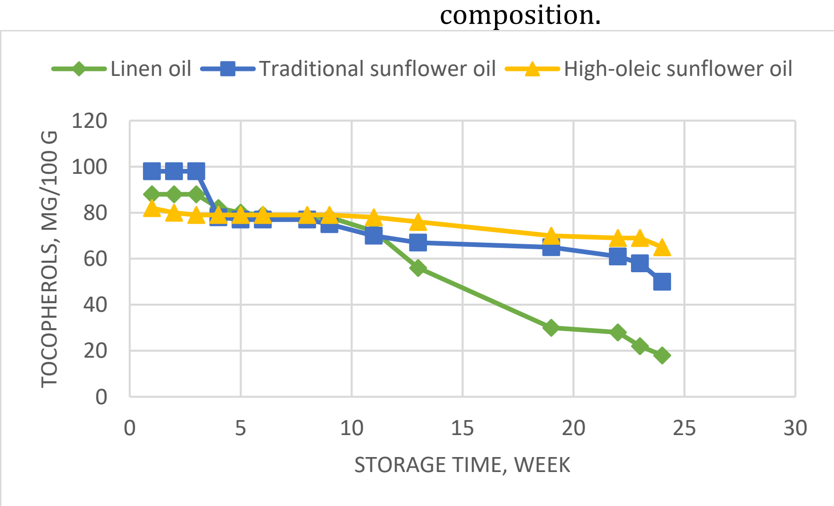

Fig. 4. Change in tocopherols during storage of oils at 22 °C

High-oleic oil was the most stable in all oxidation parameters among experimental oils. Oxidation of traditional high-linoleic sunflower oil was characterized by a predominant accumulation of primary oxidation products – hydroperoxides. Oxidation of high-linolenic linseed oil was characterized by a high rate of reactions of both initiation and formation of stable secondary oxidation products.

Given the high degree of oxidation of linseed oil, it is advisable to recommend its encapsulation or the use of inert gases in the production process to reduce contact with air oxygen, as well as the design of oxystable mixtures of linseed oil with other oils.

Conclusions

As a result of the study of oxidation processes of edible vegetable oils – linseed, sunflower high-oleic and traditional – it was found that the degree of oxidative stability differs between oils depending on their unsaturation.

1. The ratio of average rates of accumulation of peroxide compounds in linseed, traditional sunflower and sunflower high-oleic oils was 54 : 43 : 1, which confirms the proportionality of this process to the degree of unsaturation of oils.
2. The primary oxidation products formed in oils are unstable, which leads to their decomposition and the formation of secondary oxidation products.
3. Determination of carbonyl compounds using the anisidine number index revealed that linseed oil has an outstripping increase in anisidine number compared to traditional sunflower and high-oleic oils, which indicates the relative instability of its hydroperoxides.
4. The high content of polyunsaturated fatty acids in flaxseed oil makes it vulnerable to oxidation, but mixing with high-oleic sunflower oil can increase its oxidative stability and, consequently, the stability of food products.

Thus, the results of the study emphasize the need to consider the dynamics of oxidative processes when choosing vegetable oils for food products and the possibility of increasing their stability by mixing different types of oils.

References

[1] Nieva-Echevarría B, Goicoechea E, Guillén MD. (2020). Food lipid oxidation under gastrointestinal digestion conditions: A review. *Crit Rev Food Sci Nutr*., *60*(3), 461–478 https://doi.org/10.1080/10408398.2018.1538931

[2] Lashko, N., Chausovsky, N., Brazhko, O. (2019). Effect of light on the kinetics of oxidation reactions in vegetable oils. *Food science and technology, 13*(3), 54–62. https://doi.org/10.1039/b922183m

[3] Bayram, I., Parra-Escudero, C., Decker, E. (2024). Mathematical Modeling of Alpha-Tocopherol Early Degradation Kinetics to Predict the Shelf-Life of Bulk Oils. *Journal of Agricultural and Food Chemistry.* 72. 4939–4946. https://doi.org/10.1021/acs.jafc.3c08272

[4] Sytnik, N., Mazaeva, V., Bilous, O., Bukhkalo, S., Glukhykh, V., Sabadosh, G., Natarov, V., Yarmysh, N., Kravchenko, T., Zakharkiv, S. (2021). Research of oxidative stability of vegetable oils for use in sport nutrition. *Technology Audit and Production Reserves*, *6*(3(50), 30–34. https://doi.org/10.15587/2312-8372.2019.187673

