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EFFECT OF THE INFLUENCE OF HYDROLYZATE OF MOLLUSCS ON THE OXIDATION OF VEGETABLE OIL

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Abstract. Given the results of research of antioxidant properties of the hydrolyzate of molluscs; determined by the induction period the oxidation of sunflower oil and the constant of chain termination, which show the effectiveness of the use of hydrolyzate of molluscs as an inhibitor of oxidation processes.

Keywords: oxidation of lipids, oxidation inhibitors, hydrolyzate of molluscs

1. Statement of the problem

Oxidation of food fats is harmful process which causes them unsuitable for food application.

The modern technology of processing of vegetable oils provides a complete cycle of refining, during which they seized part of the natural substances, including antioxidants, which slow down intense oxidation of the oils [1].

The result of fat oxidation is a loss of essential nutrients such as unsaturated fatty acids, fat soluble vitamins, natural anti-oxidants and it's a change in the organoleptic characteristics of the product (taste, colour and consistency). Such changes have a negative impact on the nutritional value and quality, leading to a decrease in of expiration dates of fatty foods. [2]. Among the research priorities in the field of food processing and production of restaurant business, the solution for problem of ensure environmental cleanliness of the product and reduce the degree of oxidation of oils and products based on them is one of the most important problems.

Simple and effective methods of inhibition of oxidative deterioration of fat (especially during storage) are using the antioxidants. According to current trends in the development of foods as antioxidants is recommended to use natural antioxidant supplements that also increase the nutritional value of the product. Antioxidant is expedient to select an experimental way, determining the efficiency of the induction period largest oxidative transformations of fat - an antioxidant. [3].

2. Analysis of recent research and publications

On the question of inhibition of oxidation in vegetable oils using antioxidants worked many scientists. Among the Ukrainian researchers can be distinguished the works of Dr. Prof. I. Demidov, Kharkiv Polytechnic Institute Ukraine, doctoral research candidate of technical sciences V. Afanasyeva, M. Kamsulina, O. Korneyko, M. Ignatenko and others. Demidov I. experimental studies of antioxidant activity of the oil extracts of various plants, as well as the influence of tocopherol on their effectiveness. V. Afanasyeva proposed the use of antioxidant phytonutrients from natural herbs in the formulation of mayonnaise.

A significant contribution to the study of the oxidation of oils and the use of antioxidants made by scientists Prof. Jan Pokorn′y, Prague Institute of Chemical Technology; Dr. Honglian Shi, Cornell University Medical College; Dr. Noriko Noguchi and Professor Etsuo Niki, The University of Tokyo.

Despite the close attention to the protection of fats from oxidative damage by the researchers, this issue is far from complete solution. Step oxidation inhibitors (antioxidants) appear to increase the induction period and reduce the rate of oxidation. Depending on the origin inhibitors are divided into natural and synthetic [4, 5, 6]. Natural antioxidants according to the requirements of the Ministry of Health of Ukraine should be non-toxic, affordable and recommended for stabilization of edible oils. Some natural antioxidants compared with synthetic not only safe to use, but also increase the biological and physiological value of the stabilized products. That is why there is urgent study of the effect of natural antioxidants in the process of oxidation of fats in order to develop evidence-based process measures for their use.

Authors of the article suggest the use of the hydrolyzate of molluscs as the functional and

technological additive in emulsifying system based on vegetable oils. Composition of mollusc hydrolyzate is a mixture of amino acids and peptides simple, polyunsaturated fatty acids, macro- and microelements in a biologically active form. The primary raw materials for its preparation are complete proteins clams and mussels Rapana Black Sea. In the hydrolysis of proteins are broken down into amino acids and simple peptides, which are easily absorbed by the human body.

Studies have confirmed the health effects of the hydrolyzate on the human body, which includes an increase in immunity, prevent diseases that are the result of stress and physical exhaustion. It has antioxidant, allergies and radioprotective properties, has a positive effect on the cardio - vascular and hematopoietic systems, display the body of toxic elements and radionuclides.

Nutritional value of the hydrolyzate of mollusks as follows: in 100 g of molluscs hydrolyzate contain protein - 15 g, carbohydrates - 10 g, fats - 1 g, ash - 6 g, 109 kkal/456 kJ [7].

