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DEGUMMING OF SUNFLOWER OIL WITH DEGUMMING AGENTS BASED ON FLOUR

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One of the main directions of development of the food industry is to increase the safety and quality of products, the development of new technologies that use soft treatment regimes with the rejection of the use of additional chemicals. The article proves the effectiveness of degumming of sunflower oil when using aqueous suspensions of wheat and pea flour: degumming in the presence of 0.1% wheat flour and 0.06% citric acid reduces the phospholipid content in refining oil to 0.04% in terms of stearooleolecitin (when using 0.1% pea flour and 0.06% citric acid –up to 0.045%, respectively). The efficiency of degumming when using starch solutions is much lower: under the same conditions of degumming (0.1% starch and 0.06% citric acid), the final phospholipid content in refining oil is 0.075%. Degumming agent based on polyvinyl alcohol was the most effective (phospholipid content in refining oil – 0.039%), but due to its synthetic nature, we consider more promising to use moisturizing agents based on flour. The obtained refining oils meet all the main quality indicators, and such indicators as phospholipid content, acid value, peroxide value, color are significantly lower compared to the results of traditional degumming (aqueous or acidic). Also, degumming cleansing with wheat or pea flour can be recommended for oils of low quality, with the alignment of quality indicators to values that meet the requirements of regulatory documents. Equalization of oil quality due to the adsorption effect of flour looks like a promising approach due to safety and low cost. The possibility of delamination of the wet gum with the separation of 40% of the aqueous phase by heating it to 70 °C in the presence of 5% sodium chloride was investigated. It is proposed to use the obtained wet gum with high protein content without drying. Such a phospholipid product will be characterized by a higher biological value as a result of the absence of destructive thermal exposure.

Keywords: *degumming, phospholipids, sunflower oil, flour, wet gum, sodium chloride.*

ГІДРАТУВАННЯ СОНЯШНИКОВОЇ ОЛІЇ З ГІДРАТУЮЧИМИ АГЕНТАМИ НА ОСНОВІ БОРОШНА

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Доведено ефективність гідратування соняшникової олії за умови використання водних суспензій борошна пшеничного та горохового. Гідратування за наявності 0,1% пшеничного борошна та 0,06% лимонної *кислоти приводить до зменшення вмісту фосфоровмісних речовин у гідратованій олії до 0,04% у перерахунку на стеаролеолецитин. Досліджено можливість розшарування фосфоліпідної емульсії в разі застосування деемульгатора (хлористого натрію).*

Ключові слова: *гідратування, фосфоліпіди, соняшникова олія, фосфоліпідна емульсія, хлорид натрію.*

Statement of the problem. Phospholipids are the main polar lipids of vegetable oils. They have an amphiphilic nature – they consist of a polar hydrophilic part (phosphate group with a nitrogen-containing residue) and a non-polar lipophilic part (two fatty acid residues) – Fig. 1. Phospholipids are widely used in food, pharmaceutical, leather, textile, paint, chemical, cosmetic, perfume industry, agriculture and medicine [1]. In most cases, the use of phospholipids is associated with their surface activity.

The main functions of phospholipids in food are related to emulsification. Phospholipids are able to form and maintain in a homogeneous state both direct and inverse emulsions (depending on the ratio of hydrophilic and hydrophobic groups in their molecules). Also often used the ability of phospholipids to anti-splash, stabilization of various systems, defoaming, the ability to prevent adhesion of products to different materials, etc. [2]. Phospholipids improve the taste and smell, the consistency of food, so they are of interest to workers in the confectionery industry during the development of new recipes for chocolate and flour products.

Commercial phospholipids are mainly derived from vegetable oils. Due to the presence of a hydrophilic part, they are able to separate from oils when exposed to water.

