# CHAPTER 11

# Sunflower lecithin as an alternative to soy lecithin: technological approaches to improving its rheological, sensory and functional properties

Anastasiia Demydova
Svitlana Panasyuk
Yurii Hunko

**Abstract**

Soy lecithin remains the primary industrial source of lecithin; however, increasing concerns regarding its GMO origin have driven interest toward alternative sources. Among them, non-GMO sunflower lecithin has emerged as a high-quality and economically viable substitute. Despite its advantages, sunflower lecithin presents several technological drawbacks, including an intense flavor and odor, dark color, and high viscosity, which can lead to a plastic, non-flowable consistency.

The objective of this study was to develop technological strategies to produce decolorized, deodorized, and liquid sunflower lecithin. Deodorization was achieved by dissolving lecithin in ethyl alcohol at concentrations ≥ 40% (w/w), resulting in the complete removal of characteristic fatty, sweet, and nutty notes, while caramel and floral undertones became barely perceptible. This process led to the fractionation of lecithin into alcohol-soluble and alcohol-insoluble components. The use of absolute ethanol significantly reduced the yield of the alcohol-soluble fraction (from 23% to 13%).

Furthermore, it was found that the incorporation of specific diluents into wet gum prior to drying prevented the formation of a plastic consistency and ensured a stable liquid state during storage. Among the diluents tested, calcium salts proved to be the most effective. The optimal concentrations for maintaining lecithin liquidity were identified as follows: calcium acetate – 0.4%, calcium orthophosphate – 0.4%, and calcium chloride – 0.35%.

Decolorization conditions were also optimized, with the most effective parameters being 0.7% hydrogen peroxide (calculated as 100% $H_2O_2$), a temperature of 90°C, and a treatment time of 120 minutes. Under these conditions, the color value of sunflower lecithin decreased from 18 to 4–6 mg$J_2$/100 $cm^3$.


DOI: 10.21303/978-9908-9706-2-2.ch11

To evaluate the role of individual phospholipid groups in thermal darkening, fractionation was performed. Results indicated that phosphatidylcholines were most susceptible to darkening upon heating, followed by phosphatidylinositols, while phosphatidylserines and phosphatidylethanolamines exhibited the least color change. No correlation was observed between the sugar content of phospholipid fractions and their tendency to darken under thermal treatment.

**Keywords**

Sunflower lecithin, lecithin refining, resource-saving technologies, wet gum, color changes in lecithin, deodorization of lecithin, viscosity changes in lecithin, physicochemical properties of lecithin, lecithin quality parameters.

## 11.1 Introduction

Over the past few years, consumers have begun to redefine the desired attributes of food and dairy products. Lecithin combines a variety of technological functions with full safety for the human body. They are widely used in food, medical, cosmetic and other industries. Lecithins are effective emulsifiers, dispersers, antioxidants, anti-splattering, and releasing agents with application in multiple food systems [1].

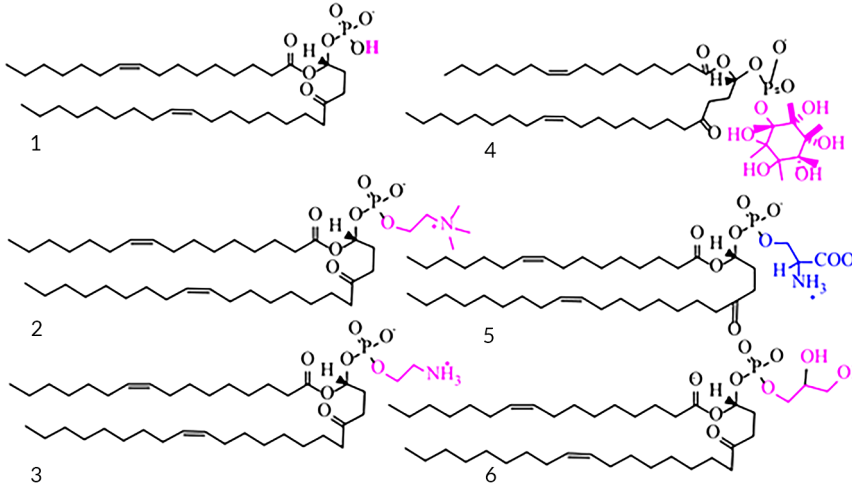
Lecithin is defined as a mixture of various phospholipids extracted from foods of different origins (animal or vegetable), containing at least 60% of acetone-insoluble substances [2].

The life of organisms without phospholipids is absolutely impossible. They deliver the necessary substances to the cells and remove the slag from them, take them in complex processes occurring inside the cage and between the cells, are the structural basis of all without exception of cell membranes, organelles, intracellular matrix. With age, as well as a result of various negative effects on the body (unfavorable ecology, stress, intense physical activity) cells are unable to synthesize phospholipids, causing cells to lose the ability to exchange metabolites with the environment and remove slag [3].

Known therapeutic and preventive effect of phospholipids in relation to several groups of diseases: hypercholesterolemia and hyperlipidemia, renal failure and diabetes [1]. Phospholipids have antioxidant effect, reducing the formation of toxic free radicals in the body (they have complex-forming properties and are able to inactivate heavy metal ions, as well as phospholipids prevent autoxidation) delay the development of cancers in 2 times. The second group of diseases includes all variants of liver pathology. The third group is neurological diseases – with regular intake of phospholipids, there is a gradual strengthening of the central nervous system:

the tendency to stress decreases, memory and productivity of thinking are improved [4]. The fourth is different cosmetic programs for correction of skin dryness, as well as some skin diseases. Lecithin can improve the texture of the skin by moisturizing it and reducing yellow fat deposits on the skin and around the eyes [5].

Commercial lecithins are mainly represented by products of plant origin – from soybeans, rapeseed, sunflower, corn, etc. Technologies for obtaining lecithins from egg yolk, brain, liver, etc. are known, but such commercial products are much more expensive. Lecithins from plant sources are represented mainly by glycerolipids (**Fig. 11.1**).




