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THE INFLUENCE OF THERMAL PROCESSING ON OXIDATION STABILITY AND FATTY ACIDS COMPOSITION OF VEGETABLE OIL MIXTURE

The effect of thermal influence duration (45, 75°C) on the resistance to oxidation on sunflower and rapeseed oil mixture (ratio of mixture 55 : 45) has been investigated. It is shown that rise in temperature and an increase in the time of heat treatment (from 0 till 80 minutes) causes the oxidation processes: acid and peroxide numbers of oil mixture are increasing. In the process, the acid number of the blend after 40 minutes of treatment at 40°C and after 20 minutes at 75°C exceeds the permissible value (0.4 mg KOH/g); peroxide value meets the requirements (less than 10 mmol ½ O/kg) under all modes of heat treatment.

Fatty acid composition of individual oils and their mixture before and after heat treatment was set by chromatographic analysis. It was determined that the mixture examined does not provide recommended ratio of fatty acids Omega-6 and Omega-3. Heat treatment under the studied parameters has essentially no effect on the fatty acid composition of oils.

Key words: sunflower oil, rapeseed oil, compound oil, heat treatment, oxidation, peroxide number, acid number, fatty acids composition.

Introduction. Vegetable oils are widely used in the food industry because biologically active substances (BAS) comprise their composition [1, 2]. The most important biologically active substances to the human body are polyunsaturated fatty acids, among which the group of omega-6 and omega-3 acids are recovered (the first double bond is located, respectively, in the third or sixth carbon atom away from the terminal methyl group).

Polyunsaturated fatty acids, such as linoleic C18:2 (omega-6), linolenic C18:3 (omega-3), arachidonic C20:4 (omega-6), also relate to essential components of food; acids mentioned above are not synthesized in the body and must proceed with food. Deficiency of unsaturated fatty acids is one of the major deficiencies in the diet of modern man [3, 4].

PUFA can proceed to the body in different quantities, but for the best biological effect it is necessary to observe the ratio of omega-6 and omega-3 of fatty acids in the human dietary (5–10) : 1 [5]. However, none of the vegetable oils can ensure supply of essential fatty acids to the organism of human in the right quantities and ratio. One may achieve this by mixing (blending) vegetable oils containing polyunsaturated fatty acids of different groups. Examples of blends, balanced on fatty acid composition, consisting of two or more kinds of vegetable oils are given in the work [6–8]. According to the authors, the blends obtained can be used as salad oil as well as fat substrate for mayonnaises, sauces and other products.

To obtain fat products, vegetable oils almost always are subjected to thermal effect. This increases the intensity of the oxidizing processes caused by the presence of a large number of unsaturated fatty acids in oils, and has a negative influence on oil quality rating and product oils.

Main part. The work aims at studying the influence of the duration of the thermal effect on the oxidation stability and fatty acid composition of a mixture of sunflower and rapeseed-oil at a ratio of 55 : 45. This oil ratio in blending, in accordance with [5] must provide ratio, close to recommended for consumption ratio of omega-6 and omega-3 fatty acids.

Refined deodorized oil soft he brand II (the Republic of Belarus) were used for studies. Physical and chemical parameters of original vegetable oils and mixtures were predefined (Table 1).

Table 1

Physical and chemical parameters of oils

Designation of parameter	Rapeseed oil	Sunflower oil	Blending
Acid number, mg KOH/g	0.40	0.22	0.27
Saponification number, mg KOH/g	192.7	188.5	–
Peroxidate number, mmol ½ O/kg	2.44	2.86	2.57
Color value, mg J_2/g	14.3	8.7	–

Table 1 shows that the analyzed systems meet the requirements in edible oils by acid (less than 0.4 mg KOH/g) and peroxide number (not more than 10 mmol ½ O/kg) [9–10]. The saponification

number and color value are comparable with the data given in the literature [2].

Oxidation stability of oils was graded taking into consideration the change of the acid and peroxide numbers. Peroxide value describes the content of peroxides and hydroperoxides formed in the first stage of fat oxidation (primary products of oxidation), and the acid value – the content of free fatty acids, which are some of the secondary oxidation products of vegetable oils [1]. Definition of parameters was carried out in accordance with the reduced procedure [11].

