

Research of high oleic sunflower oil properties under the hydrothermal effect

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Abstract

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Introduction. The modern life trend causes necessity of formation of the profile of choux pastry products consumer properties according to the principles: available, tasty, useful, comfortable. Studying the properties of the fat recipe component of the choux pastry in the conditions of technological process modeling will allow to control and provide the obtaining of competitive products.

Materials and methods. To evaluate the transformations that occur in the high oleic sunflower oil-water model systems during hydrothermal effect physicochemical research methods, namely the determination of acid (AV), peroxide (PV) and saponification values, were used.

Results. Obtained data confirm the growth of rate of hydrolysis and the accumulation of free fatty acids in the oil-water model systems due to medium's temperature (from 20 to 100 °C) and pH increase. AV magnitude is in the range 0,22...0,41 mg KOH/g at pH 4,5, 0,19...0,34 mg KOH/g at pH 6,0, 0,32...0,38 mg KOH/g at pH 8,0. The rapid growth of peroxide values is observed due to the temperature increase from 80...100 °C and is 3,90...4,70 mmol 1/2O/kg. The saponification values of model samples depends on the medium reaction and does not change in the temperatures' range from 20 to 100 °C. Those oil samples that were subjected to hydrothermal treatment at the alkaline medium (pH = 8,0) are characterized by almost unchanged acylglycerols' composition compared to the untreated oil and SN value of 191,0±06 mg KOH/g. The SN value of treated samples is some less and amounts at pH 4,5 – 186,0±0,5; pH 6 – 184,0±0,4 mg KOH/g. Thus obtained dependences of AV, PV, SV of high oleic sunflower oil on medium reaction of oil-water (1,0:2,5) model system and hydrothermal effect temperature evidence of its sufficient stability. The values of these indicators are within 0,19...0,41 mg KOH/g, 0,95...4,70 mmol 1/2O/kg, 184,0...191,0 mg KOH/g, respectively.

In the oil-water model system at pH=6,0 and hydromodule 1,0:2,5 insignificant accumulation of free fatty acids and primary oxidation products is observed, and AV and PV do not exceed 0,17 mg KOH/g and 1,55 mmol 1/2O/kg respectively at 20 °C.

The largest triacylglycerol oxidation rate during the first 20-60 s of hydrothermal treatment is observed for model system with pH 8,0, where PV increases in 2,3 times. PV increases in 1,4 and 1,2 times in systems with pH 4,5 and 6,0.

Conclusions. High oleic sunflower oil using as a source of fat in culinary products technology, particularly in technology of products based on choux pastry was experimentally proved extremely perspective.

Introduction

In the structure of human nutrition an important place is occupied by culinary products, among which the choux pastry products are in high demand [1-2]. Market research has shown that the range of culinary and pastry products with choux pastry at the domestic market is limited, the quality does not meet the requirements of today and their production technology needs an improvement. The modern trend of life dictates necessity of creation of a clearly formed profile of choux pastry products consumer properties, which will meet modern requirements: available, tasty, useful, comfortable. Performing of the aforementioned requirements will provide obtaining of the competitive products with high quality characteristics. It is known, that the realization of technological process of choux pastry products manufacturing is determined mainly by technical and technological properties of the fat component. The undisputed fact is that the final product's quality depends on the behavior of recipe components in the technological stream. The aim of this research was to study high oleic sunflower oil properties under the hydrothermal effect.

Analysis of scientific studies

Theoretical and practical aspects of the high oleic sunflower oil properties were studied by such scientists as K.M. Schaich, Xiaoqing Yang, Robin A. Boyle, S.M. Ghazani, A.G. Marangoni, Olesea Roman, G. Talbot, Bertrand Heyd, Bertrand Broyart, Roberto Castillo, Maria Teresa Rodriguez-Estrada, Claudia Belingheria, Barbara Giussani, Antonio Ferrillo, Elena Vittadini, . Analyze of existing technologies of choux pastry products determined that the fat component performs the following functions: recipe component, softener, complexing agent, baking powder, and a source of food and nutritional value [3, 8, 12-16].

