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THEORETICAL ASPECTS OF OBTAINING OXIDATION-STABLE VEGETABLE OILS

ZUFAROV OYBEK

Tashkent Chemical Technological Institute, Tashkent, Uzbekistan
E-mail.: zufarovoybek81@gmail.com

ISROILOVA SHOIRA

Tashkent Chemical Technological Institute, Tashkent, Uzbekistan
E-mail.: sherliverpool.211@gmail.com

YULCHIEV ASLBEK

Andijan State University, Andijan, Uzbekistan
E-mail.: yulchiev@mail.ru
Corresponding author

SERKAYEV KAMAR

Tashkent Chemical Technological Institute Tashkent, Uzbekistan
E-mail.: serkayev@mail.ru

Abstract: The purpose of the research was to theoretically substantiate the principles of oxidation and directions in the development of ways to prevent the appearance of derivatives of oxidation of vegetable oils based on existing modern concepts and patterns. The article substantiates the sequence of oxidation stages and the factors influencing the intensity of the process. The authors, relying on the results of numerous studies conducted by scientists, argue that high-temperature treatment in the presence of enzymes, metal ions, phospholipid residues and various pigments, especially in a relatively humid environment, is a very important component in initiating the process of autooxidation of fatty acids. It is noted that inhibition or at least reduction of the factors of initiation of the primary oxidation process by forrafination in the presence of highly effective reagents leads to an increase in the shelf life of vegetable oils.

Keywords: oxidation, initiation, peroxides, aldehydes, malondialdehyde, inhibition.

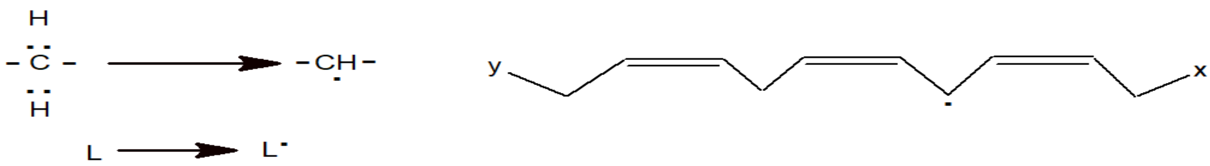
Introduction. As is known, autooxidation of lipids of native vegetable oils is a rather slow process, which is slowed down by natural antioxidants. However, by creating conditions under which lipids can be exposed to free-radical action, the cis-configuration loses a hydrogen atom from the chain and turns into a free radical L• and the possibility of interaction with molecular oxygen appears. When interacting with oxygen, lipid peroxidation occurs and the fatty acid is peroxidized by the formation of the LO• structure.

At the first stage, i.e. when the oxidation reaction is initiated, a free hydrogen radical and a free radical of fatty acids are formed by homolytic decomposition of covalent compounds of the hydrocarbon chain C-H. Vegetable oils always contain trace amounts of hydroperoxides, which are formed under the influence of lipoxygenases in plants and pass into the oil during production.

The energy needed to decompose fatty acid molecule compounds can come from various sources, such as thermal energy during heating, ultraviolet radiation, or light.

The decomposition of the molecule can also be caused by reactions with other free radicals or metals.

Initiation: The reaction is most often initiated by the hydroxyl radical, which removes hydrogen from the CH2 groups of the polyenoic acid, which leads to the formation of a lipid radical.



The resulting free radical of fatty acids is very active and easily reacts with an oxygen molecule, resulting in a peroxyl radical. The resulting radical separates a hydrogen atom from an unsaturated fatty acid molecule, resulting in hydroperoxide and a free radical of fatty acids.

The second stage of autoxidation is called propagation. The two stages of the propagation stage can be repeated several times (we are talking about a chain reaction) [1, 2]. At the beginning of this stage, the first organoleptic signs of fat spoilage begin to appear [3, 4].

