Influence of Phosphatide Content in the Unrefined Sunflower Oil on Its Thermal and Rheological Properties

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Abstract. The results of a study of the effect of the content of phosphatides in sunflower oil on its heat capacity and viscosity are presented. These studies are needed for more accurate calculations of thermal and hydrodynamic conditions in the technology of production and processing of sunflower oil. New results can become the basis for further understanding of the nature of the structure of sunflower oil under various conditions in real processes. This complements the fundamental knowledge and theory of heat and mass transfer. The adaptation of general experimental and data processing techniques to the conditions of the task is presented. Recommendations for reducing the time of experiments are proposed. New data on heat capacity and viscosity values have been obtained for unrefined sunflower oil with different fatty acid composition, for a wide range of operating parameters from 20 to 140 °C, with a phosphatide content from 0.005 to 0.9683 g/100 g. An unambiguous correlation has been established between the thermal and rheological properties of unrefined sunflower oil. The results show that these properties can have a significant impact on equipment efficiency and oil quality. The developed and repeatedly tested research methodology can be successfully applied to other oils and other conditions.

1. Introduction

It is known that sunflower oil is one of the most demanded in the world. According to the information presented in [1] with reference to the original source, sunflower oil is the fourth most consumed vegetable oil in the world. For example, in the most productive year of 2015, it was produced 14.91 million tons, that is, 3 times more than peanut oil and almost 6 times more than olive oil. Currently, this trend continues. To ensure the growth of sunflower oil production, it is necessary to intensify all stages of the technology, subject to the preservation of quality.

Sunflower oil plays an essential role in human nutrition. The article [2] describes aspects of its dietary value and health effects. Sunflower oil is prized for its high content of unsaturated fatty acids and the presence of relatively high amounts of vitamin E and phytosterols [3].
In addition to the main food use, all vegetable oils are used in cosmetics, pharmaceuticals, cutting fluids for mechanical processing, environmentally friendly heat transfer fluids, like biodiesel and other industries. A wide range of applications of vegetable oils should contribute to a detailed study of their thermophysical and rheological properties in various temperature ranges, which ultimately will help to form an accurate understanding of the processes of heat and mass transfer and obtain an equation of the liquid state of vegetable oils.

The non-edible use of vegetable oils is generating interest in detailed studies of their physical properties. These properties include density, heat capacity, viscosity, thermal conductivity, flash point, freezing point, calorific value. The article [4] presents an experimental analysis of the use of biodiesel fuel from waste sunflower oil and a mixture of sunflower oil with palm oil as fuel for aircraft turbo engines.

We specialize in research on sunflower oil, which is the main vegetable oil in Russia. The volume of sunflower oil production increased in 2020. Russia produced 5.9 million tons of unrefined and 2.5 million tons of refined sunflower oil, which is 11.2% and 10.3% more than a year earlier.

Vegetable oils are formed on the basis of triglycerides of higher fatty acids. Mass fraction of triglycerides in oils is 92–98%. The rest of the substances dissolved in the oil and got into it in the process of extraction from oilseeds are usually called accompanying. These substances, like triglycerides, are part of plant cells. They are essential for plant life. Among the accompanying substances, phosphorus-containing substances are of particular importance. Phosphatides or phospholipids are found in the tissues of animals and plants. Phosphatides are esters of phosphoric acid. Depending on the composition of the alcohol esterified with phosphoric acid, phospholipids are divided into glycerophospholipids and sphingophospholipids. Phospholipids form the basis of cell membranes, which exchange substances and energy with the external environment and determine the internal architecture of the cell. In particular, phospholipids regulate fat metabolism in the body of animals, that is, they have a lipotropic effect. The lack of phospholipids in the diet contributes to the obesity of the body. At the heart of cell membranes is a two-layer lipid structure, a significant part of which is phospholipids. About half of this structure is covered or permeated with proteins that perform transport or metabolic functions. The content of phosphatides in a particular oil is different.

Sunflower oil contains different amounts of phosphatides depending on the variety of seeds from which it is produced. Studies in [5] showed that the relative concentration of phospholipids in oils depends on the extraction method and the type of degumming. The oil extraction method has a significant effect on the phosphorus content and the profile of phospholipids, of which phosphatidic acid is the most significant. It was found that heat treatment of whole and crushed seeds increases the phosphorus content and the proportion of phospholipids (including phosphatidic acid). Cold-pressed oil samples obtained from seeds with a lower heat treatment were characterized by a lower phosphorus content and a lower proportion of phospholipids [6]. This may be due to the fact that most of these compounds remained in the cold-pressed cake.