1 – phosphatidic acid, 2 – phosphatidylcholine, 3 – phosphatidylethanolamine, 4 – phosphatidylinositol, 5 – phosphatidylserine, 6 – phosphatidylglycerol

**Fig. 11.1** Types of plant phospholipids
*Source: [6]*

The process of obtaining lecithin begins at the degumming stage, when water or an aqueous solution of acids is added to the unrefined oil or enzymatic degumming is carried out. The details of the degumming process, advantages and disadvantages of individual approaches are discussed in detail in [7]. As a result of this process, in addition to degummed oil, a wet gum is formed – a mixture of water, phospholipids and oil. It is microbiologically unstable, and to obtain a marketable product, water must be removed. As a result of gentle evaporation of water under low pressure, the final product is obtained – lecithin.

Degumming is possible due to the diphilic nature of phospholipid molecules. They contain a hydrophobic part – two fatty acid residues ($R_1$ and $R_2$, **Fig. 11.1**) and a hydrophilic part – glycerol and a residue of phosphoric acid esterified by a nitrogen group. When water (in quantities greater than 0.1%) enters the oil, phospholipids gradually concentrate on the surface of its droplets as a result of dissolving their hydrophilic part. Phospholipids and water form a dispersed phase and, due to their greater density than oil, precipitate into a precipitate called wet gum. However, phospholipid molecules also contain a hydrophobic part and also extract a significant amount of triglycerides into the wet gum. These are the so-called losses of neutral oil, which account for approximately 50% of the mass of extracted phospholipids.

Also, not all phospholipids are hydrophilic, i.e. those that are removed from the composition of oils by water. Phospholipids are also represented in non-hydrophilic forms. These are mainly complexes of phospholipids with metals. Phosphatidylinositol and phosphatidylcholine are completely eliminated in the process of aqueous degumming (under conditions of sufficient water, mixing of phases, etc.). Phosphatidic acid in an acidic environment forms complexes with metals and is not hydrophilic. It becomes hydrophilic in an alkaline environment. Phosphatidylethanolamine is non-hydrophilic only in a neutral environment [7]. Extracted oils contain much larger amounts of phospholipids that are not hydrated compared to pressed oils.

The reason for the difficulty of carrying out the degumming stage is that it is desirable to remove all groups of phospholipids from the oils and, at the same time, to remove the minimum amount of neutral oil.

A whole list of commercial phospholipid products is obtained from the wet gum obtained at the hydration stage of vegetable oils. Today, commercial preparations of vegetable phospholipids are divided into four main groups: standardized lecithins (with a phospholipid content of at least 50–60%), deoiled lecithins (phospholipid content of up to 98%), hydrolyzed lecithins (lysoforms of phospholipids, characterized by increased emulsifying effect), individual phospholipid fractions and technological functional composites based on lecithins (these are composites based on mono– and diglycerides of fatty acids (E 471), polyglycerol esters of fatty acids (E 475), lecithin (E 322), also on a protein basis) [8].

The technology for obtaining sunflower lecithin needs to be improved to increase its quality and production efficiency. The main disadvantages of sunflower lecithins include:

1) high content of mechanical impurities;

2) strong and characteristic (although pleasant) taste and smell;

3) high viscosity;

4) dark color;

5) slightly lower phospholipid content compared to soy lecithin and, related to this, slightly.

Let's consider these technological disadvantages and the results of research on their improvement separately.

## 11.2 Materials and Methods

### 11.2.1 Materials

Samples of sunflower lecithin containing 62.8% phospholipids, as well as a sunflower phospholipid emulsion, were provide by a Ukrainian manufacturer. Sunflower lecithin was characterized by the parameters summarized in **Table 11.1**. The emulsion had the following composition: water – 65.5%, phospholipids – 19.7%, and neutral lipids – 12.1%. Fractional composition: phosphatidylcholine – 15.8%, phosphatidylethanolamine – 7.5%, phosphatidylinositol – 13.9%, phosphatidic acid – 3.1%.

**Table 11.1 Quality indicators of sunflower lecithin**

| Indicator | Sunflower lecithin |
|---|---|
| Mass fraction of substances insoluble in acetone, % | 62.8 ± 0.8 |
| Mass fraction of moisture and volatile substances, % | 0.84 ± 0.02 |
| Acid number of oil isolated from lecithin, mgKOH/g | 5.9 ± 0.04 |
| Peroxide value of oil isolated from lecithin, mmol1/2O/kg | 3.05 ± 0.09 |
| Mass fraction of substances insoluble in ethyl ether, % | 0.6 ± 0.03 |
| Viscosity at 25°C, Pa·s | 10 ± 0.05 |
| Color, mg of iodine | 8 ± 0.1 |

The qualitative parameters of lecithins were assessed according to the national standard SOU 15.4-37-212:2004 "Phosphatide concentrates. Technical specifications".

### 11.2.2 Deodorization of sunflower lecithin

A 30 g portion of lecithin was dissolved in a mixture of ethyl alcohol and water (solvent ratio 96:4, 99.9:0.1, respectively). The samples were kept under constant

stirring (60 rpm) in a water bath at 60°C for 30 min, and then centrifuged at 1000 rpm for 10 min. Alcohol-insoluble and alcohol-soluble fractions were obtained, from which ethanol was eliminated by evaporation under reduced pressure to a volatile content of < 0.5%. The obtained fractions were stored at 10°C in a closed glass vessel and their sensory analysis was performed.

To conduct the organoleptic evaluation of sunflower lecithin, a tasting panel was formed, comprising 10 volunteers (5 men and 5 women aged between 23 and 60 years). All participants completed at least 10 hours of training aimed at developing skills to identify variations in the sensory characteristics of lecithins from different manufacturers at various storage stages, as well as for comparison with soy lecithins. Based on the training results, a sensory panel was developed, including the following typical aromas and flavors of lecithins: nutty, caramel, sweet, fatty, and fruity. The intensity of aroma was assessed using a five-point scale, where 1 represented minimal intensity and 5 corresponded to the intensity typical for fresh standard sunflower lecithin. Lecithin samples were placed in transparent glass containers (Petri dishes), which were sealed and labeled with coded numbers before evaluation. Prior to analysis, samples were heated to 50°C (the melting point of lecithin) and assessed under natural daylight conditions. Sample evaluation was randomized and conducted on different days.

