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OBTAINING ANTIOXIDANTS FROM FOOD INDUSTRY WASTE AND THEIR USE IN FATS

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Abstract. The food industry generates a large amount of waste and by-products of processing, which becomes a problem for the environment. Potato and onion peel, tomato seeds and peel are agro-industrial wastes of the world's main vegetable crops. However, the potential for antioxidants from them is not yet fully known. In this work, the influence of extracts obtained from these wastes on the process of inhibition of the rate of oxidation of sunflower oil was studied. Regression equations describing the process of extraction of biologically active substances from crop production waste as a result of water-ethanol extraction at a temperature of 60°C were obtained. It was established that the optimum concentration of ethanol in the water-ethanol mixture of extractants is in the range of 70–80%. Increasing the extraction time has a positive effect on the yield of extractive substances (at an interval of 2–15 hours). The kinetics of oxidation of sunflower oil by the accelerated method was studied and the antioxidant activity of the obtained antioxidants was determined, which is: for onion peel 2.29 (ie at a concentration of antioxidant 200 mg/kg oil the induction period of sunflower oil oxidation is more than doubled). For potato peels, this figure is 3.17, and for tomato peels – 1.85. All antioxidants obtained from plant waste were no less effective than butylhydroxyanisole (antioxidant activity – 1.93). The effectiveness of antioxidants varied as follows: onion peel > potato peel > butylhydroxyanisole > tomato residues. The expediency of using ascorbic acid in the course of water-alcohol extraction of antioxidants from vegetable raw materials has been proven. It has a positive effect on increasing the output of antioxidants and on extending the induction period of sunflower oil as a result of its own antioxidant properties. The existence of a synergistic effect between ascorbic acid and substances extracted from potato, onion and tomato peel has been proven, which in numerical value is 163, 126, and 180%, respectively.

Key words: oxidation, antioxidants, antioxidant activity, potato peel, onion peel, tomato seeds and peel, sunflower oil.

Introduction. Formulation of the problem

An important part of a sparing approach to the resources of our planet is the use of waste from various industries. Such wastes of the agro-industrial complex as potato skins, onion skins, seeds and peels of tomatoes are found in landfills in gigantic volumes every year [1]. Taking into account the global trend of reducing individual processing of vegetables and increasing industrial or restaurant processing methods, the problem of not using these wastes can be solved, for example, by obtaining antioxidants from them. Today it is known that the peel of many plants contains a large amount of antioxidants [2]. Therefore, agricultural waste is a source of natural antioxidants.

Analysis of recent research and publications

One of the main problems in maintaining high quality fats is inhibiting their ability to oxidize spoilage. They easily enter into auto-oxidation, polymerization, etc. reactions. under the influence of oxygen, heat, light, oxidation catalysts [3]. This leads to a decrease in the nutritional value, quality and safety of foods containing fats, as well as changes in their sensory and physiological properties. The primary oxidation products are hydroperoxides. Under the influence of temperature and other factors, they quickly turn into secondary oxidation products (aldehydes, ketones, spits, hydroxy acids, epoxy compounds, etc.), which are significantly more toxic, have a certain taste and aroma, lead to a burning sensation in fat. Secondary oxidation products (as well as hydroperoxides themselves) in the human body cause mutagenesis, carcinogenesis, accelerate aging, cardiovascular disease [4]. Therefore, effective inhibition of the oxidation process in fats remains an urgent task of the food industry.

Antioxidant (AO) is a type of food additive used in the food fat industry to extend their shelf life, improve the appearance of various foods containing lipids / fats [4].

Synthetic antioxidants are derived from petroleum-based foods. They are economical, easy to process, effective, pure, readily available and harmless (if added in concentrations permitted by law). The recommended maximum level for butylhydroxyanisole (BHA), butylhydroxytoluene (BHT), tert-butylhydroquinone (TBHQ) and propylgalate in edible oils and fats is 200 mg / L (ppm) [5]. But synthetic antioxidants have many disadvantages: they are not easily metabolized by the human body, do not impart nutritional value to food products, do not exhibit antioxidant properties in human tissues [6], and cause liver damage and carcinogenesis [7]. BHT, TBHQ, PG and BHA exhibit toxic effects when taken for a long time and when taken in high concentrations [8]. Due to the various side effects of BHA and BHT, they are banned in the UK, Japan and other European countries. TBHQ is banned in European countries, Canada and Japan [9]. Therefore, there is a global trend away from the use of synthetic antioxidants in favor of natural. Despite the higher cost of natural antioxidants and their sensitivity to environmental factors (destroyed under the influence of high temperatures, radiation, pH, etc.), the following benefits of natural antioxidants should be highlighted: high consumer acceptability, safety, potential benefits for human health, increased biological food values and lack of safety requirements [4]. The problem of the high cost of natural antioxidants can be reduced by using plant waste as a raw material for their production.