The thermal treatment of vegetable oils and blending was carried out at 40 and 75°C under continuous stirring, on a magnetic stirrer of IKA RCT (Germany, 650 min^{-1}). The temperature and duration of heat treatment (20, 40, 60 and 80 min) are selected based on production mode parameters. Fig. 1 shows dependence of peroxide value on the duration of heat treatment.

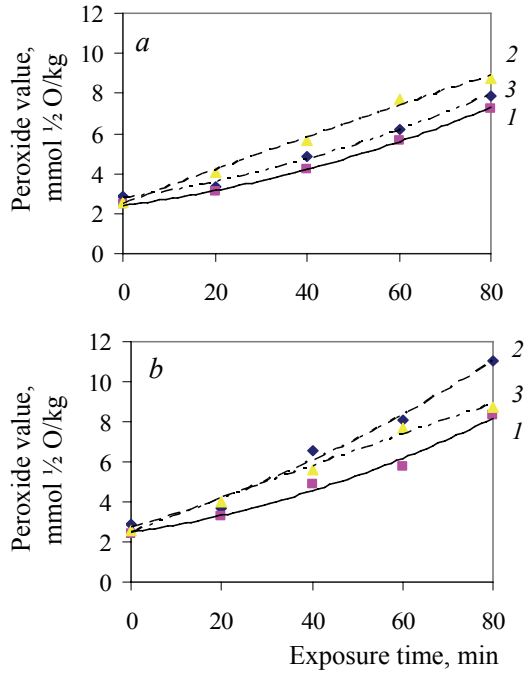

Fig. 1. The dependence of the peroxide value of rapeseed (*1*), sunflower (*2*) oil and their mixture (*3*) on the duration of heat treatment at temperature 40 (*a*) and 75°C (*b*)

The data given show, that with the increase of temperature and duration of thermal exposure, peroxide value increases for all systems. Most significantly this index increases for vegetable oil at the temperature of 40°C after 80 minutes it increases by 3.1 times, and at 75°C – 3.9 times compared with the rapeseed oil and the blending: under similar conditions the peroxide number increases for blending by 3.0 and 3.3 times, and for rapeseed oil by 2.9 and 3.2 times respectively.

It should be noted that after thermal treatment at temperature of 40°C (20–80 min) peroxide value of individual oils and their mixture does not exceed the standard. A similar result has been obtained after thermal treatment of rapeseed oil and blending at temperature of 75°C (20–80 min). The peroxide value of sunflower oil after 80 minutes of heat treatment at 75°C made 11.02 mmol $^1/_2$ O/kg, which does not meet the requirements to edible vegetable oils.

The data obtained testify the accumulation in all systems of primary oxidation products being unstable peroxides of different types. The oxidation of saturated fatty acids gives saturated hydroperoxides, while the oxidation of unsaturated fatty acids being present in vegetable oils in large amount gives unsaturated hydroperoxides. Hydroperoxides are unstable; they convert into secondary oxidation products – oxides and epoxy compounds, alcohols, aldehydes and others. Secondary products of oxidation of fats are acids formed in the result of destruction of the carbon chain of triglyceride molecules [1], so it was determined acid number of the studied systems. The data obtained are presented in Fig. 2.

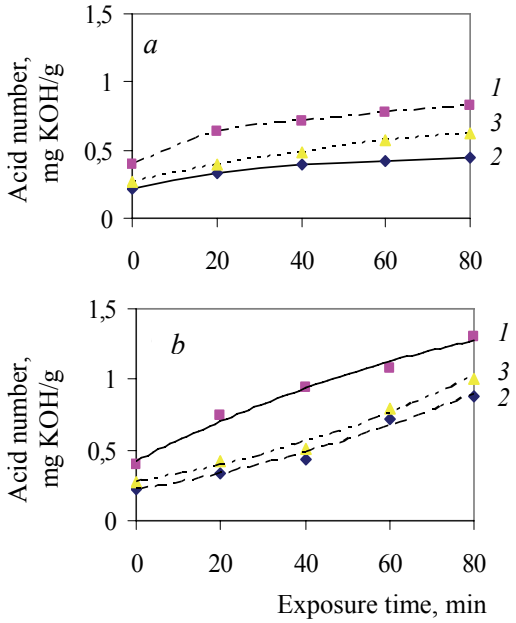

Fig. 2. Dependence of acid number of rapeseed (*1*), sunflower (*2*) oils and their mixture (*3*) on the duration of heat treatment at temperature 40 (*a*) and 75°C (*b*)