The phospholipid fractional composition was analyzed by thin-layer chromatography using a solvent system of chloroform – acetic acid – water in a ratio of 70:36:4 on "Silufol-254" plates (Czech Republic).

### 11.2.3 Method for determining the rheological properties of sunflower lecithin

Samples of sunflower lecithin were initially heated above their melting point (exceeding 60°C), after which predetermined amounts of modifying agents, including sunflower oil, oleic acid, or ethyl oleate, were incorporated. Homogenization was performed in a water bath at 60°C using a propeller mixer operating at 120 rpm for 10 minutes. Following homogenization, the mixtures were cooled to ambient temperature and stored for 14 days before viscosity analysis.

For the preparation of sunflower phospholipid emulsions, designated volumes of diluents were added, and the mixtures were stirred at 60°C for 10 minutes. The resulting emulsions were subsequently dried using a rotary-film evaporator at 80°C under reduced pressure until the moisture content fell below 1%. The lecithin

concentrates obtained were cooled and stored at 5–10°C for 14 days to facilitate plastification processes, after which viscosity was determined.

The experimental procedure involved the use of 30% aqueous solutions of calcium salts, namely calcium chloride, calcium acetate, and calcium orthophosphate. Viscosity measurements were conducted using a Brookfield Viscometer LVT (USA) at 25°C, with the sample immersed in a thermostatic bath (TS-1/80 SPU). The measurement principle was based on determining the torque required to maintain a constant spindle rotation within the tested medium.

### 11.2.4 Method of extracting individual fractions from sunflower lecithin

In this work, a combined improved method was used, consisting of the following stages:

– method of degreasing phosphatide concentrate: isopropyl alcohol is added in small portions to a portion of sunflower lecithin at a ratio of 1:5 ÷ 6, respectively. The oil solution in isopropyl alcohol that has separated is separated from lecithin by filtering through a Buchner funnel, which is connected to a vacuum pump using a Bunsen flask. The degree of lecithin degreasing was recorded visually (light, non-sticky powder was obtained) and by grinding the powder on a calcine (it should not leave greasy traces);

– method of extracting the phosphatidylcholine fraction: 96% ethyl alcohol is added to the defatted lecithin (ratio 1:4). Mix thoroughly for 20 min. at a temperature of 50–60°C and leave to form a precipitate. The alcohol-soluble fraction is separated by decantation and volatile substances are distilled from it in a vacuum at a temperature not higher than 40°C. Then degrease again as described above, add ethyl alcohol again, decant the fractions and also distill the alcohol residues from the alcohol-soluble fraction. Fraction I is obtained, which contains mainly phosphatidylcholines. Ethyl alcohol is added twice more to the alcohol-insoluble fraction II, the alcohol-soluble fraction is separated and not used;

– method of extracting fractions of phosphatidylinositols and phosphatidylethanolamines: a portion of fraction II is dissolved in an eightfold excess of chloroform and the same amount of ethyl alcohol is added. Precipitate III (phosphatidylcholine fraction) is obtained. Fraction IV (a mixture of phosphatidylethanolamines and phosphatidylserines) is separated in the same way as in the previous methods. Further separation of phosphatidylethanolamines and phosphatidylserines was not performed due to their low separation coefficient (according to all known methods).

### 11.2.5 Method for determining the optical density of heat-treated lecithins

0.5 g portions of sunflower lecithin or its fractions with a known phospholipid content were dissolved in 9.5 $cm^3$ of refined sunflower oil and subjected to heat treatment at a temperature of 200°C for 2 hours. The samples were placed in heat-resistant glass test tubes with an expanded neck and hung on a tripod that was lowered into a bath filled with heat-resistant silicone oil. Constant stirring and temperature control within ± 0.1°C were maintained. Then, after cooling the test tubes, the optical density of the obtained samples was determined using an electrophotocalorimeter (KFK-2) relative to refined deodorized oil, which was added to the lecithin portions.

### 11.2.6 Method for decolorizing sunflower lecithin

A portion of lecithin (100 g) is placed in a round-bottomed flask and heated in a water bath (VB-4 MIKROMED) to a given temperature (70–90°C). Constant mixing of lecithin is carried out with constant stirring, without stopping the stirring, concentrated hydrogen peroxide (33%) is added in small portions and the reaction mixture is kept.

### 11.2.7 Statistical processing of experimental results

Analysis of variance (ANOVA) was used to determine the statistical significance of the effects of hydrogen peroxide content ($X_1$), duration of lightening ($X_2$) on lecithin clarification efficiency. 9 experiments were conducted in a given factorial space: $X_1$: from 1 to 5% hydrogen peroxide (33%); $X_2$: from 30 to 90 min. The range of variation was chosen based on previous experiments.

The data were analyzed using three-way ANOVA to assess: the effect of each independent variable ($X_1$, $X_2$), two-factor interactions ($X_1X_2$). The significance level was $\alpha = 0.05$.

The results of the experiment are a regression equation of the form

$$Y = b_0 + b_1X_1 + b_2X_2 + b_{12}X_1X_2,$$

where $Y$ – color number of lecithin, mg $J_2$/100 $cm^3$; $b_0$ – intercept; $b_1$, $b_2$, $b_{12}$, $b_{23}$, $b_{23}$ – interaction coefficients.

At 4 points, the calculated response value ($Y$ – color number of lecithin) was determined according to the obtained regression equation. Experimental studies were conducted at the same points (with the same values of the parameters $X_1$, $X_2$). The obtained values of the experimental results and the theoretical ones (according to the regression equation) were compared and the coefficient of determination ($R^2$) value was established. In this way, it was assessed how well the model describes the obtained results. In scientific and technical research, $R^2 > 0.70$ is usually considered acceptable. Mathematical modeling was carried out using the Python programming language and the Sklearn libraries to determine the regression equation and Scipy for optimization.