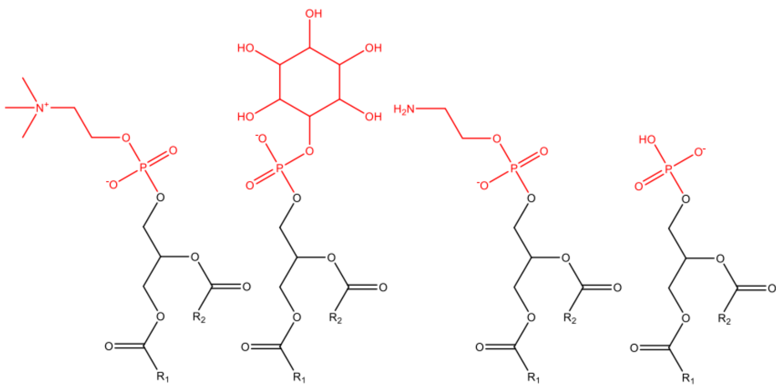

Fig. 1. Structure of glycerophospholipids (from left to right: phosphatidylcholine, phosphatidylinositol, phosphatidylethanolamine, phosphatidic acid)

This process is called hydration. A lipid layer of phospholipids and triacylglycerols is formed on the surface of water droplets introduced into the oil during hydration. Phospholipid molecules, which are highly hydrophilic, diffuse from the bulk of the oil to this surface and gradually displace neutral lipids, saturating the layer on the droplet surface. As a result of different densities, phospholipids with water (as well as a part of neutral lipids) gradually concentrate in the lower part of the hydration reactor and are separated, as a rule, by centrifugation. The thus obtained wet gum (water ≈70%, phospholipids ≈18%, oil ≈12%) is dried and a commercial product is obtained –lecithin (phospholipid content ≈60%, oil ≈35%, water – 1%).

The simplest cheap and environmentally friendly way to refining is to use water. However, it is impossible to achieve low values of phospholipids in degumming oil. Only the phosphatidylcholine and phosphatidylinositol groups are completely hydrophilic. The hydrophilicity of others depends on the pH of the medium (Table 1): the molecule of phosphatidylethanolamine has a positive charge (ie becomes hydrophilic) at pH = 2. The molecule of phosphatidic acid in an acidic medium will not dissociate, when the pH rises to values greater than 5, the molecule acquires a negative charge, which makes it hydrophilic. Alkaline earth metal salts of phosphatidic acid remain in the oil at any pH value, because divalent calcium or magnesium form a salt with two dissociated hydroxyl groups of the phosphate residue. They are part of the so-called non-hydrated groups of phospholipids (NGF).

Table 1

Charging of phospholipid groups at different pH values [3]

pH	Phosphati-dyl-choline	Phosphatidyl-ethanolamine	Phosphati-dyl-inositol	Phosphatidic acid	Salts of phosphat idic acid
2	+	+	0	0	0
3	(+)	(+)	(0)	(0)	0
4	(±)	(±)	(–)	(–)	0
5–7	±	±	–	–	0
8–9	±	±	–	(2–)	0
>10	±	–	–	2–	0

Review of the latest researche and publications. Degumming aims to remove phospholipids from the oil as completely as possible. The industry most often uses degumming with solutions of acids (phosphoric, sulfuric, citric, etc.), which allow to remove phosphatidylethanolamine, phosphatidic acid from its salts, ie convert NGF into hydrophilic form. The main disadvantage of their use is the introduction of additional chemical compounds into the oils, which as a result of refining remain in the phosphatide concentrate. Recently, enzymatic degumming has become more common, using phospholipases A (PLA1 and PLA2) and phospholipase C (PLC), which increase the hydrophilicity of phospholipids by separating fatty acids (PLA1 and PLA2) or phosphatidic acid containing a group with nitrogen (PLC) [4]. Significant disadvantages of the enzyme approach to degumming are its price, process duration (4–8 hours), complexity of control, etc.

Other common refining methods, such as super-degumming and caustic refining, use a combination of acid refining and alkaline neutralization [5].

Modern technologies must meet the requirements of low cost, safety, no harsh effects (temperature, extractant, etc.) on the oil.

It is known that phospholipids and proteins form all cell membranes without exception due to the presence of hydrophilic and hydrophobic groups in phospholipid molecules. On the same features of the structure of phospholipids is based the now popular direction – the construction of liposomal systems based on phospholipids for drug transfer [6] Liposomes are microscopic fat particles filled with liquid, the shell of which consists of molecules of the same natural phospholipids [7].