According to the Food and Agriculture Organization (FAO), onions are grown in 126 countries [10]. The amount of waste from onion peeling is from 5 to 30% of the mass of raw materials. In [11], the antioxidant activity of ethanol extracts of yellow onion husks was studied in relation to aging laboratory rats. Oral intake of onion peel extract had a positive effect on the indicators of the antioxidant system of the liver and brain, but not on blood and plasma, mainly due to an increase in the activity of catalase and superoxide dismutase in the liver by 44% and 79%, respectively, and in the brain by three and 79% respectively. The extract contains Phenol, 2,4-bis (1,1-dimethylethyl), Phenol, 2,4-bis (1,1-dimethylethyl), 4-(3-Amino-1H-1,2,4-triazol-5-yliminomethyl) resorcinol, 2,6,10,14,18-Pentamethyl-2,6,10,14,18-eicosapentaene related to antioxidants [11].

The is characterized by a low economic value, which is a waste. However, this provision could be revised. According to the results of scientific research, in addition to carbohydrates (88.56%), proteins (0.88%) and fats (0.04%), onion skins contain high concentrations of biologically active substances with antioxidant activity [12]. In [13] it was proved that dry husk has a greater antioxidant activity in comparison with the juicy part of the onion. Contained in the peel of onions biologically active substances with antioxidant capacity, numerous and in their chemical structure belong to different classes: phenolic acids and their derivatives (gallic acid, vanilla acid), phenylpropanoids (ferulic acid), flavonoids of different classes: flavonols quercetin, kaempferol), proanthocyanidins (leukocyanidin), anthocyanidins (cyanidin, peonidine, delphinidine), and finally carotenoids (β-carotene) [14].

Potato peel is an agro-industrial waste of one of the world's major crops (ranked fifth in world agricultural production after cereals [1]). In the process of potato processing 100–120 kg/t of potato peels are formed [15]. Potato peel extract contains phenolic acids, mainly represented by chlorogenic acid, as well as gallic, ferulic, p-hydroxybenzoic, p-coumaric and trans-o-hydroxycinnamic acids [16]. Although other phenolic acids such as gallic, ferulic, p-hydroxybenzoic, p-coumaric, and trans-o-hydroxycinnamic can also be found [17].

Seeds and peels of tomatoes are waste of tomato processing, which are formed in quantities of 20–50 kg/t. These tomato residues are characterized by a high content of carotenoids (approximately 950 mg/kg): mainly lycopene, lutein and β-carotene, as well as phenolic compounds of quercetin and camferol [15,18]. Phenolic compounds have an ideal structure for neutralizing free radicals, since they contain phenolic hydroxyl groups that tend to donate a hydrogen atom or an electron to a free radical and have a conjugated aromatic system to delocalize a damaged electron [19]. On the other hand, carotenoids can interact with free radicals and are able to bind singlet oxygen due to their system of conjugated double bonds.

Thus, the high concentration of flavonoids and carotenoids in the peels of onions, potatoes and tomatoes makes these wastes of the agro-industrial complex a promising source of natural AO. Taking into account the data obtained on the antioxidant properties of these food production wastes, it is necessary to establish their effect on the inhibition of the oxidation of vegetable fats. It is necessary to study the kinetics of sunflower oil oxidation (the main commercial fatty product of Ukraine) in the presence of extracts from plant waste. The data obtained by different methods for determining the kinetics of oxidation have disagreements in absolute values. Therefore, it was decided to compare the obtained data on the antioxidant activity of plant extracts with the data on the kinetics of sunflower oil oxidation in the presence of a standard synthetic antioxidant, butylhydroxyanisole.

The purpose – to investigate the effectiveness of aqueous-alcoholic extracts from potato skins, onion skins, seeds and tomato skins in inhibiting the oxidation of sunflower oil, to evaluate their antioxidant activity in comparison with the effectiveness of the synthetic antioxidant butylhydroxyanisole (BHA) and propose options for increasing the efficiency of antioxidant extraction.

Objectives of the research:

1. Investigation of the process of water-alcohol extraction of antioxidants from potato skins, onion skins, seeds and skins of tomatoes, establishment of optimal extraction conditions.