Fat component of choux pastry is an important complexing agent. It interacts with other recipe components of the dough. By adsorbing at the surface of starch grains and wheat protein micelles fat screens part of hydrophilic groups, preventing their interaction with water and the formation of strong flour paste. Fat increases the plasticity of dough by weakening the connection between protein micelles and also starch polysaccharides of wheat flour. Found that in the process of making dough and baking it the intensive binding of lipids occurs – more than 75% of free lipids, including 90% of glycolipids and phospholipids and 66% of glycerides [4].

The activity of fat in the process of complexation greatly depends on its chemical composition, so different choux pastry fat components take part in forming of the structure of choux pastry and baked semi-finished products in different ways. Fats, that contain the mixture of triglycerides with the following composition: saturated fatty acids – 10...20% and unsaturated – 80...90%, show the greatest activity in interaction with flour proteins. The vegetable oil is characterized by this ratio of fatty acids.

Fat products, which are used in technology of dough products, perform the role of softeners of dough structure and improvers of product quality. Fats, which are included to recipe composition of choux pastry semi-finished products, perform the similar function. Monoglycerols show plastic characteristic more than diglycerols. According to the researches of Mikhailov V.S., Chekmariova I.B. and others the melting temperature and physical state of fat during the dough making process largely determine the degree of dough plasticizing.

One of the traditional fat components in the technology of choux pastry semi-finished product cooking is butter. Fatty acid composition of butter mainly comprises saturated fatty acids (63...65%) – palmitic and stearic, less monounsaturated (33...34%) – oleic acid and very small amount of polyunsaturated (1,1...3,6%) – linoleic acid. Deficiency of essential fatty acids and high price for butter urge consumers to search for alternative replacement to other raw material, despite butter's high nutritional value.

In world practice, there is some production experience of floury confectionery products with the oil addition. The use of oil allows to enrich products with unsaturated fatty acids, primarily the essential, and to reduce its cost by excluding butter and margarine products and attracting domestic raw materials [5-7].

S.M. Ghazani, A.G. Marangoni (Healthy Fats and Oils) discussed the main healthy minor components present in fats and oils, as well as their fatty acids composition. The major oils produced in the world were discussed, focusing on beneficial compounds naturally present in these oils. The effects of refining on the removal of desirable and undesirable minor components are also reviewed [8].

Gruner B.C. and Scherbova E.A. investigated the possibility of vegetable oil use instead of butter in the manufacturing of choux pastry semi-finished products. The researchers used sunflower and corn oil for this purpose. The oil pressing off didn't occur during baking the dough pieces. The taste and smell of cooked choux pastry semi-finished products did not changed significantly. The specific volume of choux pastry semi-finished products increased by 5-10% compared to the control samples, made using butter (replacement was equivalent 1:1, i.e. excluding the content of lipids in fat products) [9].

Mikhailov V.S. and Borodina T.P. showed the influence of vegetable oil (50 to 100%) amount on the quality of choux pastry semi-finished products [10]. In mentioned work it was revealed that the volume of semi-finished products increases with the increasing of vegetable oil content. However, the authors baked semi-finished products in non-traditional way, i.e. by dough pieces portioning at the pastry sheet, but in the forms, so these data can not be the basis for the development of choux pastry semi-finished products recipe, that uses vegetable oil as a fat component. Seeing during the baking at the pastry sheet, i.e. with the bigger surface of water yielding, the increase of vegetable oil amount in the dough would lead to a sharp decrease in dough's viscosity which would not let to obtain the semi-finished products of satisfactory quality.