Hydrolyzate of molluscs is recommended as a dietary supplement as a secondary raw material biologically active substance - essential amino acids, taurine, glucosamine biopolymer type and melanoidyniv, macro-and micronutrients (especially calcium, zinc, manganese, copper) for total body strengthening and improving immunity prevention of diabetes and more. Protein hydrolyzate of molluscs is a patented dietary supplement [8].

The purpose of the article is to study antioxidant properties of molluscs hydrolyzate and possibility of using it not only as a dietary additive, but also as a processing additive of fat emulsion systems, for example as an antioxidant.

3. Material and methods

Authors of the article conducted a study of the antioxidant properties of the hydrolyzate of molluscs "Rapamid" [9].

The authors conducted a study of the properties of the hydrolyzate of molluscs as an antioxidant of the second group, the use of which is an important and effective action to prevent food spoilage due to the oxidation of fats in the presence of atmospheric oxygen. Analysis of the content of antioxidants in the hydrolyzate shellfish conducted by the method which consists in calculation according to the amount of oxygen absorbed by the time on the time during initiated oxidation of fat (oils) at elevated temperature. [9] Using this method, a certain amount of inhibitor added to cumene and the oxidation was conducted at volumetric installation at various concentrations of initiator (azoisobutyronitrile - AIBN).

4. The results of the research

It is known that depending on the rate of free radical chain oxidation of organic matter (in this case oil) on the rate of initiation can determine the nature of the oxidation of substances that determine the presence (or absence) of inhibitor in the system.

Depending on the rate of oxidation of fat (oil) from the initiation rate of oxidation can determine the nature of matter oxidation. In the presence of inhibitors of this dependence is described by the equation:

$$V_{o_2} = \frac{k_2 \cdot [RH]}{k_7 \cdot f \cdot n \cdot [InH]} \cdot V_i \qquad (1)$$

where

V_{O2} – oxidation rate, 10^{-7}mole/(dm^3 s);

V_i - –the rate of initiation of oxidation, 10^{-7}mole/(dm^3 s);

k_7 – the rate constant of chain termination;

k_2 – the constant of chain initiation, dm^3/(mole s);

f - coefficient of inhibition, which is equal to the number of chains, terminating one molecule of antioxidant;

[In] - concentration of antioxidants, mole/dm^3.

If the nature of the inhibitor is unknown (as in our case), then calculate its concentration, based on the known specific inhibitor (e.g., tocopherol). In this case, if the oxidation is carried out with different speeds substances to initiate, and then build the plot coordinates in $V_{O2} - V_i$ If the experimental points will form a straight line, this will indicate the presence of inhibitors in the system.

Antioxidants concentration (mole/dm^3) calculated by the formula:

$$[InH] = \frac{1 \cdot [AIBN] \cdot (1 - e^{-K_p \tau})}{f} = \\ = 0.48 \cdot [AIBN] \cdot (1 - 0.9999^{\tau}) \qquad (2)$$

where

[$AIBN$] – the initial concentration of the initiator, mole/dm^3;

K_i – the rate constant of decomposition of the initiator, which is calculated for the formula:

$$K_i = \lg A - \frac{E}{\Theta} \qquad (3)$$

where A – constant, A = 15.00;

E – activation energy of the reaction, E = 30.45 kcal/mole;

$\Theta = 4.575 \cdot T/1000$ - reduced temperature;

T – temperature, in °K;

$1 / f = 0.48$ – (1 – output radicals in one molecule of initiator decomposition); f – inhibiting factor which equals the number of circuits, which snap one molecule of antioxidant;

τ – the experimentally determined induction period, in seconds.

In calculating the concentration of antioxidants, in the formula (2) substituted molar initiator concentration, which was used in the experiment and calculated, and the induction period, which is determined experimentally. Repeatability of experience - five times.

During of experimentation beforehand modelling experiments were performed to cumene, hereinafter - the oxidation of sunflower oil. In cumene conducted four experiments (Table 1) depending on the concentration of the initiator and the rate of oxidation at a temperature of 69 °C. Before adding to the reactor hydrolyzate dissolved in xylene at a ratio of 1:3.