The samples were randomized and tested on different days, with all measurements repeated three times. The statistical significance of differences between the mean values of all measurements was assessed at a significance level of $p < 0.05$ (5%).

## 11.3 Results

The possible high content of mechanical impurities in sunflower lecithin (insoluble in hexane or insoluble in toluene, or insoluble in ethyl ether according to the standards of different countries) is a known problem. However, it is solved by effective filtration of the oil before refining (separators are used for this purpose). Therefore, there is no need to investigate the removal of mechanical impurities from lecithin in this study.

### 11.3.1 Deodorization of sunflower lecithin

Deodorization of lecithin is a complex process. The industrial method of lipid deodorization is based on the different volatilities of triacylglycerols and other fat components, the total concentration of which can reach 5%. These include fatty acids, pigments and volatile compounds. This process is carried out at high temperatures (220–260°C), low pressure (3–5 mPa) and in the presence of 3–5% of acetic steam as a solvent for volatile components [9].

However, this approach is not suitable for lecithins, since they are thermolabile and prone to melanoidin formation, oxidation and other undesirable reactions. High temperatures cause oxidation of fatty acids, the formation of Maillard reaction products and the formation of aldehydes, which negatively affects the quality of lecithin. This leads to darkening of the product and the appearance of unpleasant odors, such as burnt or rancid [10].

Most of the volatile compounds contained in lecithins are products of autocatalytic decomposition of unsaturated fatty acids of phospholipids. The main source of the undesirable odor of defatted soy lecithin is isophorone, which is likely formed as a result of contact of lecithin with acetone. In addition, nitrogen-containing substances, including nitriles, acetoxime and 4.5-dimethylisoxazole, have been identified among the unique volatile compounds of phospholipids [10]. Among the volatile components of lecithin, aldehydes are characterized by the lowest perception thresholds, therefore, they are most likely to significantly affect the sensory characteristics of lecithins.

A feature of ethyl alcohol is its high selectivity with respect to substances that give lipids taste and odor (aldehydes, ketones, hydrocarbons, etc.). When lecithins are treated with ethyl alcohol, they are fractionated into an alcohol-insoluble fraction (mainly containing phosphatidylcholine) and an alcohol-insoluble fraction (mainly containing phosphatidylinositol, phosphatidic acid). Phosphatidylethanolamine is contained in both fractions. Since different phospholipids have different properties, lecithin is usually fractionated with solvents to obtain fractions with the desired functionalities.

During our own research on fractionation of sunflower lecithin, the effect of deodorization of the alcohol-soluble fraction was noticed. This result requires additional research. 5, 10, 20, 30, 40, 50% of 96% ethyl alcohol was added to sunflower lecithin. The results of the change in the sensory characteristics of the alcohol-insoluble fraction were as follows:

– when adding 30% ethanol (by weight to lecithin), the intensity of the lecithin odor significantly decreased;

– when adding 40% and higher amounts of ethanol, the odor and taste of sunflower lecithin could not be identified (**Fig. 11.2**).

The removal of odorants from lecithin is likely to occur by eliminating them in a mixture with ethanol.

The qualitative characteristics of the obtained lecithin are given in **Table 11.2**. Treatment of sunflower lecithin with 96% ethyl alcohol in an amount of 40% relative to lecithin leads to the formation of an alcohol-soluble fraction (phosphatidylcholine) in an amount of 23% and an alcohol-insoluble (phosphatidylinositol) in an amount of 77%.

The alcohol-insoluble fraction meets the requirements of the regulatory document. The alcohol-soluble fraction must be degreased to increase the content of acetone-insoluble substances. It was treated with acetone at a ratio of alcohol-soluble fraction:acetone as 1:1. As a result, the content of phospholipids in it increased to 63%.

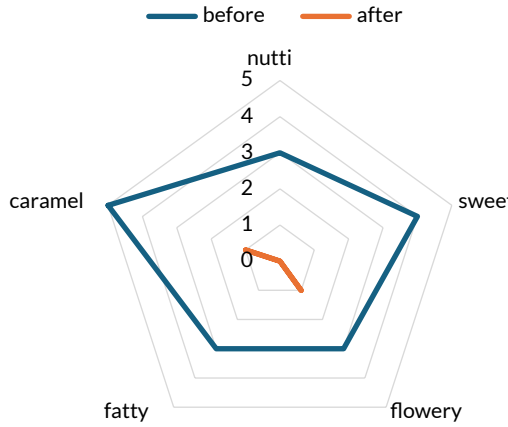



**Fig. 11.2** Sensory characteristics of sunflower lecithin before and after treatment with ethyl alcohol (40% relative to lecithin)

**Table 11.2 Qualitative indicators of lecithin fractions obtained as a result of treatment with 96% ethyl alcohol**

| Qualitative indicator | Requirements of the Ukrainian standard SOU 15.4-37-212:2004 | Alcohol-insoluble fraction | Alcohol-soluble fraction |
|---|---|---|---|
| Mass fraction of substances insoluble in acetone, % | ≥ 60 | 72.4 ± 0.4 | 25.5 ± 0.2 |
| Mass fraction of moisture and volatile substances, % | ≤ 1.0 | 0.38 ± 0.04 | 0.11 ± 0.02 |
| Mass fraction of substances insoluble in ethyl ether, % | ≤ 1.5 | 0.30 ± 0.04 | 0.30 ± 0.05 |
| Acid number of oil isolated from lecithin, mgKOH/g | ≤ 10 | 3.8 ± 0.05 | 5.2 ± 0.06 |
| Peroxide value of oil isolated from lecithin, mmol1/2O/kg | ≤ 10 | 1.8 ± 0.05 | 2.5 ± 0.06 |
| Color, mg of iodine | ≤ 8 | 4 ± 0.1 | 6 ± 0.2 |

The alcohol-soluble fraction after evaporation of ethyl alcohol also significantly reduced the intensity of the aroma. However, to a lesser extent compared to the alcohol-insoluble. Nevertheless, the intensity of the smell (2 on the developed scale) of the alcohol-soluble fraction is no more than that of soy lecithin. The qualitative indicators of the resulting product meet the requirements for fractionated phospholipid products [11].