2. Investigation of the influence of equal quantities of obtained antioxidants, as well as butylhydroxyanisole on the kinetics of sunflower oil oxidation.

3. Research on the influence of ascorbic acid on the efficiency of antioxidant extraction, as well as on the kinetics of sunflower oil oxidation. The search for synergistic effects between ascorbic acid and a complex of antioxidants from crop production waste.

4. Investigate the effect of the obtained antioxidants on the quality indicators of the oil as a result of its storage.

Research materials and methods

The work investigated potatoes of the Gala variety. Potato peels were obtained using a manual vegetable peeler to obtain a uniform peel thickness. Then the waste was crushed to obtain a powdery state (laboratory mill RRH-100 (Ukraine)) and dried in a vacuum desiccator connected to a vacuum pump at ambient temperature. The resulting raw materials were stored at a temperature of 5°C without access to light for no more than 2 weeks.

For research, only dry and clean peel of yellow onions was collected, crushed with the help of a laboratory mill brand RRH – 100 (Ukraine). The number of revolutions per minute – 28000, power – 700 W), after which the samples were sieved through a laboratory sieve with holes = 1 mm.

The seeds and peel of tomatoes were separated from other components of tomatoes of the Red Date variety by grinding through a sieve with a hole diameter of 1 mm. The resulting mixture was crushed and dried in a vacuum desiccator connected to a vacuum pump at a temperature of 40°C until constant weight. The resulting dry mixture was ground using a laboratory mill RRH-100, after which the samples were sieved through a laboratory sieve with holes 1 mm.

Refined deodorized oil (TM "Oleyna") with a volume of 1 dm^3 was used. The bottle was opened before the start of the study and stored at a temperature of 5°C without access to light for not more than 2 weeks.

To obtain extracts, the raw material prepared as described above was soaked in a mixture of ethyl alcohol – water in a glass flask, which was immersed in a water bath, heated to 60°C using a heating element of a magnetic stirrer and extracted for 6–24 hours with constant stirring. The temperature was controlled by a thermocouple. The flask was connected to a reflux condenser. The obtained extracts were stored at 5°C without access of light for no more than 2 weeks. An extract with an antioxidant content of 200 ppm was used in the study of the oxidation kinetics of sunflower oil.

Extraction in the presence of ascorbic acid was performed in the same way, but ascorbic acid in an amount of 4% relative to the weight of vegetable raw materials was first dissolved in a mixture of solvents ethyl alcohol – water.

The antioxidant activity (AOA) of the extracts was studied by volumetric method in the presence of an inert octane solvent in a manometric apparatus by oxidizing sunflower oil. Manometric unit measures the uptake of small amounts of oxygen by the sample. The unit consists of a reaction cell with a volume of 5 cm^3 thermostatic manometer, a system of connecting glass tubes and taps, which are connected to a source of pure (99.9%) oxygen and a vacuum pump, as well as a thermostat. Work with the installation includes the following stages: 1) preparatory stage: by connecting to the vacuum pump (through the two-way crane greased with vacuum greasing) there is an extraction of air mix from system of glass pipes of installation; by connecting to a source of pure oxygen (two-way valve) filling of installation with pure oxygen is reached. Such sequential operations are performed 5–8 times; 2) working stage: measuring the volume of oxygen absorbed by the sample in mm3 for a certain time by monitoring the change in the level of the column of colored liquid attached to the oil sample. By determining the constants of the reaction vessels of the installation, the obtained data of the oxidation kinetics of the samples in mm^3/min are converted into mol/s.

The study was performed under conditions of initiated oxidation, ie due to thermal decomposition of the AIBN solution (2,2′-azo-bis-iso-butyronitrile). Purification of AIBN was performed before a series of experiments. To do this, it was recrystallized from anhydrous ethanol, then acetone, then benzene. The introduction of the same number of AIBN achieved a constant rate of initiation. The study was carried out at a temperature of 70 ºC (± 0.1ºC). Concentration [AIBN] = $2 \cdot 10^{-3}$ mol / L for all samples. AIBN was dissolved in o-xylene (non-oxidizing solvent). The value of the induction period (τ_i) was determined by the graphical method [20] as a segment of the abscissa axis, cut off by a perpendicular from the point of intersection of those in contact with the kinetic curve.