Propagation (development): The chain develops with the addition of O2, resulting in the formation of a lipoperoxy radical LOO• or lipid peroxide LOOH. Lipid peroxidation is a free radical chain reaction, i.e. each radical formed initiates the formation of several others:

$$L^{\bullet} + O_2 \rightarrow LOO^{\bullet}\ LOO^{\bullet} + LH \rightarrow LOOM + LR^{\bullet}$$

The resulting peroxide radical reacts with the next fatty acid molecule to form a hydroperoxide molecule and a new fatty acid radical:

$$ROO^{\bullet} + RH \_\_\_\_\_ ROOH + R$$

The enthalpy of propagation reactions is low compared to the enthalpy of the initiation reactions. That is why the chain oxidation reaction at the second stage occurs at an accelerated rate

Research methods. The color number of the cottonseed oil under study was determined in red units using a Lovibond tentometer (Model E), in a 1 cm thick cuvette and at a constant 35 yellow units [7]. The color number of sunflower oil was determined using the iodine scale in mg iodine.

When determining the acid number of the oils under study, it was assumed that this indicator characterizes the presence of free fatty acids in the fat and is expressed by the amount of potassium hydroxide (mg) required to neutralize free fatty acids and alkali-neutralized accompanying substances contained in 1 g of fat (mg KOH/g). The acid number for refined vegetable oils should not exceed 0.4 mg KOH/g [8].

Since free fatty acids are oxidized faster than bound ones, an increase in the acid number accelerates the processes of both chemical and enzymatic oxidative rancidity of unsaturated fatty acids. On the other hand, oxidation of free unsaturated fatty acids by lipoxygenases promotes an increase in the acid number. However, an increased acid number does not always indicate fat spoilage. Fats with a high acid number are often not rancid, while the acid number of rancid fats can be low.

To determine the acid number, an oil sample was first dissolved in a neutralized mixture of ethanol and diethyl ether (1:2). Ethyl alcohol is used not only for dissolution formed during soap titration, but also to eliminate the reverse reaction - soap hydrolysis. About 3 g of vegetable oil were weighed into a 100 ml flask on an analytical scale, 50 ml of an alcohol-ether mixture (1:2) were added, and 1-2 drops of an alcohol solution of phenolphthalein were introduced. The analyzed solution was carefully titrated (one drop at a time) with 0.1 N aqueous potassium hydroxide solution until a faint pink color was obtained. The acid number (AN, mg KOH/g) was determined using formula (1):

$$\text{Кч} = \frac{5{,}611 \cdot V_{KOH}}{m} \qquad (1)$$

The peroxide value serves as a quantitative indicator of the presence of primary oxidation products of peroxides and hydroperoxides, i.e. oxidative changes occurring in fats.

In the experiments, a titrimetric method was used to determine the peroxide value, based on the ability of peroxides to oxidize hydroiodic acid with the release of free iodine [9]. Hydroiodic acid is formed as a result of the reaction of potassium iodide and acetic acid (2):

$$KJ + CH_3COOH \rightarrow HJ + CH_3COOK \qquad (2)$$

If the fat does not contain peroxide compounds, then free iodine is not released for 3-5 minutes. After this time, the release of free iodine becomes noticeable due to the oxidation of hydroiodic acid by atmospheric oxygen. The released iodine was titrated with sodium thiosulfate (3):

$$4\,HJ + O_2 \rightarrow 2J_2 + 2H_2O \qquad (3)$$

If the release of free iodine occurred immediately after adding acetic acid and potassium iodide to the fat solution, this indicated the presence of peroxide compounds in the fat.

To do this, a sample of oil was weighed into a flask with a ground stopper on an analytical scale based on the degree of expected oxidation of the oil being studied. 10 ml of ethyl alcohol and 15 ml of glacial acetic acid were poured along the wall of the flask, washing away traces of fat. Then 1 ml of freshly prepared 50% potassium iodide solution was added. The mixture was thoroughly mixed, then closed with a stopper and left in a dark place at a temperature of 15-25 °C. After 3 minutes, 75 ml of distilled water was poured into the flask, to which 5 drops of a 1% starch solution were added in advance, until a violet-blue color appeared. The released iodine was titrated with a 0.01 N sodium thiosulfate solution until a milky white color was obtained, which was stable for 5 seconds.