The presence of water in ethyl alcohol affects the dissolution of phospholipids and related compounds in it. In order to reduce the yield of the alcohol-soluble fraction, sunflower lecithin was treated with 99.9% absolute ethyl alcohol (in amounts of 5, 10, 20, 30, 40, 50% relative to lecithin). The effect on the sensory characteristics of lecithin is the same as that of 96% ethyl alcohol. The deodorizing effect was also observed at 40% absolute ethanol. The yield of the alcohol-soluble fraction compared to the use of 96% ethyl alcohol under the same conditions is significantly reduced – from 23% to 13%, respectively. Thus, in order to reduce lecithin fractionation, it is advisable to use 99.9% ethyl alcohol. The fractional composition of the obtained lecithins (preliminarily defatted) is given in **Table 11.3**.

**Table 11.3 Fractional composition of phospholipid products obtained after deodorization of sunflower lecithin with ethyl alcohol**

| Faction name | Composition, % | | | |
|---|---|---|---|---|
| | Ethyl alcohol-rectified | | Ethyl alcohol, absolute | |
| | Alcohol-insoluble fraction | Alcohol-soluble fraction | Alcohol-insoluble fraction | Alcohol-soluble fraction |
| Phosphatidylcholine | 10.5 ± 0.06 | 40.3 ± 0.9 | 12.8 ± 0.1 | 43.6 ± 1.0 |
| Phosphatidylinositol | 14.6 ± 0.1 | 9.8 ± 0.7 | 14.0 ± 0.9 | 7.7 ± 0.5 |
| Phosphatidylethanolamine | 21.8 ± 0.9 | 11.9 ± 0.1 | 22.6 ± 0.8 | 8.3 ± 0.7 |
| Phosphatidic acid | 8.9 ± 0.5 | 8.8 ± 0.4 | 8.5 ± 0.3 | 7.1 ± 0.4 |

The alcohol-soluble fraction meets the requirements for fractionated lecithins in terms of choline content (according to regulatory requirements – from 39%) and inositol (up to 3%).

The fraction enriched with phosphatidylcholine is characterized by improved emulsifying properties for oil-in-water (o/w) emulsions, which are necessary for the food, pharmaceutical and cosmetic industries. Such products are in wide demand. The fraction enriched with phosphatidylinositol is considered a high-quality emulsifier for water-in-oil emulsions.

### 11.3.2 Reducing the viscosity of sunflower lecithin

Sunflower lecithin is always liquid after production (drying wet gum), but after a few days it plasticizes and ceases to be liquid. This is inconvenient for its transportation, unloading, dosing and use in various food technologies, for uniform distribution

in food products, etc. Therefore, most buyers require a liquid state of lecithin, including sunflower. This corresponds to a viscosity value of 8–12 Pa·s. Sunflower lecithin has a higher viscosity than soybean and rapeseed due to the presence of long-chain waxes. Liquid lecithins, as a rule, correspond to Newtonian characteristics. An increase in the content of phospholipids gives an increase in viscosity, oils – vice versa. The highest viscosity of sunflower lecithin during its drying is observed at a water content of 0.7%. The presence of salts reduces the viscosity of lecithins [12]. The cheapest and safest diluent is table salt, but it increases the value of the "mechanical impurities" indicator, because it does not dissolve in either hexane or ethyl ether.

In order to determine the optimal conditions for obtaining liquid sunflower lecithin, diluents of different types were used. Related substances of lipid nature with lower viscosity were added to lecithin – sunflower oil, oleic acid and ethyl ester of oleic acid. Another way is to use salts of divalent metals, calcium derivatives were used as an element that is vital for the human body: chloride, acetate and calcium orthophosphate. According to our studies, the introduction of diluents into already plasticized lecithin

The results are given in **Table 11.4** (column 2).

Diluents were incorporated into the wet gum (produced by the same manufacturer as the sunflower lecithin), followed by drying under reduced pressure. The goal was to reach a final moisture content of approximately 0.7%, a level at which lecithin is most likely to undergo plasticization. The lecithin samples with added diluents were then stored for 14 days to enable potential plasticization processes. After this storage period, viscosity measurements were performed, and the results are presented in **Table 11.4** (column 3).

Comparing the data of columns 2 and 3 of **Table 11.4**, it can be concluded that the introduction of diluents should be carried out in a wet gum. In this case, the effective amount of diluents (to achieve a viscosity of 12 Pa·s) can be halved.

**Table 11.4 The amounts of diluents required to reduce the viscosity of already plasticized sunflower lecithin (column 2) and lecithin obtained from wet gum to 12 Pa·s (at 25°C)**

| Diluent | Quantity, % in relation to sunflower lecithin | |
|---|---|---|
| Sunflower oil | 26 ± 0.6 | 14 ± 0.4 |
| Oleic acid | 11 ± 0.2 | 6 ± 0.1 |
| Ethyl ester of oleic acid | 10 ± 0.3 | 4 ± 0.09 |
| Calcium chloride | 0.7 ± 0.03 | 0.35 ± 0.01 |
| Calcium acetate | 0.8 ± 0.04 | 0.40 ± 0.01 |
| Calcium orthophosphate | 0.8 ± 0.04 | 0.40 ± 0.01 |

The use of sunflower oil cannot meet the requirements of modern standards for sunflower lecithins due to the excess of the content of neutral lipids in lecithin. In the work, lecithin with an acetone-insoluble (phospholipid) content of 62.8% was used. The introduction of 14% of sunflower oil leads to a triglyceride content in lecithin of 49%. The amount of acetone-insoluble substances is thus less than 60%, which is unacceptable in the production of competitive natural lecithin.