The inhibition efficiency of the oxidation process of sunflower oil was determined by the set of reactions of the inhibitor and was designated as antioxidant activity, quantified by the formula AOA = τ_i / τ_s, де τ_i і τ_s, where τ_i and τ_s are the periods of induction of sunflower oil oxidation with and without an antioxidant, respectively.

The AOA of the studied antioxidants was compared with the AOA of the standard antioxidant, which was taken as butylhydroxyanisole in an amount of 200 ppm relative to oil.

To remove tocopherols from refined sunflower oil, it was passed through a layer of activated carbon (a filter with a layer of carbon was placed in a Buchner funnel, which was attached to a Bunsen flask. Then the oil was passed through a layer of coal several times – 10–20 using a vacuum pump).

To establish the nature of the combined effect of two inhibitors, we compared the simple sum of the induction periods of individual components (additive effect $\Sigma\tau_i$) and the gross efficiency of their mixture (τ_Σ) [20]. If, as a result of the combination of inhibitors, a greater value was obtained in the periods of induction ($\Delta\tau$) in comparison with the additive effect of inhibitors, that is, ($\tau_\Sigma > \Sigma_{\tau i}$), then a synergistic effect is established in the combined effect of inhibitors. Under conditions where the combined effect of antioxidants was less than the sum of the inhibition effects of two separate substances ($\tau_\Sigma < \Sigma_{\tau i}$), it is necessary to conclude that antagonism was detected in the combined effect of inhibitors.

The effect of synergism was evaluated by the difference $\Delta\tau = \tau\Sigma - \Sigma_{\tau i}$ and in relative units $\Delta\tau/\Sigma\tau_i$*100%.

Acid number (AV), peroxide number (POV) and p-anisidine (p-AnV) values were determined according to official AOCS 3d-63, Cd 8-53 and Cd18-90 methods, respectively.

Each experiment was performed twice, the article shows the average values between the two studies. The root mean square error of determining the induction period did not exceed 5%.

Results of the research and their discussion

Ethyl alcohol is a food solvent (biosolvent), safer compared to other organic solvents (acetone, chloroform, etc.), it is also proven that it gives high yields of phenolic compounds [21], its extracts have maximum antioxidant activity compared to other solvents [15]. Therefore, only ethyl alcohol and another environmentally friendly solvent, water, were used in the research [22]. Used during the extraction of a mixture of water and ethanol can be reused after distillation from the removed biologically active substances.

Investigated the effective parameters of the extraction of antioxidants from potato peels, onion peels, seeds and peels of tomatoes (Table 1). The maximum amount of extracted substances was evaluated as the desired result. The factors considered were the concentration of ethanol in the mixture of solvents (ethanol-water) and the duration of the extraction. Hydro modulus was equal to 1:5 in relation to dried and crushed raw materials. The extraction temperature is 60ºC. A higher temperature was not used due to destructive processes for phenolic compounds, which at the same time begin to occur in moderate amounts. The results of an active experiment by means of regression equations are shown in Table 1.

It was assumed that the dependence on the duration of extraction is logarithmic, and the dependence on the concentration of ethyl alcohol in the solvent mixture is quadratic (the presence of an extremum is possible). The values of the correlation coefficients (high) indicate the correctly chosen functional dependence. With an increase in the amount of ethyl alcohol, the amount of extracted substances also increases. However, when using 100% ethanol, the amount of extracted substances is not the maximum. The optimum lies in the range of 70–80% ethanol. The lengthening of the extraction time also has a positive effect on the yield of extractives.

The process of sunflower oil oxidation was studied by an accelerated method at 70°C under the conditions of initiated oxidation. The study of this process in native conditions (at ambient temperature and access to atmospheric oxygen) would require a long time (weeks for one sample). Establishing the content of oxidation products according to Codex Alimentarius standards does not give a complete picture: the peroxide number measures the content of only the primary oxidation products – hydroperoxides, the anisidine number – only aldehydes. The influence of other secondary oxidation products when the results of these methods are combined (which is also not correct) is not established, as is their role in the general process of oil oxidation kinetics. In the conditions of researches by a volumetric method we see results of the general process of oxidation - absorption of oxygen, an exit from the period of induction. The period of induction is a time interval when the oxidation process is very slow (oxygen is practically not absorbed). At the end of the induction period, the so-called catalytic oxidation begins, which is characterized by a high rate of oxidation (absorption of oxygen by the sample in large volumes). As a result of catalytic oxidation, fat quickly loses its nutritional value, accumulates significant amounts of oxidation products and no longer meets the requirements for food products. Therefore, setting the duration of the induction period corresponds to the shelf life of fat.