The peroxide value (PV, mmol ½O/kg) of fat was calculated using formula (4):

$$\text{ПЧ} = \frac{(V_0 - V_k) \cdot 0{,}001269}{m} \cdot 100 \qquad (4)$$

Where: Vo is the volume of 0.01 N sodium thiosulfate solution used to titrate the test sample, ml;

Vк is the volume of 0.01 N sodium thiosulfate solution used to titrate the control sample, ml;

0.001269 is the titer of 0.01 N sodium thiosulfate solution, g/ml; 100 is the conversion factor for 100 g of the analyzed oil;

m is the mass of the studied oil, g.

The oxidizing agent was an air flow in the amount of 20 l per hour. Samples of vegetable oils were taken at 3 g, and a parallel analysis was carried out for each sample. The criterion of antioxidant activity is the protective factor (PF), which is calculated by the difference in the induction period (an increase in the induction period indicates stable oxidative stability, the higher the induction period, the higher the oxidative stability of vegetable oils and fats) of vegetable oils treated with different reagents to reduce the iron content in them [11-13].

Results and discussion. As shown by the analysis of the conducted works on lipid oxidation, the sequence of the oxidation stage occurs according to the following mechanism of chain reaction: At the beginning of initiation, the methylene group of fatty acids is attacked by the hydroxyl radical located between the double bonds and releases the hydrogen atom. Then there is a rearrangement of the double bonds of the fatty acid, a shift of the radical group and its interaction with active oxygen, as a result of which an intermediate oxidation product appears - an unstable lipoperoxide radical. These radicals are often presented in the form of hydroperoxides and diene conjugates (primary oxidation products) of fatty acids. The resulting lipoperoxide radical reacts with other fatty acids in the medium, which leads to its neutralization and the formation of new lipoperoxide radicals, causing a chain reaction with the formation of new oxidized forms of fatty acids.

However, radiation in the presence of metal ions in the environment leads to the formation of branched forms of peroxides, which is facilitated by the production of electrons of metals by hydroperoxides according to the scheme shown in Fig. 2.

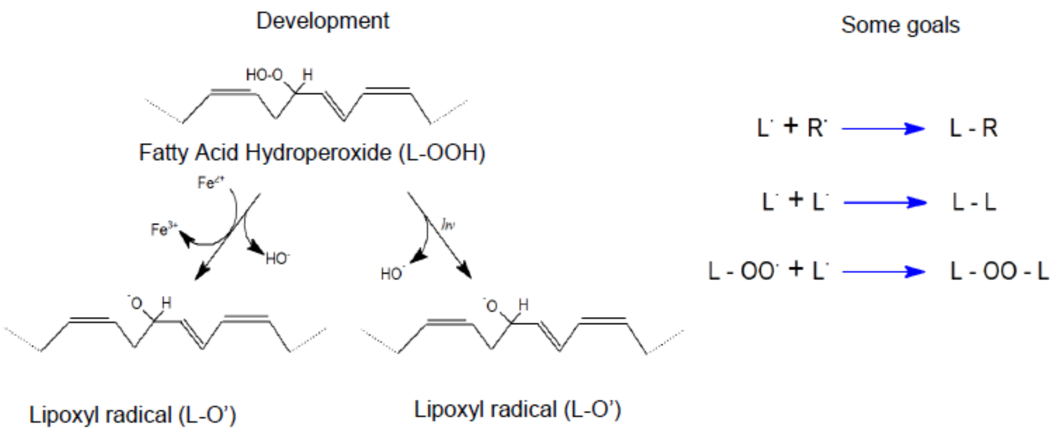


Figure 2. The fluttering reaction of the appearance of lipoperoxides

The primary products of peroxidation of fatty lipid systems are hydroperoxides, which undergo further decomposition to form secondary products of peroxidation, which include alcohols, aldehydes, ketones, and epoxy compounds. The most significant secondary product of peroxidation is malonic dialdehyde, the sequence of appearance of which is shown in Fig. 3.