Table 1. Characteristics of experimental conditions on the cumene

No. of experiments	Concentration, cm^3			Oxidation rate (Wo_2) mole / (dm^3 s)
	AIBN	hydrolyzate	cumene	
1	0.2	0.1	3.0	$0.69 \cdot 10^{-7}$
2	0.3	0.1	3.0	$1.26 \cdot 10^{-7}$
3	0.4	0.1	3.0	$3.66 \cdot 10^{-7}$
4	0.5	0.1	3.0	$4.62 \cdot 10^{-7}$

To generate the graph in the coordinates of $O_2 \cdot 2.97 \cdot 10^{-7}$ mole – t·60s accepted the arithmetic mean of the results of the five experiments. Diagrams of dependence oxygen consumption by the time are shown in Figure 1.

Analysing the dependence can be judged on the linear dependence of the reaction of oxygen uptake solution of cumene. According to the experimental data calculated the rate of oxidation of cumene solution for different rates of initiation. Graph of these values is shown in Figure 2.

The straight line in Figure 2 indicates the proportional nature of the dependence, which is characteristic of a system with linear chain termination, that is, almost all of the free radicals "killed" by the molecules of the inhibitor, which means molluscs hydrolyzate manifest itself as an inhibitor of oxidative processes.

In the next phase of work it was tested the impact of the molluscs hydrolyzate on the oxidation of sunflower oil, which is held on a volumetric unit. For the oxidation reactor is placed in sunflower oil, initiator (AIBN) inhibitor, and a solvent.

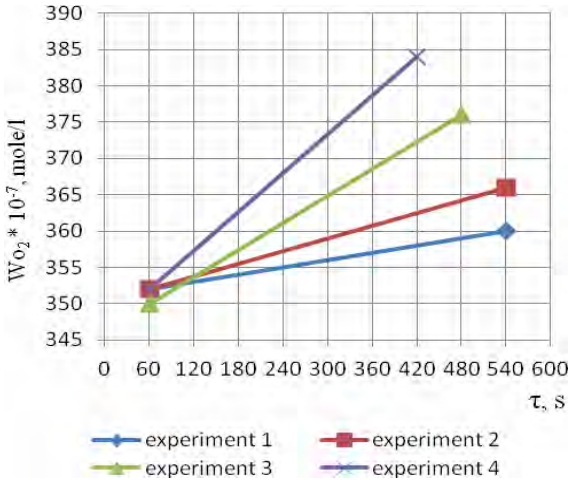

Figure 1. The dependence of the amount of oxygen absorbed by solution of cumene and oxidation reaction time

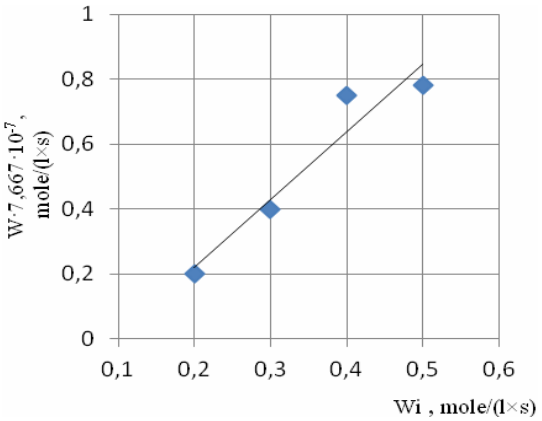

Figure 2. The dependence of V_{O2} - V_i for the solution of mollusks hydrolyzate in cumene

In the next phase of work was tested the impact of the molluscs hydrolyzate on the oxidation of sunflower oil, which is held on a volumetric unit. For the oxidation reactor is placed in sunflower oil, initiator (AIBN), inhibitor, and a solvent. At first conducted oxidation of sunflower oil in the mode initiated oxidation inhibitors, without supplements. Further, it was defined the induction period of the solution molluscs' hydrolyzate in sunflower oil. Graph of oxygen absorption sunflower oil sample times shown in Figure 3.