The obtained kinetic curves of the oxidation process are presented in Fig. 1. To study the antioxidant efficiency of the obtained extracts, samples with the maximum amount of extracted substances were selected. Butylhydroxyanisole (BHA) is one of the most common synthetic antioxidants [23], so it was decided to compare the antioxidant activity of the studied AO from crop waste with it.

According to Fig. 1 can be seen that the rate of oxidation of sunflower acid samples with the addition of restrained antioxidants is essentially reduced, with the greatest effectiveness of the antioxidant from the onion peel. The studied antioxidants in descending order of AOA look like this: onion peel> potato peel> BHA> tomato residues.

Table 1 – The results of an active experiment on the extraction of vegetable raw materials with aqueous-alcoholic solutions

Raw materials	Intervals of variation		The amount of extracted substances (y), % of raw materials (range of obtained values)	Regression equation describing the extraction process
	The amount of ethanol in the solvent (Mass fraction of ethanol in solution – x_1), %	Extraction time (x_2), hours		
Potato peels	0 40 70 100	2 5 7 10 15	2.88 – 5.02	$1.26+0.023*x_1+2.6*lg(x_2)+0.0058*x_1*lg(x_2) – 0.0002*x_1^2$, $R^2= 0.958$
Onion peels			1.5 – 3.1	$0.75+0.03*x_1+0.97*lg(x_2) – 0.00017*x_1^2$, $R^2= 0.964$
Seeds and peels of tomatoes			2.06 – 3.65	$1.77+0.017*x_1+0.32*lg(x_2)+0.0095*x_1*lg(x_2) – 0.00012*x_1^2$, $R^2= 0.867$

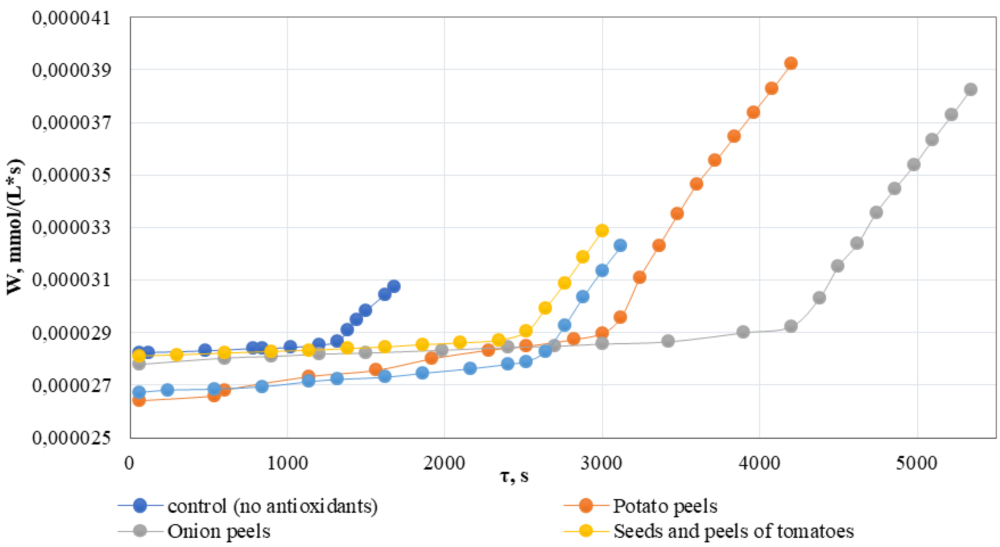

Fig. 1. Kinetics of initiated oxidation of sunflower oil without AO and in the presence of 200 mg/kg oil AO

Table 2 shows the obtained kinetic data of the initiated oxidation of sunflower oil in the presence of AO. All antioxidants obtained from plant waste were no less effective than butylhydroxyanisole (column 3 of Table 2).

Table 2 – Periods of induction of oxidation of sunflower oil without AO and their presence

The name of the antioxidant	The period of induction of oxidation of sunflower oil in the presence of plant extracts (200 mg/kg oil), s	Antioxidant activity (AOA)
Potato peels	3110 ± 40	2.29
Onion peels	4310 ± 50	3.17
Seeds and peels of tomatoes	2510 ± 40	1.85
Butylhydroxy anisole	2620 ± 70	1.93
Without the addition of antioxidants	1360 ± 60	-

The values for tomato residues and BHA are similar (AOA = 1.85 and 1.95, respectively), these AOs prolong the period of induction of sunflower oil oxidation almost twice. Potato peel extract slightly exceeds BHA in antioxidant activity (AOA = 2.29). And onion peel was twice as effective in inhibiting oil oxidation compared to VNA: AOA = 3.17.