Andrews S.L., Harte J. B.(Ingredient Functionality and Dough Characteristics) considered that fat contributes tenderness, or shortness, to pastry. 0004 Depending on the type of pastry, the fat content can range from 25% to almost 75% of the dough. Fat tenderizes pastry by waterproofing flour particles. The polar groups in water have an affinity for the polar groups in both the protein and starch. Polar carbonyl groups and the double bonds in unsaturated fatty acid moieties make it possible for fat to unite with polar groups on the surface flour particles. The remaining portions of the fat molecule have no affinity for the flour or water and act as a mechanical barrier, preventing contact of the water and protein in the flour. A fat's ability to interfere with gluten formation is 0005 known as its shortening power. Pure fats have more shortening power than do butter or margarine which contain 16% water. Even pure fats, such as lard, hydrogenated shortenings, and oils, exhibit different characteristics in a pastry product. Oil is more dense than lard, which is more dense than shortening. In addition, liquid fats have more spreading power and are able to coat flour more evenly and completely. The higher the ratio of liquid to crystals, the greater the covering power of the fat. [17].

Analytical data showed that the studies are preliminary, it is impossible to give scientifically grounded choux pastry semi-finished products recipe, which provides full or

partial butter replacement with vegetable oil, on their base. However, giving preference to vegetable oil including choux pastry semi-finished products technology will let to get a number of advantages. Therefore, the question of butter replacement with vegetable oil in choux pastry semi-finished products recipe is actual.

All this created the preconditions for searching for oil with the required properties. Researchers of the Plant Production Institute nd. a. V. Ya. Yuryev of NAAS managed to create sunflower hybrid whose oil is characterized by significantly increased oleic acid content and has similar to olive oil properties. The high oleic sunflower oil (HOSO) use will provide high nutritional value and oxidative stability of finished products. It should be noted HOSO's high ability to form complexes because of the peculiarities of the fatty acid composition, which affects the reactivity and the ability to form complexes with starch and protein substances contained in the dough.

Materials and methods

The dynamics of chemical reactions of high oleic sunflower oil under the conditions of hydrothermal process was studied in the oil-water model systems with volume ratio of 1,0:0,5; 1,0:2,5; 1,0:3,0. The composition and the ratio of fat and water (hydromodule) in a model system are chosen on the base of traditional choux pastry recipe, according to which it is 1,0:2,1, and with less and larger part of water in the system.

To estimate changes in oil-water model systems that occur during hydrothermal effects physicochemical research methods were used. Data of acid value (AV) showed the rate of hydrolysis of triacylglycerol in oil. AV was determined according to standard procedure as the number of potassium hydroxide milligrams required to neutralize free fatty acids contained in 1 gram of oil. For what oil sample was dissolved in a neutral mixture of ethanol with diethyl ether to further titration with alcoholic solution of potassium hydroxide in the presence of phenolphthalein.

Determination of primary triacylglycerol oxidation products in oil was carried out with standard iodometric method by peroxide value (PV). PV was determined by the number of active oxygen ($1/2O$) millimoles equivalent to I_2 separated from potassium iodide in glacial acetic acid by peroxides and hydroperoxides contained in 1 kg of oil. The peculiarity of the method was that sample after adding of the aqueous solution of potassium iodide to oil dissolved in a mixture of glacial acetic acid and chloroform was kept for 40-60 s in the darkness. Further formed iodine was titrated with sodium thiosulfate in the presence of starch solution.

In order to detect the possible deepening of hydrolysis with change of acylglycerol composition of oil due to hydrothermal influence an important for identification of fat indicator – saponification value (SV) was studied. SV as the number of potassium hydroxide milligrams required for saponification of acylglycerols and free fatty acids contained in 1 gram of oil was determined according to standard procedure. Samples of oil were treated with a solution of potassium hydroxide in ethanol and heated for 60² s in a boiling water bath, further the sample was titrated with hydrochloric acid solution in the presence of phenolphthalein.

The transformation of triacylglycerols of high oleic sunflower oil during hydrothermal influence was studied at different medium reaction pH (4,5; 6,0; 8,0), temperature (20...100 °C) and the duration of the process (5, 10, 20, 40-60 s).

The required medium reaction 4,5; 6,0; 8,0 of model system was provided by the addition to the water of citric acid, salt, baking soda accordingly in a certain quantity to achieve pH.