Oleic acid and its ethyl esters are more effective in reducing the viscosity of lecithin, but they are quite expensive substances. Also, 6 and 4%, respectively, again underestimate the phospholipid content to a value of less than 60%. Thus, the optimal use of calcium salts is. Both chloride and acetate and calcium orthophosphate are known food additives permitted for use in the food industry in these quantities. All three of these diluents should be recommended for use in industry.

It is necessary to determine whether the recommended diluents do not negatively affect the quality indicators of sunflower lecithin. 0.4% of calcium orthophosphate was introduced into the wet gum, the quality indicators were established after drying. In parallel, the wet gum was dried without the introduced diluent. The results are given in **Table 11.5**.

**Table 11.5 Quality indicators of dried sunflower lecithin**

| Indicator | Sunflower lecithin with calcium orthophosphate content of 0.4% | Sunflower lecithin | Requirements of SOU 15.4-37-212: 2004 "Phosphatide concentrates. Specifications" |
|---|---|---|---|
| Mass fraction of substances insoluble in acetone, % | 62.8 ± 0.09 | 62.8 ± 0.1 | ≥ 60 |
| Mass fraction of moisture and volatile substances, % | 0.73 ± 0.05 | 0.85 ± 0.04 | < 1.0 |
| Acid value of oil isolated from lecithin, mgKOH/g | 5.6 ± 0.11 | 5.4 ± 0.09 | < 35 |
| Peroxide value of oil isolated from lecithin, mmol1/2O/kg | 2.8 ± 0.18 | 3.4 ± 0.10 | ≤ 10 |
| Mass fraction of substances insoluble in ethyl ether, % | 0.6 ± 0.10 | 0.6 ± 0.13 | ≤ 1.5 |
| Viscosity at 25°C, Pa·s | 10 ± 0.20 | 18 ± 0.26 | ≤ 12 |
| Color, mg of iodine | 6 ± 0.50 | 10 ± 0.55 | ≤ 8 |

The obtained sunflower lecithins with the recommended content of calcium acetate and calcium orthophosphate were stored at a temperature of 10°C (at this temperature, the maximum probability of forming a plastic consistency is) for 0.5 year. The lecithins were constantly in a liquid state, and their plasticization was not observed.

### 11.3.3 Sunflower lecithin clarification

Lecithin can be found in various colors and forms, ranging from light brown to dark reddish brown [13]. Dark brown color (sunflower lecithin) or a yellow-amber color (soybean lecithin).

The use of sunflower lecithin due to its dark color (color number is 18 mg $J_2$/100 $cm^3$ and above) is not possible in all food products, but only in dark-colored products. Therefore, the clarification of the establishment of optimal conditions for obtaining light sunflower lecithin is an important task. It is also of interest to determine the causes of lecithin darkening under the influence of elevated temperatures. It is known that the darkening of phospholipids during heat treatment is associated with the appearance of melanophospholipids – "brown pigments". There are several theories explaining the mechanism of their appearance, most of which point to: the interaction of phospholipids with free fatty acids and sugars with the formation of amines (this reaction occurs at temperatures below 80°C); the interaction of hydroperoxides and amino groups of phosphatidylethanolamine with the formation of imine; the reaction of adol condensation of phosphatidylcholine with the formation of macromolecular brown products (the reactions occur at temperatures higher than 80°C).

The corresponding part presents the developed method for separating sunflower lecithin fractions, the method for heat treatment of fractions and determination of optical density.

It turned out that the fractions of phospholipids, according to the degree of change in their color after heat treatment, create the following series: phosphatidylcholines – phosphatidylinositols – phosphatidylserines and phosphatidylethanolamines (**Fig. 11.3**).

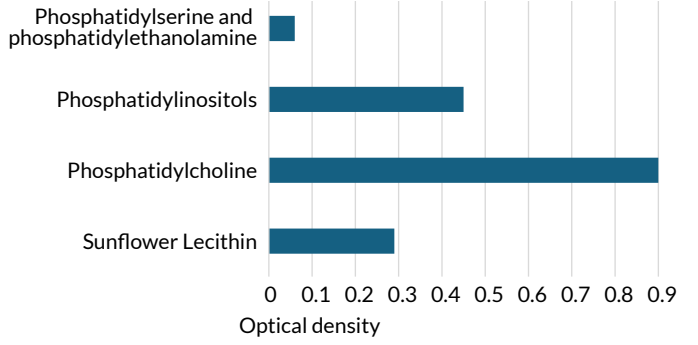



**Fig. 11.3** Optical density of sunflower lecithin and its fractions after heat treatment

It is known that the content of sugars in phospholipids also leads to their darkening [14]. Therefore, to establish the probable influence of sugars on the degree of darkening of individual phospholipid fractions, their content in each of the fractions was determined. As can be seen from the data given in **Table 11.6**, there is no correlation between the values of the sugar content in the fractions and the optical density of the latter.

Thus, it is proven that the color of phosphatide concentrates at elevated temperatures is explained mainly by the influence of the phosphatidylcholine fraction.

**Table 11.6 The content of phospholipids and sugars in the isolated fractions of sunflower lecithin**

| Faction name | Optical density after heat treatment | The content of the phospholipid fraction,% in relation to the total content of acetone-insoluble | Sugar content, % |
|---|---|---|---|
| Sunflower lecithin | 0.29 | – | 0.044 |
| Phosphatidylcholine | 0.90 | 45.1 | 0.028 |
| Phosphatidylinositols | 0.45 | 21.2 | 0.051 |
| Phosphatidylserine and phosphatidylethanolamine | 0.06 | 48.9 | 0.045 |

Hydrogen peroxide is highly effective in decolorizing lecithins. A negative consequence of its use is a significant increase in the content of peroxide compounds. But some enzymes have a high ability to break down these compounds [15].