In our other work, the feasibility of using food acids, in particular ascorbic acid, in the process of extraction of AO was established. Ascorbic acid is a strong antioxidant, and due to the ability to reduce the pH of the medium can increase the yield of AO in the extract. Therefore, ascorbic acid in an amount of 4% relative to the weight of the plants was added to the extractant and extracted according to the parameters described in table 3. The period of induction of oxidation of sunflower oil in the presence of 200 mg ascorbic acid/kg of oil was 2870 ± 50 s.

In the presence of ascorbic acid, the yield of extractives increases. From the weight of the sample of the extracted substances, the weight of the introduced ascorbic acid was counted.

Table 3 – Influence on extraction of AO from plant waste and on oxidation kinetics of ascorbic acid sunflower oil

The name of the antioxidant	Extraction parameters	The amount of extracted substances, %		The period of induction of oxidation of sunflower oil in the presence of AO extracted with ascorbic acid (200 mg/kg oil), s	Antioxidant activity (AOA)
		Without ascorbic acid	As a result of the introduction of ascorbic acid *		
Potato peels	Temperature – 60°C, duration – 8 hours, ethanol – 70%, hydromodule 1: 5	4.7 ± 0.21	5.8 ± 0.15	5450 ± 60	4.01
Onion peels		2.9 ± 0.18	3.6 ± 0.09	6660 ± 30	4.90
Seeds and peels of tomatoes		3.5 ± 0.10	4.2 ± 0.23	4620 ± 70	3.40

* The amount of extracted substances was determined by subtracting the amount of ascorbic acid introduced, % in relation to the weight of plant raw materials. Purpose – to establish the effect of ascorbic acid on the extraction of antioxidants from crop waste.

The result is additional extraction of extractive substances under the influence of acid in% in relation to the weight of the sample of plant waste (column 4 of Table 3). Thus, ascorbic acid has a positive effect on the extract of biologically active substances of plants in a water-alcohol solvent.

Periods of induction (column 5 of table 3) in the oxidation of sunflower oil in the presence of mixtures of plant AO and ascorbic acid are significantly longer than the periods of induction in the presence of only extracts of plant AO (Table 2). The AOA of the mixture of onion peel and ascorbic acid is 4.90, ie the period of induction of oxidation of sunflower oil is extended almost 5 times. The AOA for mixtures of ascorbic acid and potato and tomato peel is 4.01 and 3.40, respectively. The obtained data indicate the presence of a synergistic effect between ascorbic acid and extracted AO.However, to study the interaction of these AOs, it is necessary to get rid of the effect of the third antioxidant – tocopherols, which are always present in oils (even deodorized) in significant quantities and affect the oxidation process [24]. Tocopherols and tocotrienols were extracted from sunflower oil using activated carbon. Their absence in the obtained oil was checked by determining the oxidation kinetics of the oil (Fig. 2). The nature of the dependence (direct), which we see in Fig. 2, shows no induction period, ie the oil sample does not contain any antioxidants and does not inhibit the oxidation process.

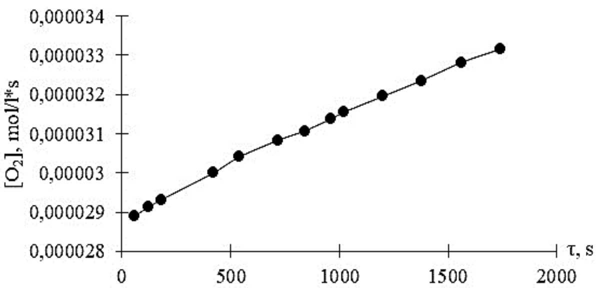

Fig.2 Kinetics of oxidation of sunflower oil from which tocopherols were extracted at a study temperature of 70°C and the amount of AIBN 2*10^{-3} mol/l

Next, the kinetics of oxidation of sunflower oil without tocopherols was investigated. To the sunflower oil was added 200 mg/kg oil AO obtained by extraction of plants, 200 mg/kg oil of ascorbic acid (an aqueous solution of ascorbic acid was added to the oil, water was evaporated under vacuum) and their mixture (100 ppm ascorbic acid and 100 ppm AO from plants). The results are given in table 4.