Maximum temperature and duration interval of hydrothermal exposure were chosen according to the traditional technology of choux pastry cooking, based on the dough boiling operation parameters (95...100 °C within no more than 10·60 s).

For an objective judgment about the degree of probability of the data obtained the mathematical treatment of the obtained results was made. The reliability of the results obtained was determined with the help of Student's coefficients for the taken statistical significance level of $P = 0.05$ and corresponding $(n-1)$ degrees of freedom.

Results and discussion

Hydrothermal processes belong to multifactorial difficult thermal processes that significantly affect the quality of the finished products. The dynamics of changes in the properties of fats in the technological system under the hydrothermal treatment depends on the temperature, time of treatment, the ratio of fat-containing products and water, i.e. hydromodule, presence of electrolytes, alkalis, acids solutions among the other food components [11-17].

Research results of high oleic sunflower oil physicochemical characteristics dependence on the pH and temperature in oil-water model systems with ratio 1,0:2,5 are presented accordingly in Fig. 1 and 2.

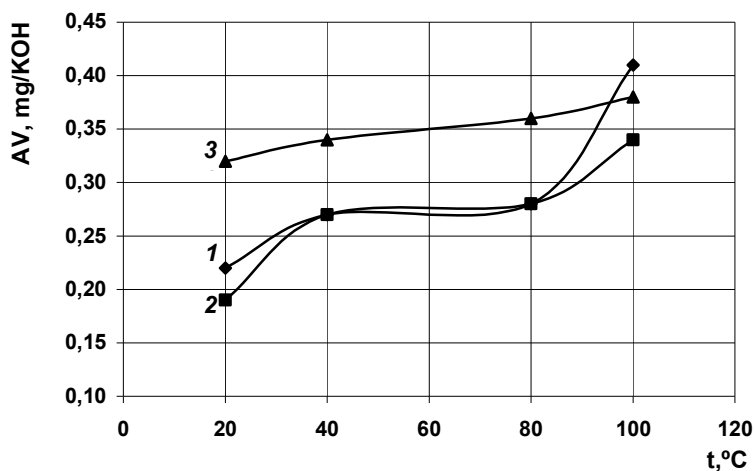
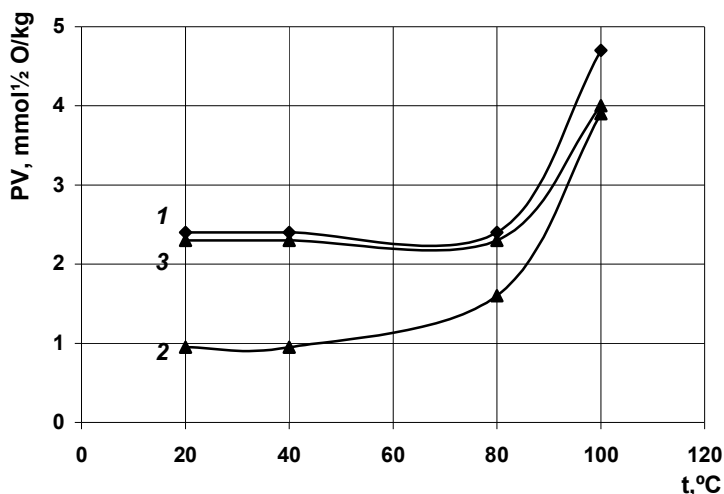


Fig. 1. Dependence of fat's acid value of oil-water (1,0:2,5) model systems on the temperature of hydrothermal influence and pH:
1 – 4,5; 2 – 6,0; 3 – 8,0

The experimental data (Fig. 1) show that the acid value of samples increases with the increase of hydrothermal influence temperature from 20 to 100 °C in model systems with acidic, slightly acidic and alkaline medium. AV magnitude is in the range 0,22...0,41 mg KOH/g at pH 4,5, 0,19...0,34 mg KOH/g at pH 6,0, 0,32...0,38 mg KOH/g at pH 8,0. Obtained data confirm the growth of rate of hydrolysis and the accumulation of free fatty

acids in model systems due to medium's temperature and pH increase. The greatest growth occurs when hydrothermal process flows in acidic medium (1) at the temperature of 100 °C. However, in alkaline medium (3) transformation is accompanied by the accumulation of more free fatty acids for the entire temperature range (20...100 °C) of hydrothermal influence.