To reduce the number of experiments and increase the reliability of conclusions, it is advisable to use experimental planning methods. An active experiment of type $2^3$ was conducted. The following factors were selected as the experimental factors: $X_1$ – concentration of 33% hydrogen peroxide, %, $X_2$ – duration of decolorization, min. and $X_3$ – temperature, °C. The response parameter is the color number, which was checked using the standard method. The model obtained as a result of calculating the factorial experiment data adequately describes the process of decolorizing lecithin with hydrogen peroxide. The regression equation is:

$$Y = 6.575 - 1.075x_1 + 1.075x_2 + 0.675x_3 - 0.275x_1x_2 - 2.475x_1x_3 + 1.675x_2x_3,$$
$$R^2 = 0.58.$$

Analysis of the obtained regression equation shows that all factors are significant, and the process of decolorization of sunflower lecithin should be carried out in accordance with the following conditions: process temperature – 90°C; amount of hydro-

gen peroxide (in terms of 100% peroxide) – 1%; duration of decolorization – 90 min. During the experiment, it was decided that hydrogen peroxide should be added in small portions to the lecithin already heated to 90°C with constant stirring. Under such conditions, the color number of lecithin decreases from 18 mg $J_2$/100 $cm^3$ to 4–6 mg $J_2$/100 $cm^3$.

During the research, it was recorded that by increasing the duration of decolorization, the same results can be obtained while simultaneously reducing the amount of hydrogen peroxide. Therefore, it was decided to decolorize lecithin under the same conditions, but with the addition of 0.5; 0.7; 1.0% hydrogen peroxide (in terms of 100% peroxide) and duration of decolorization – 90; 120; 180 min.

It was decided to introduce hydrogen peroxide into the wet gum before drying it. In this case, the unreacted peroxide will decompose under the influence of the high drying temperature.

It was found that increasing the duration of decolorization to 120 min. allows to reduce the amount of hydrogen peroxide to 0.7% (**Table 11.7**). It is possible to recommend these conditions for use in industry. The value of the peroxide value of lecithin after treatment with hydrogen peroxide under these conditions was 45 mmol1/2O/kg. After their destruction by the enzyme superoxide dismutase – 6.8 mmol1/2O/kg.

**Table 11.7 Determination of the effect of decolorization duration on the color of the lecithin**

| Amount of hydrogen peroxide (calculated as 100% peroxide) | Duration of discoloration, min. | | |
|---|---|---|---|
| | 90 | 120 | 180 |
| | Color, mg of iodine | | |
| 0.5 | 12 ± 0.1 | 8 ± 0.2 | 6 ± 0.1 |
| 0.7 | 10 ± 0.2 | 4 ± 0.1 | 4 ± 0.2 |
| 1.0 | 6 ± 0.1 | 4 ± 0.1 | 4 ± 0.1 |

During the research, it was established that when sunflower lecithin is treated with hydrogen peroxide, it deodorizes the latter – the decolorized lecithin has a characteristic smell of oil and any other odors. When phospholipids are decolorized with concentrated hydrogen peroxide, hydroxyphospholipids are also formed, which are strong hydrophilic emulsifiers.

It is advisable to combine the obtained experimental data and propose a rational scheme for obtaining light, liquid, deodorized sunflower lecithins. The scheme is shown in **Fig. 11.4**.

It is proposed to introduce hydrogen peroxide and calcium salts into the wet gum. As a result, the formation of dark-colored forms of phospholipids due to less viscosity of lecithin, which is formed during the drying process of wet gum, its other quality indicators are better. The number of peroxide compounds is significantly lower than the option of introducing hydrogen peroxide into the already dried lecithin (45 and 145 mmol1/2O/kg, respectively).

The stage of deodoration of lecithin (ethanol treatment) drives to the fractionation of lecithin with the formation of two valuable fractions in the industry – the one that mainly contains phosphatyletanolamine, phosphatidylserine, phosphatidylinositol, phosphatide acids (main in weight) and fractions containing phosphatidylcholine (**Table 11.3**).

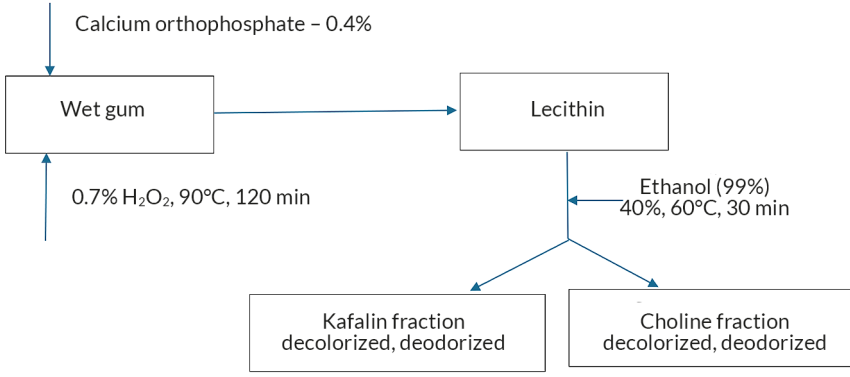



**Fig. 11.4** The rational scheme for obtaining decolorized, liquid, deodorized sunflower lecithins

## 11.4 Conclusions

As a research result, it was proven that it is possible to get rid of the main technological disadvantages of sunflower phospholipids – intense taste and smell, dark color, high viscosity with the transition to a plastic non-liquid state.

Deodorization of sunflower lecithin is possible by dissolving it in ethyl alcohol in an amount of ≥ 40% relative to lecithin. In this case, such characteristics of the smell and taste of sunflower lecithin as fatty, sweet, nutty completely disappear. Caramel and floral taste and smell become barely noticeable. In this case, lecithin is fractionated into alcohol-soluble and alcohol-insoluble fractions. The separation

of the alcohol-soluble fraction can be significantly reduced (from 23 to 13% relative to lecithin) by using absolute ethanol. The quality indicators of the alcohol-insoluble fraction (main) meet the requirements for lecithins. The alcohol-soluble fraction (with a predominant content of phosphatidylcholine) will meet the requirements of the quality indicators after increasing the content of acetone-insoluble substances. It is advisable to carry out the treatment with acetone in one stage at a ratio of alcohol-soluble fraction: acetone as 1:1, the content of phospholipids in the fraction as a result becomes more than 60%.