Fig. 2 shows that the heat treatment of oils within the analyzed study parameters leads to an increase in their acid number. Thus during the entire time interval acid number of rapeseed oil exceeds the allowable value irrespective of the processing temperature. For sunflower oil at 40°C even after 80 minutes of heat treatment index complies with the requirements, and at 75°C after 40 minutes this index comes out of range values. The acid number of the blending after 40 minutes of treatment at 40°C and in 20 min at 75°C is more than 0.4 mg KOH/g.

Table 2

The content of fatty acids in vegetable oils (%)

Fatty Acids	Rapeseed oil		Sunflower oil		Blending	
	before treatment	after treatment	before treatment	after treatment	before treatment	after treatment
Octane	0.02	0.02	0.02	0.01	0.01	0.02
Decanoic	0.01	–	–	0.01	–	–
Lauric	0.01	0.01	0.01	0.03	0.03	0.02
Myristic	0.07	0.07	0.08	0.10	0.09	0.07
Pentadecanoic	0.02	0.02	0.02	0.02	0.02	0.02
Palmitic	5.83	5.88	6.64	7.24	6.69	6.05
Palmitoleic	0.12	0.11	0.09	0.09	0.02	0.10
Cis-10-pentadecenic	0.04	0.02	0.02	0.02	0.02	0.03
Stearic	3.07	3.17	3.89	3.86	3.51	3.39
Oleic	31.27	31.10	23.52	23.93	26.97	26.72
Linoleic	53.92	53.32	63.21	62.45	59.32	58.84
Gamma-linolenic	–	0.02	–	–	0.01	–
Alpha-linolenic	2.64	2.68	0.16	0.15	1.11	1.24
Cis-11,14-eicozadienic	0.02	0.03	–	–	0.02	0.02
Erucic	0.15	0.16	–	–	0.06	0.06
Unidentified compounds	2.81	3.39	2.34	2.09	2.12	3.39

Different values of peroxide and acid numbers in the individual oils and their mixture, in our opinion, may be associated with different amounts of unsaturated acids comprising them which are more prone to oxidation, as well as having different content of tocopherols being associated components of vegetable oils referring to natural antioxidants. In the process of refining of vegetable oils the basic amount of tocopherols is removed, but in minor amounts they may be present in oils and influence their oxidation.

The increase in the acid number of vegetable oils may occur in connection with increasing of the acid content formed in the oxidation process of triglycerides. Therefore, the fatty acid composition of vegetable oils was studied before and after thermal effect (75°C, 80 min). The content of fatty acids in oils was defined by chromatographic method of analysis in accordance with [12]. The results are presented in Table 2. The results show, that the main amount of unsaturated fatty acids in the analysed systems comprise oleic and linoleic acids. They make up 86.29, 85.19 and 86.63% respectively in blending, rapeseed and sunflower oils before thermal treatment. The total content of unsaturated fatty acids after thermal processing decreased for rapeseed, sun flower oils and blending respectively by 0.79, 0.41 and 0.49%. The ratio of omega-6 and omega-3 fatty acids was almost unchanged and made: for rapeseed oil 20 : 1; for sunflower oil – 60 : 1; for blending – 53 : 1, which is significantly different from recommended (5–10) : 1.

Conclusion. The composition of sunflower and rapeseed oils selected for research on the basis of the published data did not give the desired ratio of omega-6 and omega-3 fatty acids. Since the quantitative composition of fatty acids of vegetable oils depends on various factors (plant varieties, growing conditions, the degree of maturity of seeds, etc.), one can be made a conclusion about the necessity of preliminary determination of fatty acid composition of oil before blending. Heat treatment of sunflower and vegetable oil mixture results to increasing of its peroxide and acid number (ratio 55 : 45). In the studied time interval, after thermal exposure at temperatures 40 and 75°C the peroxide number of the blending complies with the requirements for edible oils, while the acid value of the mixture is higher than the permissible one after 40 minutes of treatment at 40°C and after 20 minutes of treatment at 75°C. The data obtained also demonstrate the necessity of the introduction of antioxidants to stabilize vegetable oils subjected to thermal exposure.

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