The process of hydroperoxides' accumulation is confirmed by the results of the study of fat peroxide value change dynamics of oil-water model systems with ratio 1,0:2,5 respectively (Fig. 2).



**Fig. 2. Dependence of fat's peroxide value of oil-water (1,0:2,5) model systems on the temperature of hydrothermal influence and pH:
1 – 4,5; 2 – 6,0; 3 – 8,0**

It is clear from Fig. 2 that peroxide value increases for all samples of model systems at the investigated pH range with the temperature increase. The rapid growth of peroxide values is observed due to the temperature increase from 80...100 °C and is 3,90...4,70 mmol 1/2O/kg.

The results of dependence determination of fat's saponification number of model systems with oil-water ratio equal 1,0:2,5 respectively on high oleic sunflower oil base on medium reaction and hydrothermal treatment temperature are given in Table 1.

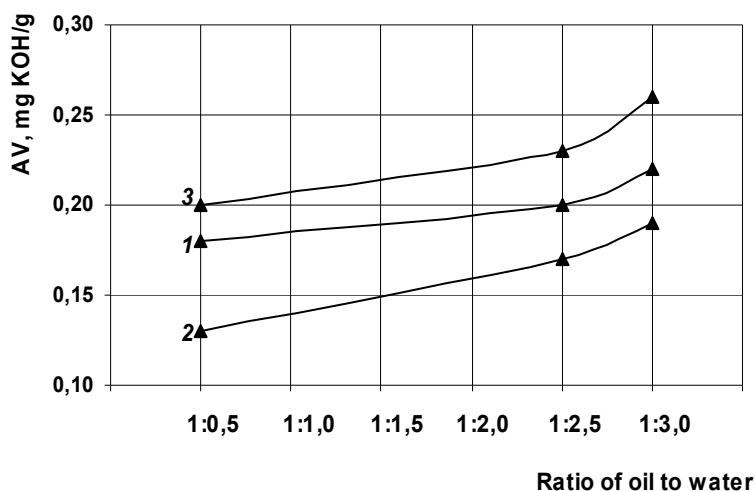
Table 1
Dynamics of the changes of fat's saponification value of oil-water (1,0:2,5) model systems due to pH and the temperature of hydrothermal influence

Temperature t, °C	Saponification value, mg KOH / g		
	pH=4,5	pH=6,0	pH=8,0
20 °C	186,0±0,5	184,0±0,5	191,0±0,6
40 °C	186,0±0,4	184,0±0,5	191,0±0,5
80 °C	186,0±0,5	184,0±0,4	191,0±0,5
100 °C	186,0±0,5	184,0±0,4	191,0±0,6

Data from Table 1 show that the saponification value of model samples depends on the medium reaction and does not change in the temperatures' range from 20 to 100 °C. Those oil samples that were subjected to hydrothermal treatment at the alkaline medium (pH = 8,0) are characterized by almost unchanged acylglycerols' composition compared to the untreated oil and SV value of $191,0 \pm 0,6$ mg KOH/g. The SV value of treated samples is some less and amounts at pH 4,5 – $186,0 \pm 0,5$; pH 6 – $184,0 \pm 0,4$ mg KOH/g.

Thus obtained dependences of AV, PV, SV of high oleic sunflower oil on medium reaction of oil-water (1,0:2,5) model system and hydrothermal effect temperature evidence of its sufficient stability. The values of these indicators are within 0,19...0,41 mg KOH/g, 0,95...4,70 mmol 1/2O/kg, 184,0...191,0 mg KOH/g, respectively.

Dependence of model systems fat's AV and PV on hydromodule and pH at the temperature of 20 °C is shown in Fig. 3 and 4.