It has been proven that under the condition of introducing certain diluents, it is possible to achieve a state when sunflower lecithin does not form a plastic consistency and is liquid throughout the shelf life. It has been proven that diluents should be introduced into the wet gum before its drying. In this case, the amount of diluents required to obtain a stably liquid lecithin is approximately halved. The effective concentrations of lipids, the addition of which to the sunflower wet gum leads to lecithin dilution to 12 Pa·s (at 25°C), i.e. to the value when lecithin does not plasticize during storage (the studies were conducted after 14 days of storage), namely: sunflower oil – 13%, oleic acid – 5%, oleic acid ethyl ester – 4%. However, such amounts of introduced lipids reduce the value of the indicator "insoluble in acetone" to a level lower than the requirements of the quality indicators, therefore their use in sunflower lecithins should be abandoned. According to the research results, the optimal diluents are calcium salts. The effective amounts of their presence for obtaining liquid lecithin are the following: calcium acetate – 0.4%, calcium orthophosphate – 0.4%, calcium chloride – 0.35%.

Rational conditions for sunflower lecithin decolorization were determined: the amount of hydrogen peroxide (in terms of 100% peroxide) – 0.7%; process temperature – 90°C; duration of decolorization – 120 min. Under such conditions, the color number of sunflower lecithin decreases from 18 mg$J_2$/100cm$^3$ to 4–6 mg$J_2$/100cm$^3$. Effective destruction of peroxide compounds formed during lecithin decolorization was carried out by the enzyme superoxide dismutase.

In order to determine the influence of different groups of phospholipids on lecithin darkening, its fractionation was carried out. It was proved that phospholipids, according to the degree of change in their color after heat treatment, create the following series (in descending order): phosphatidylcholines – phosphatidylinositols – phosphatidylserines and phosphatidylethanolamines. That is, the darkening of lecithin at elevated temperatures is primarily influenced by the phosphatidylcholine fraction. It has also been proven that there is no correlation between the sugar content in phospholipid fractions and their darkening as a result of heat treatment.

## References


1. Guo, A., Li, S., Yang, Y., Hou, F., Wu, J., Gao, Y. et al. (2022). Lecithin extraction optimisation and synthesis in Hemerocallis citrina Baroni. Scientia Horticulturae, 293, 110682. doi:10.1016/j.scienta.2021.110682
2. Gutiérrez-Méndez, N., Chavez-Garay, D. R., Leal-Ramos, M. Y. (2022). Lecithins: A comprehensive review of their properties and their use in formulating microemulsions. Journal of Food Biochemistry, 46 (7). https://doi.org/10.1111/jfbc.14157
3. Ezzat, S. M., Salem, M. A., Mahdy, N. M. E., Mahfouz, M. M. (2022). Lecithin. Antioxidants Effects in Health, 375–386. https://doi.org/10.1016/b978-0-12-819096-8.00060-4
4. Hu, G.-L., Xiong, J., Liu, Y., Yang, H.-J., Hu, L.-L., Chen, P. et al. (2022). Effects of Lecithin Supplementation in Feed of Different fat Levels on Serum Indexes and Liver Health of Laying Hens. Frontiers in Physiology, 13. https://doi.org/10.3389/fphys.2022.892585
5. Raut, S., Azheruddin, M., Kumar, R., Singh, S., Giram, P. S., Datta, D. (2024). Lecithin Organogel: A Promising Carrier for the Treatment of Skin Diseases. ACS Omega, 9 (9), 9865–9885. https://doi.org/10.1021/acsomega.3c05563
6. Alagumuthu, M., Dahiya, D., Singh Nigam, P. (2019). Phospholipid – the dynamic structure between living and non-living world; a much obligatory supramolecule for present and future. AIMS Molecular Science, 6 (1), 1–19. https://doi.org/10.3934/molsci.2019.1.1
7. Demidova, A. O., Gladkyi, F. F., Berezka, T. O. (2021). Modern methods of degumming of vegetable oils: an analytical review. Innovative Biosystems and Bioengineering, 5 (2), 105–116. https://doi.org/10.20535/ibb.2021.5.2.227359
8. van Nieuwenhuyzen, W., Tomás, M. C. (2008). Update on vegetable lecithin and phospholipid technologies. European Journal of Lipid Science and Technology, 110 (5), 472–486.. https://doi.org/10.1002/ejlt.200800041
9. De Greyt, W. (2020). Deodorization. Bailey's Industrial Oil and Fat Products, 1–44. https://doi.org/10.1002/047167849x.bio027.pub2
10. Kim, H., Ho, C., Chang, S. S. (1984). Isolation and identification of volatile flavor compounds in commercial oil-free soybean lecithin. Journal of the American Oil Chemists' Society, 61 (7), 1235–1238. https://doi.org/10.1007/bf02636260
11. Mortensen, A., Aguilar, F., Crebelli, R., Di Domenico, A., Frutos, M. J., Galtier, P. et al. (2017). Re-evaluation of lecithins (E 322) as a food additive. EFSA Journal, 15 (4). https://doi.org/10.2903/j.efsa.2017.4742

12. Szuhaj, B. F., Yeo, J., Shahidi, F. (2020). Lecithins. Bailey's Industrial Oil and Fat Products, 1–86. https://doi.org/10.1002/047167849x.bio011.pub2
13. Garba, U., Singanusong, R., Jiamyangyuen, S., Thongsook, T. (2020). Extracting lecithin from water degumming by-products of rice bran oil and its physico-chemical, antioxidant and emulsifying properties. Food Bioscience, 38, 100745. https://doi.org/10.1016/j.fbio.2020.100745
14. Chen, X., Sun, S. (2023). Color reversion of refined vegetable oils: a review. Molecules, 28 (13), 5177. https://doi.org/10.3390/molecules28135177
15. Zheng, Z., Zhu, K., Dai, Z. (2021). Preparation of Antarctic krill oil emulsion and its stability under catalase treatment. Foods, 10 (11), 2797. https://doi.org/10.3390/foods10112797