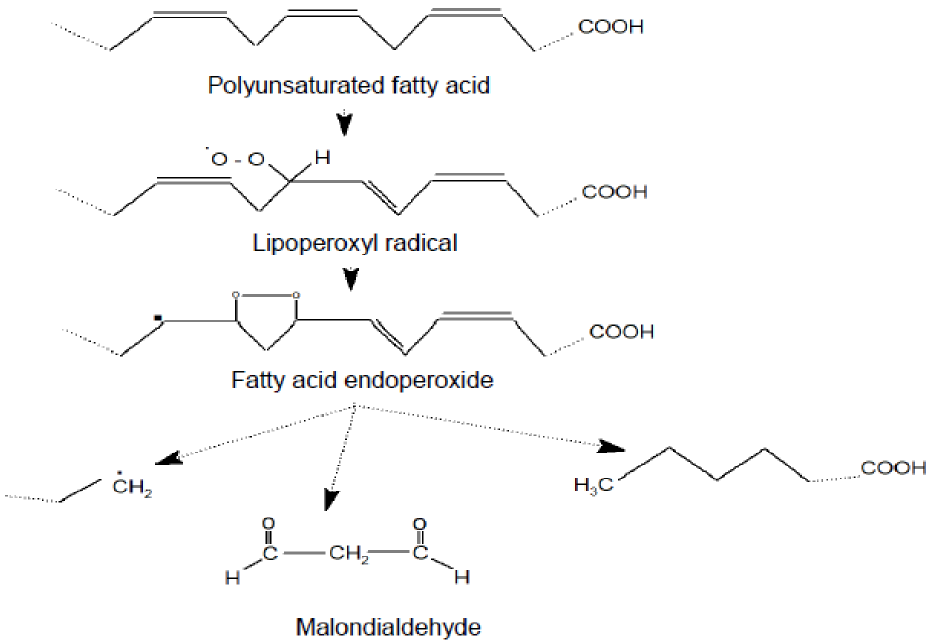


Fig. 3. The sequence of formation of malondialdehyde

Malondialdehyde promotes the formation of covalent bonds with NH2 groups of proteins and molecules of other Schiff base substances according to the scheme shown in Fig. 4

- moisture. The activity of enzymes, the activity of oxygen and hydroxyl groups, in general, the initiation of the oxidation reaction is not possible without moisture, even in small quantities;

- phospholipids. Lipid peroxidation is inextricably linked with the composition of phospholipids. Intensification of the process leads to an acceleration of phospholipid metabolism and a change in their composition. Also, the intensification of lipid peroxidation leads to the enrichment of lipids with fractions of phosphatidylcholine, sphingomneline and cholesterol that are more resistant to oxidation [21]. According to some researchers, lipid peroxidation is initiated by phospholipase. Phospholipase catalyzes the hydrolysis of phospholipid peroxides into fatty acid hydroperoxides.

- metals of variable valence. During lipid oxidation, despite their insignificant content, metals of variable valence are catalysts for the reaction, especially if during the decomposition of hydroperoxides by a single-electron mechanism [22, 23]:

$$Fe_{2}^{+} + ROOH \rightarrow Fe_{3}^{+} + RO^{\bullet} + OH^{-} \quad (6)$$

$$Fe_{3}^{+} + ROOH \rightarrow Fe_{2}^{+} + ROO^{\bullet} + H^{+} \quad (7)$$

The oxidation-reduction capacity of iron activates free hydroxyl and superoxide radicals [24]:

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^{\bullet -} \quad (8)$$

$$O_2^{\bullet -} + H^+ \rightarrow O_2 + H_2O_2 \quad (9)$$

$$Fe^{2+} + H_2O_2 \rightarrow OH^- + {}^{\bullet}OH \quad (10)$$

Accordingly, the hydroxyl radical is capable of separating a hydrogen atom from polyunsaturated fatty acids, which is the beginning of a chain reaction.