That is, when aqueous suspensions of proteins are added to the oil, they will form bonds with phospholipids on the surface of the water droplets, which will increase the efficiency of the degumming process. An important effect of several mechanisms – prevention of "sticking" of water droplets (polar substances in a non-polar medium are collected in isolated clots), the presence of proteins by reducing the surface tension between the phases will lead to a more uniform distribution of degumming agent in oil. The dispersion of the degumming agent in the fat has a very significant effect on the effectiveness of degumming. Increasing the density of these associates will facilitate their separation from the oil. The charge of proteins depends on the pH of the medium: in an acidic medium they carry a positive charge (ie can increase the yield of phosphatidylethanolamine), in alkaline – a negative charge (probably can increase the efficiency of phosphatidic acid extraction).

In general, the idea of using other emulsifiers in a mixture with degumming agents is constantly attracting the attention of experimenters [8]. There is a method of use as a degumming agent of wheat flour in a ratio of flour:oil as 1:1 [9]. However, in this way, the consumption of flour is high, and also loses an unacceptable amount of oil that remains on the flour.

It would be interesting to find out how effective the technology degumming using high molecular weight refining agents can be, that is, how low the final phospholipid content in oils can be obtained.

The objective of the research: to increase the efficiency of degumming and obtain refining sunflower oil with a phospholipid content of less than 0.05% in terms of stearooleolecithin.

*Methods.*As raw material for refining was used unrefined sunflower oil with the following quality indicators: phospholipid content,% in terms of stearooleolecithin – 0.60 %, acid value– 0.8 mg KOH/g, peroxide value – 6.7 mmol½ O/kg, moisture content, % – 0.18%, mass fraction of non-fat impurities – 0.02%, color – 18 mg of iodine.

The following were used as degumming agents: distilled water, first grade wheat flour (according to DSTU 46.004-99), polyvinyl alcohol (GOST 10779–78). Dry peas were ground in a laboratory mill brand RRH – 100 (rpm – 28000, power – 700 W), after which the samples were sieved through a laboratory sieve with holes = 0.1 mm.

Laboratory degumming was performed on 400 g samples of unrefined sunflower oil. Degumming temperature – 55 °C, mechanical stirring (magnetic stirrer) 500 rpm, duration – 5 minutes. After hydration, the oil was centrifuged at 1000 rpm for 5 min and thus a hydrated sunflower oil and a wet gum were obtained.

To stratify the wet gum, it was heated to 70 °C, 5% sodium chloride was added and kept under constant stirring for 20 minutes. Then set the degree of delamination after 4 hours.

All experimental data were obtained twice. The article gives the average values. The mean deviation did not exceed 0.1 for a confidence interval of 0.95.

Presentation of the research material. The following variants of degumming agents were added to unrefined non- degumming sunflower oil:

1) water. To obtain comparative values with the classical method of degumming;

2) aqueous suspension of wheat flour;

3) an aqueous suspension of flour with citric acid, which is an effective chelator, ie able to remove metal ions from phosphatidic acid and convert NGF into a hydrophilic form;

4) aqueous suspension of finely ground peas. Peas are the cheapest legume in our country (the cost is similar to the cost of wheat flour);

5) colloidal starch solution;

6) synthetic polymer – polyvinyl alcohol (also known as PVA, the general formula [CH_2CH (OH)] n. Of course, we do not propose to use the technology of purification of edible oil with synthetic polymer. But it is advisable to obtain comparative data on the effectiveness of hydration with different types of macromolecular compounds.The results of degumming with aqueous solutions of macromolecular compounds are given in table 2.