**Fig. 3. Dependence of fat's acid value of oil-water model systems at the temperature of 20 °C on hydromodule and pH:
1 – 4,5; 2 – 6,0; 3 – 8,0**

Acid value (Fig. 3) increases in all oil-water model systems with increasing of water share that is the defining factor of oil hydrolysis deepening. Experimentally determined that the biggest AV and accumulation of free fatty acids characterize model system with hydromodule 1,0:3,0 at pH=8, which amounts 0,26 mg KOH/g, and the least – a model system with ratio 1,0:0,5 at pH=6, which amounts 0,13 mg KOH/g.

Growth dynamics of peroxide value in all model systems (Fig. 4) has a similar character. PV for systems with acidic (pH=4,5) and alkaline (pH=8,0) medium reaction almost coincide within the limits of experimental error. Larger PV characterizes oil-water model systems with ratio 1,0:3,0 respectively, and is: 2,15 mmol 1/2O/kg at pH 4,5; 2,31 mmol 1/2O/kg at pH 8,0; 1,91 mmol 1/2O/kg at pH 6,0. The oil-water system with hydromodule 1,0:0,5 respectively has the lowest PV: at pH 4,5 – 1,36 mmol 1/2O/kg; at pH 8,0 – 1,39 mmol 1/2O/kg; at pH 6,0 – 1,24 mmol 1/2O/kg. Peroxide value increase due to increasing the share of water in the system indicates an increase of oxidation rate of oil acylglycerols and accumulation of primary oxidation products, mainly hydroperoxides.

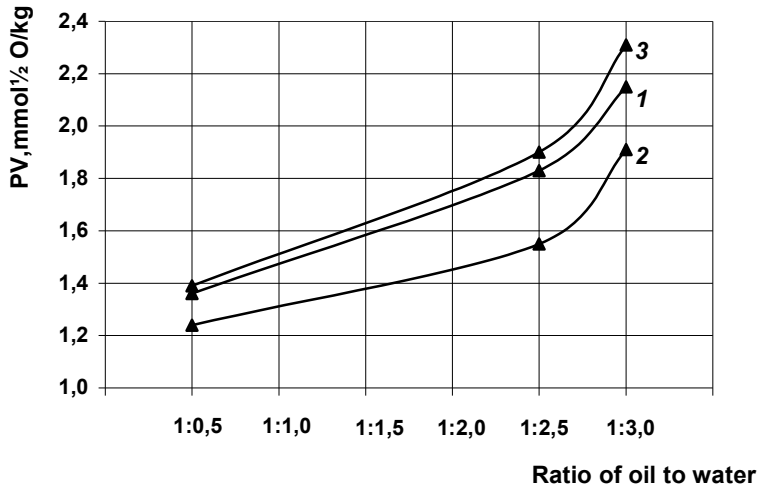


Fig. 4. Dependence of fat's peroxide value of oil-water model systems at the temperature of 20 °C on hydromodule and pH:
1 – 4,5; 2 – 6,0; 3 – 8,0

Therefore in oil-water model system at pH=6,0 and hydromodule 1,0:2,5 insignificant accumulation of free fatty acids and primary oxidation products is observed, and AV and PV do not exceed 0,17 mg KOH/g and 1,55 mmol 1/2O/kg respectively at 20 °C.

Effect of hydrothermal influence duration at the temperature of 100 °C on fat's AV and PV of oil-water model systems with hydromodule 1,0:2,5 at the different medium reaction is illustrated by dependencies, shown in Fig. 5 and 6.