When the reaction medium contains substances capable of removing radicals from the reaction medium or regenerating oxidized products of natural antioxidants, a synergistic effect is observed. Synergists can be substances that have a weak oxidation-reduction potential and easily pass from the oxidized form to the reducing one. Such synergists in vegetable oils can be ascorbic and citric acids [29, 30].

At low concentrations, when the reaction medium contains metal ions with variable valence, vitamin C acts as a catalyst for the oxidation process. At high concentrations, when there are a sufficient number of centers for binding metals, vitamin C functions as an antioxidant [15, 29].

Thus, the process of free radical oxidation of lipids caused by the free oxygen radical •OH is a consequence of a complex of circumstances:

- the rate of the process depends on the fatty acid composition of the oil, the enzyme environment, temperature and moisture of the reaction environment;

- the quantitative content of accompanying substances, including phospholipids and ions of metals of variable valence, determine the duration of the oxidation period;

- the increased reactivity of lipid oxidation products determines two different types of their action in the human body. Primarily oxidized forms have a beneficial effect on the human body, consisting in hydrophilic-hydrophobic derivatives of phospholipids, with a change in the functional state of biomembranes and activation of enzymes;

- secondary products appearing in the process of propagation of oxidative processes, i.e. aldehydes and ketones destroy the functional state of biomembranes in the body. The most significant secondary product of peroxidation is malonic dialdehyde, which promotes the polymerization of membrane components and ultimately destroys the cellular structure, which is why it is a strong carcinogen;

- lipid peroxidation is initiated mainly by the enzyme phospholipase, which catalyzes the hydrolysis of phospholipid peroxides into fatty acid hydroperoxides;

- low content of variable metal ions in oils, in particular iron, activates and, conversely, a significant content inhibits the oxidation process. However, as studies show, the content of variable metal ions in vegetable oils is relatively low (approximately 1 mg / kg) and act as catalysts for the oxidation process, and therefore, like phospholipids, should be blocked and eliminated from vegetable oils.

In our opinion, using the above-mentioned regularities and the results of studies on the effect of antioxidants on the regulation of the lipid oxidation process, it is necessary to improve the technology of processing vegetable oils.