The effect of synergism was evaluated by the difference $\Delta\tau = \tau_\Sigma - \Sigma\tau_i$, where $\Sigma\tau i$ is the sum of periods of induction of sunflower oil oxidation in the presence of ascorbic acid and plant extracts, τ_Σ is the period of induction of the sample with total administration of ascorbic acid and AO. The period of induction of sunflower oil without tocopherols from 200 mg/kg oil of ascorbic acid was equal to 480 s.

Periods of induction in the presence of a mixture of AO (column 4) significantly exceed the simple sum of periods of induction of oxidation of sunflower oil in the presence of plant extracts (column 2) and in the presence of ascorbic acid. That is, the effect of synergism between ascorbic acid and antioxidant complex and potato peelings and onion peel and tomato peel is proved. The synergistic effect is significant for all samples studied (column 5). Maximum – for ascorbic acid and tomato extract. The mechanism of the synergistic effect between the antioxidant complex of the studied plants AO and ascorbic acid is probably related to the regeneration of phenoxyl radicals formed during the oxidation of plant phenolic compounds by ascorbic acid. Thus, these radicals re-enter the reaction of breaking the oxidation chains and further inhibit this process.

The influence of AO on plant waste on the quality of sunflower oil was studied. First of all, I was interested in their influence on the possible change in the taste and smell of oil. The most effective of the obtained antioxidants from onion peel was studied. It was characterized by the most intense aroma. The introduction of this antioxidant in the studied concentrations (200 mg/kg of oil) had virtually no effect on its organoleptic characteristics.

Table 4 – Results of oxidation kinetics of sunflower oil without tocopherols in the presence of extracts from plant waste, ascorbic acid and their mixtures

The name of the antioxidant	The period of induction of oxidation of sunflower oil in the presence of plant extracts, s	$\Sigma\tau_i$, s	The period of induction of oxidation of sunflower oil in the presence of plant extracts and ascorbic acid, s	Synergism of the obtained antioxidants and ascorbic acid, % ($\Delta\tau/\Sigma\tau_i$)×100%
Potato peels	570 ± 30	1050	1710 ± 60	163
Onion peels	640 ± 20	1220	1540 ± 50	126
Seeds and peels of tomatoes	450 ± 30	930	1780 ± 70	180

Table 5 – Qualitative indicators of sunflower oil before and after the introduction of antioxidant

Indicator	Deodorized sunflower oil	Sunflower oil is deodorized after 1 month of storage	Sunflower oil is deodorized after 1 month of storage with the content of AO onion peel (200 mg/kg oil)
Acid value, mg KOH/g	0.62 ± 0.20	0,66 ± 0.22	0.69 ± 0.17
Peroxide value, mmol½O/kg	1.09 ± 0.11	14.6 ± 0.19	2.1 ± 0.09
P-anisidine value	1.22 ± 0.34	1.31 ± 0.30	1.28 ± 0.33
Color number, mg of iodine	8	8	8
Taste and smell	Taste of impersonal oil, odorless		

The change in taste and aroma was barely noticeable and almost did not intensify when the oil was heated to 180°C (frying temperature in deep-fry).

The influence of the introduced AO on the change of oil oxidation parameters during its storage was also investigated. The oil was stored with access to oxygen at an ambient temperature of 25°C for 1 month. The results are given in Table 5.

Regarding oil storage – the introduction of AO had virtually no effect on the acid number of the oil. The amount of peroxides increased in the oil sample, which was not significantly protected by AO (from 1.09 to 14.6 mmol ½O/kg) and this indicator was stable in the oil sample with AO. The anisidine number has not changed. It is known that secondary oxidation products are slowly formed during low-temperature oxidation [25]. Thus, the effectiveness of protection of sunflower oil against the oxidation process in native conditions by antioxidant from onion peel is proved.

Conclusion

The process of water-alcohol extraction of antioxidants from potato peels, onion peels, seeds and skin of tomatoes was studied and the optimal extraction conditions were established. The process is described by the following regression equations:

$$1.26+0.023*x_1+2.6*\lg(x_2)+0.0058*x_1*\lg(x_2)-$$
$$-0.0002*x_1^2,\ R^2= 0.958 \text{ (potato peel)};$$

$$0.75+0.03*x_1+0.97*\lg(x_2)-0.00017*x_1^2,$$
$$R^2 = 0.964 \text{ (onion peel)}$$

$$1.77+0.017*x_1+0.32*\lg(x_2)+0.0095*x_1*\lg(x_2)-$$
$$-0.00012*x_1^2,\ R^2= 0{,}867 \text{ (tomato skins and bones)}.$$

The optimum concentration of ethanol in the water-ethanol mixture of extractants is in the range of 70–80% ethanol. An increase in the extraction time has a positive effect on the yield of extractives (logarithmic dependence in the range of 2–15 hours).