Experimental data confirm that the hydrolyzate of molluscs "Rapamid" has antioxidant properties. This is evidenced by the dependence of the rate of oxidation of cumene (with the addition hydrolyzate of molluscs) on the rate of initiation, which is a

straight line. The tangent of the slope of this line allows to determine the value k_2 [RH] / ($k_7 \cdot f \cdot n \cdot [In]$) and to assess the value of k_7 for the inhibitor of oxidative processes hydrolyzate of molluscs.

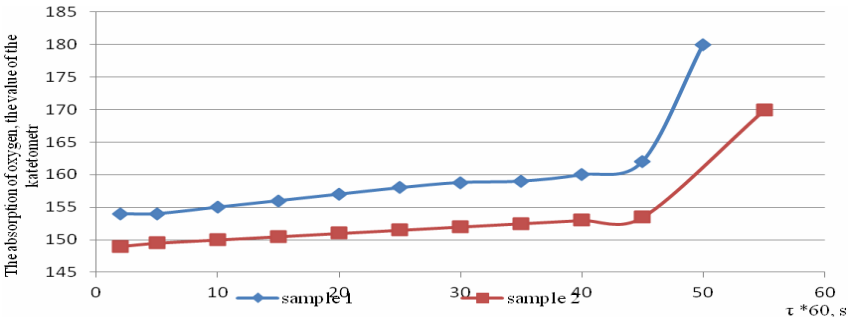

Figure 3. Graph of the oxygen absorption by the sample of sunflower oil at:
sample 1 - control (no inhibitor oil); sample 2 - oil with the addition of the hydrolyzate of molluscs

In calculating authors took into account that certain tangent of the angle incline of the straight line (Figure 2) is equal to 0.209. Inhibitor concentration (mass, on a dry solids) equal to 1.2 g/l.

In order to calculate $k_7 \cdot f \cdot n$ must use the formula:

$$k_7 \cdot f \cdot n = k_2 \cdot \frac{[RH]}{tg\alpha \cdot [In]} \qquad (4)$$

In calculating authors took into account that certain tangent of the angle incline of the straight line (Figure 2) is equal to 0.209. Inhibitor concentration (mass, on dry solids) equal to 1.2 g/l.

Since the content of antioxidant compounds in the dry matter of the hydrolyzate of molluscs is unknown, we assume that all dry solids are antioxidant substances. But it is unknown to us the nature of these antioxidant substances.

Assume (for evaluation calculation), that it's ionol (2, 6-ditert-butyl 4-methylphenol). For this substance M = 196, f = 2, n = 1. To estimate the k_7 need to know $k_2 \cdot$ [RH]. According to the reference data, the value of k_2 for cumene is

$$k_2 = 10^{6.67 \pm 0.34} \cdot e^{-\frac{(9800 \pm 400)}{RT}} \qquad (5)$$

The value of k_2, calculated for a temperature of 69 ˚C, is equal to 2.382 l/(mol·s) [10]. The concentration of cumene - [RH] is 7.17·2/5 = 2.836 mol/l. Thus the estimated value of k_7 for the hydrolyzate of molluscs, based on the ionol: k_7 = $2.6 \cdot 10^4$ l/(mole·s).

An estimate of the chain termination rate constants shows that the inhibitor contained in the hydrolyzate is effective, but its effectiveness as an inhibitor lies in the range between weak inhibitors and inhibitors of medium strength.

For comparison, the value of k_7 (dm^3/(mol·s)) for some natural antioxidants, which are used in the food industry: ionol – $1.2 \cdot 10^4$; catechol – $3.5 \cdot 10^4$; hydroquinone $5.1 \cdot 10^4$; hlorgen acid $2.6 \cdot 10^5$.

5. Conclusions

On the basis of these studies we can conclude that the hydrolyzate molluscs contain substances which give it the property of the inhibitor of oxidative processes. The induction period due to the introduction of the inhibitor is increased by 1.6 times. In terms of the rate constants of chain breaking antioxidant supplement is characterized as high strength and can be used as a complex antioxidant supplement. The prospect for further research is the analysis of molluscs' hydrolyzate as a source of antioxidants of the third kind and research of antioxidant properties of the hydrolyzate in the fat-containing foods.

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