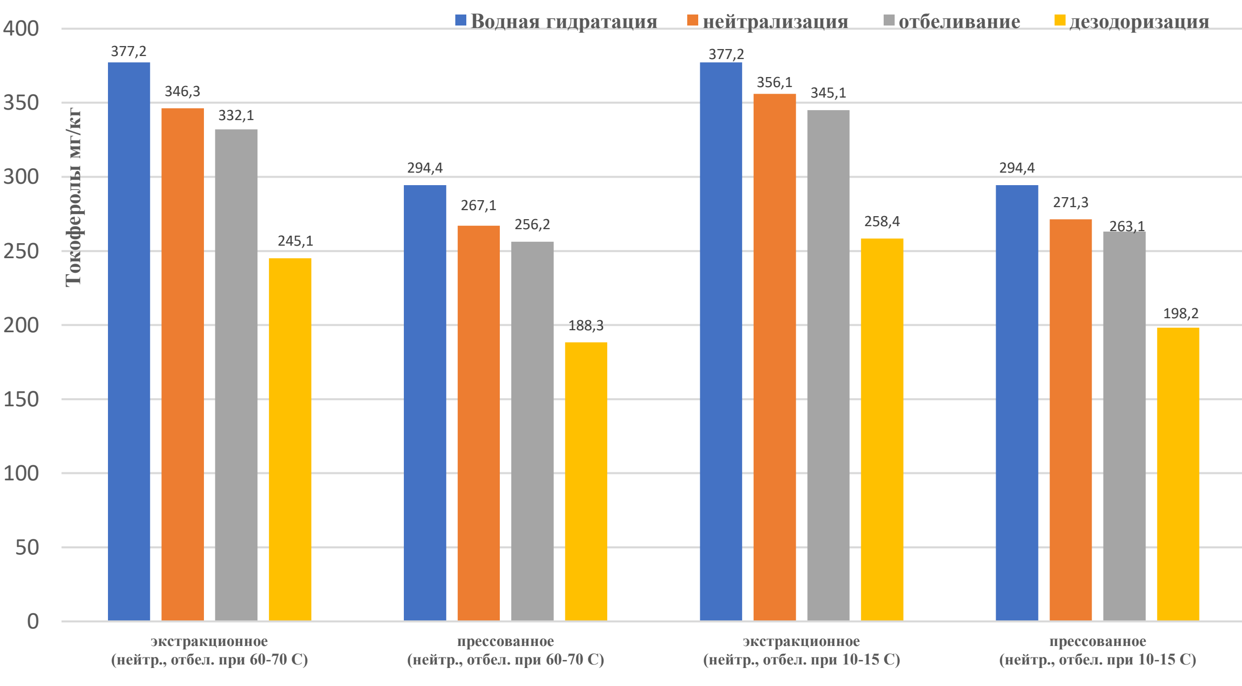


Fig. 5. Tocopherols content in rapeseed oil after each refining stage

Also, by carrying out various effects on unrefined rapeseed oil, the change in the content of phosphorus and iron in the oil was determined. Table 1 shows data on the change in the content of phosphorus and iron with different methods of processing rapeseed oil.

Table 1. Changes in the content of phosphorus and iron in rapeseed oil with different refining methods

Processing method	Content phosphorus	in iron	oil phosphorus	(mg/kg): iron
	Press	oil	Extraction	oil
Water hydration	61,4	0,5	85,6	0,9
Processing with MEA	7,5	0,2	9,6	0,4
Processing with DEA	12,3	0,3	18,9	0,7
Processing with TEA	14,3	0,4	21,5	0,8
TOP hydration	10,4	0,2	15,8	0,3
Neutralization (60-70 °C)	17,1	0,4	24,2	0,7
Neutralization (10-15 °C)	15,1	0,2	21,1	0,4

As can be seen from the data given in Table 1, monoethanolamine treatment was the most effective for removing phospholipids from sunflower oil, since this treatment reduced the phosphorus content to 7.5 mg/kg.

Iron ions are effectively reduced by TOP hydration and low-temperature neutralization at a temperature of 10-15°C.

Conclusions. Analysis of numerous studies by scientists on the nature of oxidation of vegetable oils shows that high-temperature treatment in the presence of enzymes, metal ions, phospholipid residues and various pigments, especially in a relatively humid environment, is a very important component in initiating the process of fatty acid autoxidation. Inhibition, or at least a decrease in the factors initiating the process of primary oxidation by forrefining in the presence of highly effective reagents leads to an increase in the shelf life of vegetable oils.

The refining process is complicated by the fact that it requires the preservation of some necessary substances, such as tocopherols, and at the same time the removal of accompanying substances that interfere with stability, such as iron ions, residues of phosphorus-containing substances, etc.

We have experimentally determined that water hydration of vegetable oils removes only a certain portion of phospholipids and iron. However, complete removal of iron can be a difficult task, and the degree of its removal depends on the specific method of processing vegetable oils.

Processing oils with ethanolamines (MEA, DEA, TEA) forms complexes with metals by chelation, which helps to reduce the iron content in the oil.

Neutralization and bleaching of vegetable oils at a temperature of 10-15°C leads to a lower iron content compared to processing at higher temperatures.

The method of processing MEA oils, TOP hydration and neutralization at 10-15°C followed by bleaching of vegetable oils is the most effective for removing iron, where the content in the oil is reduced by less than 0.2 mg/kg, which in the presence of tocopherols ensures long-term inhibition of oxidative processes activated by iron ions.

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