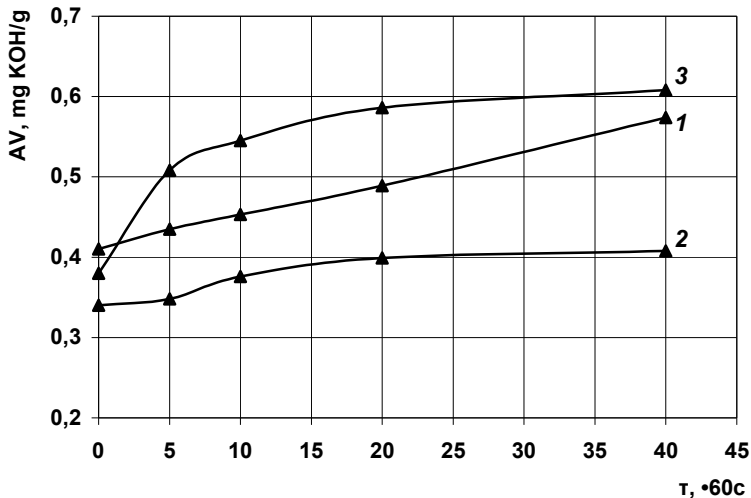


Fig. 5. Dependence of fat's acid value of oil-water (1,0:2,5) model systems on temperature treatment duration (100 °C) and pH: 1 – 4,5; 2 – 6,0; 3 – 8,0

Hydrothermal treatment duration increase leads to fastening of oil hydrolysis, what is demonstrated by the AV increase in model systems. Acid value increases during 40·60 s of hydrothermal influence at pH 4,5 in 1,4 times; pH 6,0 in 1,2 times; pH 8,0 in 1,6 times.

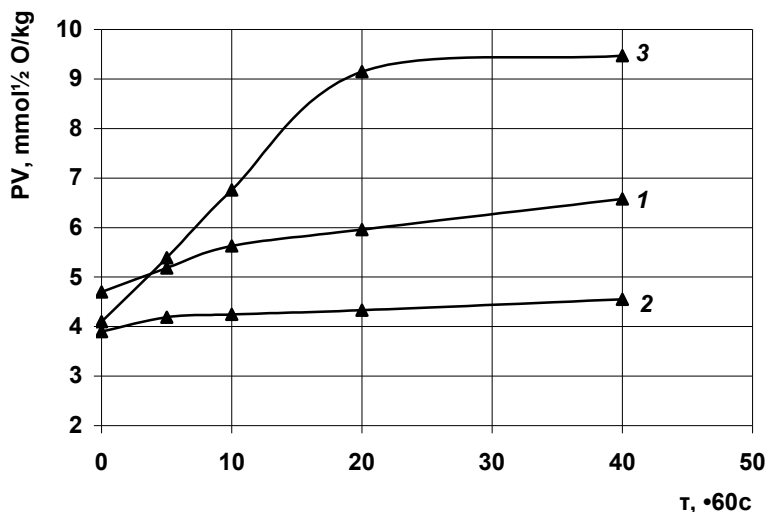


Fig. 6. Dependence of fat's peroxide value of oil-water (1,0:2,5) model systems on temperature treatment duration (100 °C) and pH:
1 – 4,5; 2 – 6,0; 3 – 8,0

The largest triacylglycerol oxidation rate during the first 20·60 s of hydrothermal treatment is observed for model system with pH 8,0, where PV increases in 2,3 times. PV increases in 1,4 and 1,2 times in systems with pH 4,5 and 6,0.

Conclusions

It was determined that chemical transformations of high oleic sunflower oil triacylglycerols, such as hydrolysis and oxidation, are not accelerated so significant during hydrothermal processes in oil-water model systems with different medium reaction (pH 4,5; 6,0; 8,0). Oil reveals sufficient thermal stability and resistance to peroxidation, and maximum AV and PV values do not exceed 0,61 mg KOH/g and 9,50 mmol 1/2O/kg respectively under the conditions of increasing of water proportion in the system (1,0:0,5; 1,0:2,5; 1,0:3,0), raising of the temperature to 100 °C and thermal treatment duration to 40·60 s. Rational conditions for hydrothermal process for model systems oil-water were determined, under which the AV and PV do not exceed 0,34 mg KOH/g and 4,10 mmol 1/2O/kg respectively. According to these conditions temperature is 95...100 °C, duration is 5·60 s, oil-water hydromodule– 1,0: 2,5. High oleic sunflower oil using as a source of fat in culinary products technology, particularly in technology of products based on choux pastry was experimentally proved extremely perspective.

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