New data have been obtained on the effect of extracts of potato peels, onion peels, tomato peels and seeds on the process of sunflower oil oxidation. All antioxidants obtained from plant waste were found to be no less effective than butylhydroxyanisole. AOA tested at a concentration of 200 ppm antioxidant / kg oil for seeds and peel of tomatoes and BHA is practically the same, equal to 1.85 and 1.93, respectively. AOA for potato peels slightly exceeds this value for BHA (AOA = 2.29), and onion peel extract turned out to be the most effective antioxidant, AOA = 3.17, i.e. its introduction more than three times extended the induction period of sunflower oil oxidation.

The positive effect of ascorbic acid on increasing the yield of biologically active substances in the extraction of the studied plants and the positive effect on the prolongation of the periods of induction of oxidation of sunflower oil.

The AOA of the mixture of onion peel and ascorbic acid is 4.90, ie the period of induction of oxidation of sunflower oil is extended almost 5 times. The AOA for mixtures of ascorbic acid and potato and tomato peel is 4.01 and 3.40, respectively. The presence of a synergistic effect between ascorbic acid and extracted from potato peel, onion peel, tomato peel substances, which in numerical value is 163, 126, 180%, respectively.

As a result of research it is proved that AO from the wastes of the most common crops is not inferior in antioxidant activity to synthetic AO BHT, ie is a qualitative and safer replacement for synthetic AO. It is important that the introduced antioxidants in the studied concentrations did not change the quality and organoleptic characteristics of sunflower oil, so they can be recommended as antioxidants for fatty products for various purposes. Availability, cheapness and high AOA of onions, potatoes and tomatoes processing waste qualify them as a good source of antioxidants.

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ОТРИМАННЯ АНТИОКСИДАНТІВ З ВІДХОДІВ ХАРЧОВОЇ ПРОМИСЛОВОСТІ ТА ЇХ ВИКОРИСТАННЯ В ЖИРАХ

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Анотація. Харчова промисловість генерує великий обсяг побічних продуктів переробки та відходів, що стає проблемою для навколишнього середовища. Картопляна шкірка, лушпиння цибулі, кісточки та шкірка томатів – це агропромислові відходи одних з основних світових культур. Однак потенціал одержання антиоксидантів з них ще не до кінця відомий. В цій роботі досліджувався вплив екстрактів, отриманих з цих відходів на процес гальмування швидкості окиснення соняшникової олії. Одержано рівняння регресії, що описують процес екстрагування біологічно активних речовин з відходів рослинництва в умовах водно-етанольного екстрагування при температурі 60°С. Було встановлено, що оптимум концентрації етанолу в водно-етанольній суміші екстрагентів знаходиться в інтервалі 70–80%. Подовження часу екстрагування позитивно впливає на вихід екстрактивних речовин (на інтервалі 2–15 годин). Досліджено кінетику окиснення соняшникової олії прискореним методом та визначено антиоксидантну активність одержаних антиоксидантів, що становить: для антиоксидантів з екстракту лушпиння цибулі 2,29 (тобто при концентрації антиоксиданту 200 мг/кг олії період індукції окиснення соняшникової олії подовжується більше ніж у два рази), картопляних шкірок – 3,17, шкірки томатів – 1,85. Всі одержані з відходів рослин антиоксиданти виявились не менш ефективними за бутилгідроксіанізол (антиоксидантна активність – 1,93). Порядок ефективності антиоксидантів був таким: лушпиння цибулі > картопляна шкірка > бутілгідроксіанізол > залишки томатів. Доведено доцільність застосування в ході водно-спиртового екстрагування антиоксидантів з рослинної сировини аскорбінової кислоти. Вона впливає позитивно на збільшення виходу антиоксидантів і на подовження періоду індукції соняшникової олії в результаті власних антиоксидантних властивостей. Доведено наявність синергетичного ефекту між аскорбіновою кислотою та екстрагованими з шкірки картоплі, лушпиння цибулі, томатної шкірки речовинами, який у численному значенні становить 163, 126, 180% відповідно.

Ключові слова*:* окиснення, антиоксиданти, антиоксидантна активність, картопляна шкірка, лушпиння цибулі, кісточки та шкірка томатів, соняшникова олія