Table 2

The results of degumming with macromolecular compounds

The composition of the degumming agent relative to the oil	Phospholipid content, % in terms of stearoleolecitin	Degummingoil moisture, %
Water (2%)	0.095	0.070
Wheat flour (0.5%), water (2%)	0.038	0.046
Pea flour (0.5%), water (2%)	0.040	0.044
Starch (0.5%), water (2%)	0.057	0.066
Polyvinyl alcohol (0.5%), water (2%)	0.036	0.050

The efficiency of degumming with macromolecular compounds is high. Slightly higher degummingefficiency with wheat flour compared to pea flour is probably due to the smaller diameter of wheat flour particles – about half are smaller than 40–50 microns, and others – from 45–50 to 190 microns, while pea flour was obtained by grinding and passing through a sieve with a diameter of 0.1 mm.

However, the introduction of 0.5% of such substances leads to the loss of the flour itself and neutral oil, which is also removed from the degumming agents. Therefore, it was decided to reduce the amount of high-molecular compounds in the degumming agent by 5 times (Table 3) and add citric acid. Citric acid lowers the pH of the degumming agent, and this leads to the elimination of large amounts of phosphatidylethanolamine. Also, the logarithms of the stability constants of citric acid with ions of iron, calcium, magnesium are higher than the same logarithms of metals with phosphatidic acid. That is, the presence of citric acid will lead to the elimination of a significant part of NGF.

According to table 3, the results of using as a degumming agent mixtures of food protein-containing macromolecular substances and citric acid meet the conditions of the task – the final content of phospholipids in the refined oil is less than 0.05% in terms of stearooleolecithin.

The results of degumming with starch do not meet the objectives of the study. The low efficiency of phospholipid excretion is probably due to the insufficient reduction of the interfacial surface tension in the lipid-water system.The most effective moisturizing agent among those studied was polyvinyl alcohol, due to its ability to emulsify. Although E 1203 is approved for use in the food industry as a moisture retainer, due to its synthetic nature and potential danger to human health, subsequent studies have decided to focus on flour-based degumming agents. The macromolecular compounds introduced into the system also affect other indicators of oil quality (IOQ) (Table 4). It should be noted the positive effect of degumming with pea flour on all studied indicators.

Table 3

Degumming results with macromolecular compounds and acid

The composition of the degumming agent in relation to the oil	Phospholipid content, % in terms of stearoleolecitin	The composition of the degumming agent in relation to the oil	Phospholipid content, % in terms of stearoleolecitin
Water (2%)	0.095		
Wheat flour (0,1%), water (2%)	0.052	Wheat flour (0.1%), citric acid (0.06%), water (2%)	0.040
Pea flour (0,1%), water (2%)	0.058	Pea flour (0,1%),citric acid (0.06%), water (2%)	0.045
Starch (0,1%), water (2%)	0.1	Starch (0.1%), citric acid (0.06%), water (2%)	0.075
Polyvinyl alcohol (0,1%), water (2%)	0.048	Polyvinyl alcohol (0.1%), citric acid (0.06%), water (2%)	0.039

Table 4

Qualitative indicators of sunflower oil before and after degumming

Indicator	IOQbefore degumming	IOQ after water degumming	IOQafter degumming with citric acid (0.06 %)	IOQafter degumming with pea flour (0.1%) and citric acid (0.06 %)
Acid value, mgKOH/g	0.8	0.8	0.91	0.55
Peroxide value, mmol½O/kg	6.7	4.5	4.1	2.8
Phospholipid content, % in terms of stearooleolecithin	0.60	0.095	0.075	0.045
Moisture content, %	0.18	0.07	0.06	0.05
Mass fraction of non-fat impurities, %	0.02	Not detected	Not detected	Not detected
Color, mg of iodine	18	15	15	13
Taste and smell	Inherent in sunflower oil without foreign odor, taste and bitterness	Inherent in refined sunflower oil without foreign odor, taste and bitterness	Inherent in refined sunflower oil without foreign odor, taste and bitterness	Inherent in refined sunflower oil without foreign odor, taste and bitterness

The resulting wet gum is probably spherical conglomerates of denatured wheat or pea proteins and phospholipids arranged so that their hydrophilic parts are oriented outward into a dispersion medium – water, and the hydrophobic parts are immersed in a dispersed phase – oil, that is, it is located inside the spheres of proteins and phospholipids. This configuration is energetically favorable and gives the system a high stability, the phospholipid emulsion does not delaminate over time.