[5] Bakhmach V., Peshuk L., Chernushenko O., Savchenko A., Petrenko S. (2022). [Execution of innovative technologies and components in the manufacture of emulsion products]. *Visnyk NTU «KhPI»*. *1*(1363) 18–22 https://doi.org/10.20998/2220-4784.2022.01.03

[6] Laguerre, M., Bily, A., Birtic, S. (2020). Lipid oxidation in food, *Properties, Processing, and Applications, 2020*, 243–287. https://doi.org/10.1016/B978-0-12-817105-9.00007-0

[7] Frankel, E.N. (2005). *Lipid oxidation.* The Oily Press, Dundee. https://doi.org/10.1533/9780857097927

[8] Shahidi, F., Zhong, Y. (2020). Lipid oxidation and improving the oxidative stability. *Chemical Society Reviews, 39*, 4067–4079. https://doi.org/10.1039/b922183m

[9] Choe E., Min D. (2021) Mechanisms and factors for edible oil oxidation. *Comprehensive Reviews in Food Science and Food Safety*, *5*(4), 169–186 https://doi.org/10.1111/j.1541-4337.2006.00009

[10] Gunstone, F.D. (2021). *Vegetable oils in food technology: Composition, properties and uses.* Wiley-Blackwell. https://doi.org/10.1002/9781444339925

[11] Logrén, N., Hiidenhovi, J., Seppälä, T., Välimaa, A.-L., Mäkinen, S., Rintala, N., Mattila, P., Yang, B., Hopia, A. (2022). Effects of Weak Acids on the Microbiological, Nutritional and Sensory Quality of Baltic Herring (Clupea harengus membras). *Foods.* 11, 1–17 https://doi.org/10.3390/foods11121717

[12] Velasco, J., Dobarganes, M. (2021). Oxidative stability of virgin olive oil. *European Journal of Lipid Science and Technology, 104*, 661–676. https://doi.org/10.1002/1438-9312%28200210%29104%3A9/10%3C661%3A%3AAID-EJLT661%3E3.0.CO%3B2-D

[13] Jacobsen, C. (2021). *Oxidative stability and shelf life of foods containing oils and fats*. Elsevier. https://doi.org/10.1007/s00216-016-987

[14] McClements, D.J., Decker, E.A. (2020). Lipid oxidation in oil-in-water emulsions: Impact of molecular environment on chemical reactions in heterogeneous food systems. *Journal of Food Science*, *65*(8), 1270–1282 https://doi.org/10.1111/j.1365-2621.2000.tb10596.x

[15] Porter, N.A., Caldwell, S.E., Mills, K.A. (2020). Mechanisms of free radical oxidation of unsaturated lipids. *Lipids*, *30*(4), 277–290. https://doi.org/10.1007/BF02536034

[16] Pokorny, J., Yanishlieva, N., Gordon, M. (2020). *Antioxidants in food: Practical applications*. CRC Press. https://doi.org/10.1079/BJN2001510

[17] Warner, K., Eskin, M. (1995). *Methods to Access Quality and Stability of Oils and Fat-Containing Foods.* AOCS Publishing. https://doi.org/10.4324/9781003040958

Journal of Chemistry and Technologies, 2025, *33*(2), 493-499

[18] Nieva-Echevarría, B., Goicoechea, E., Guillén, M.D. (2020) Food lipid oxidation under gastrointestinal digestion conditions: A review. *Crit Rev Food Sci Nutr*., *60*(3), 461–478. https://doi.org/10.1080/10408398.2018.1538931

[19] Nashchansky, D., Demidov, I., Demidova, A. (2024). Study of the features of fat oxidation in the solid state. *Scientific Bulletin of the Tavria State Agrotechnological University, 14*(1), 1–8. https://doi.org/10.32782/2220-8674-2024-24-1-8

[20] [20] Syed, A (2016) Oxidative stability and shelf life of vegetable oils. In: Hu M, Jacobsen C (eds) Oxidative stability and shelf life of foods containing oils and fats. *AOCS Press,* 187–207. https://doi.org/10.1016/B978-1-63067-056-6.00004-5