Table 5

Qualitative indicators of wet gum

Indicator	TU 9147-005-55514306-2003	Wet gum obtained by degumming with pea flour and citric acid
Acid value, mgKOH/g	8,0	2.8
Moisture content, %	70,0	62.5
Mass fraction of neutral fat,%	12	14.5
Phospholipid content,% in terms of stearooleolecithin	6,0	22.0
Mass fraction of non-fat impurities, %	≤1,5	0.66

In traditional processes for producing lecithin, the wet gum is dried to a water content of less than 1%. However, this process is traumatic for phospholipids and also energy consuming. It is advisable to try to delaminat the wet gum into an aqueous and a lipid phase. The thermodynamic stability of emulsions can be reduced by raising the temperature and introducing certain substances, such as dietary sodium chloride.

At a temperature of 95 °C it is possible to destabilize such an emulsion system as whey [11] and the production of whey protein dispersion. However, at temperatures around 80 °C, the processes of lipid oxidation begin to intensify rapidly, so to obtain a quality product, lower temperatures should be adhered to (a temperature of 70 °C was used for experimental delamination). As a demulsifier used sodium chloride in an amount of 5%. The wet gum obtained by traditional aqueous degumming contains proteins, the protein content in such an emulsion obtained during degumming with flour is even higher. Proteins are characterized by a positive charge in an acidic medium (characteristic of a wet gum), due to electrostatic attraction they form a shell around phospholipids, which contain a negative charge, which increases the stability of these emulsions in an aqueous medium. With increasing pH, proteins lose charge, the ability to emulsify phospholipids and precipitate.

Based on previous experiments, it was observed that the delamination the wet gum is more effective when using not a salt solution, but a pre-mixed mixture of salt and wet gum. The results of delamination of the wet gum under the influence of a temperature of 70 °C, 5% sodium chloride (introduced as a solution in the wet gum) are given in table. 6.

Table 6

Delamination the wet gum

The duration of settling after the introduction of the demulsifier	The amount of aqueous phase separated,% (relative to the wet gum)
4	23
8	40
12	42

The separation of this amount of water makes this method of delamination the wet gum interesting. According to the table. 6, the delamination time is expedient – 8 hours (provided that sodium chloride is introduced in the form of a solution in a wet gum).

It is known that phospholipids have a positive effect on the quality of flour products: the yield of bread increases, the process of making products intensifies, the process of staling slows down, and the biological value of the product improves [12; 13].

It is proposed to use the obtained wet gum with reduced water content, increased protein and salt content in the production of flour products. Such a wet gum, although somewhat stabilized against microbiological spoilage by the presence of sodium chloride, cannot persist for a long time (its significant drawback), however, it has not been subjected to the destructive thermal effects of drying, contains salt and an increased amount of proteins, therefore it will have a positive effect on the characteristics of flour products.

Conclusion. According to the obtained data, degumming agents based on aqueous solutions of wheat or pea flour and citric acid are effective, reduce the content of phospholipids to low final values less than 0.05% in terms of stearooleolecithin. The obtained refined oils meet all the main quality indicators, and such indicators as phospholipid content, acid value, peroxide value, color are significantly lower compared to the results of traditional degumming (aqueous or acidic).

Also, degumming cleaning with wheat or pea flour can be recommended for oils of low quality, while there will be an improvement of quality indicators to values that meet the requirements of regulatory documents. Improving the quality of oil due to the adsorption effect of flour looks promising due to safety and low cost.

The effectiveness of the use of demulsifiers (sodium chloride) to delaminat the wet gum has been studied. The purpose of this approach is to reduce the amount of water that is distilled off during the drying of the wet gum.

The use of a phospholipid product that has not been destructive to drying, contains increased amounts of protein and salt in the composition of mixtures for baking flour products looks promising. The cost of such a product will be lower than standard lecithin, and the efficiency of use for the production of flour products is likely to be higher.

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