In the production technology, sunflower oil is repeatedly exposed to thermal and hydrodynamic effects. Thermal and rheological properties of sunflower oil are important initial information for the construction of rational technological processes. In dynamic heat treatment processes, the most important thermal property is the heat capacity of sunflower oil. This is necessary to calculate the energy balance. Correct knowledge of this physical quantity determines the amount of heat energy supplied to heat or cool sunflower oil. As a result, the lowest possible temperature of the thermal process can be calculated or the exposure time can be shortened. This has a beneficial effect on the quality of the finished sunflower oil. Among the rheological properties that determine the hydrodynamics of the process of movement of sunflower oil inside the equipment, we have chosen dynamic viscosity. The dynamic viscosity of an oil is highly dependent on temperature and composition. The structure of phosphatides affects the formation of hydrodynamic layers of oils. In [7], two theoretical models of rheological characteristics are determined for changing the dynamic viscosity from the temperature of refined sunflower oil. The dynamic viscosity of sunflower oil decreases exponentially with increasing temperature and shear rate. Based on experimental measurements of the viscosity of vegetable oils, the
researchers propose convenient mathematical formulas. Another study [8] proposed four dependences of dynamic viscosity on temperature for vegetable oils.

The composition of oils significantly affects the formation of physical and physicochemical properties. Thus, according to publications [9], [10] and [11], an increased interest is evident and confirm the relevance of the research topic we have chosen. The article [12] deals with the problems of mass and energy transfer in complex media.

As written in other publications, such as [13], sunflower oil has been extensively studied in recent years because it can be a feedstock for biodegradable lubricants that become organic. These oils are an alternative to synthetic and mineral oils.

Our scientific research is currently focusing on the important physical properties of unrefined sunflower oil. These oils necessarily contain phosphatides. Phosphatides significantly affect the structure and quality of sunflower oil and products of their processing. The ratio of free and bound phosphatides can vary from 1:10 to 1:5, depending on the type of seeds, their place of growth, degree of maturity, storage conditions, transportation and other various factors. In the process of processing oil seeds with such methods as pressing and extraction, free phosphatides are also extracted together with oil, while bound ones, under the influence of hydrothermal treatment and hot solvent, are partially removed from the complexes and thereby pass into oil. For these reasons, the content of phosphatides in crude oils can vary over a wide range, which depends on various factors such as oil recovery, processing mode, phosphatide content in the oilseeds themselves.

Phosphatides are usually referred to as amorphous substances. However, using X-ray structural analysis in synthetic products, clear signs of a crystal lattice were found [14].

Phosphatides are hygroscopic. When interacting with water, they first swell, then form a mucous mass and eventually pass into a turbid, coarsely dispersed system. Since phosphatides contain both hydrophilic and hydrophobic parts, when in contact with water, their molecules are arranged in such a way as to occupy an approximately parallel position relative to each other. At the same time, their polar (hydrophilic) groups tend to submerge in water, while hydrophobic ones remain at the interface between water and air [14]. If a preparation of pure phosphatides is placed in water, and then this mixture is placed between a glass slide and a cover slip, the formation of cylindrical continuously growing fibers can be observed under a microscope [14]. These fibers almost always have the same diameter. This phenomenon is explained with the fact that the non-polar side of the oriented monomolecular layer attracts hydrocarbon radicals of other molecules with the help of van der Waals forces, forming a double layer, which increases in size over time. The same forces cause the formation of other identical layers, separated from the first with some, quite definite number of water molecules.

These phenomena occur simultaneously in all planes. Ultimately, the aforementioned “fiber” is formed with a series of coaxial cylindrical double layers. Fiber has liquid crystal properties. It contains a lot of water, but does not pass spontaneously into a dispersed phase and does not merge with other fibers [14].

Phosphatides are polar. The “end” of the phosphatide, at which the phosphoric acid residue is located, connected to a nitrogenous base or serine, has hydrophilic properties. Its other “end”, containing residues of fatty acids, exhibits hydrophobic properties. This affects the configuration of their molecules. The hydrophilic part of phosphatides forms a polar “head”, while the hydrophobic part forms two non-polar “tails” [15].

2. Objects of research
For experimental studies, two series of samples of unrefined sunflower oil were formed: series no. 1–5 and series no. 5–5.4.

A series of samples no. 1–5 are various samples of unrefined sunflower oil of various origins and different compositions. The data on the fatty acid composition of the studied series of samples were obtained in a similar way as in [16] and are shown in table 1. To determine the fatty acid composition, a Bruker-Sci-on 436 GS gas-liquid chromatograph was used. In this case, a BR-Swax capillary column
(catal. no. BR 89377) with a length of 30 m, a diameter of 0.25 mm, and an active phase based on polyethylene glycol, was used.

**Table 1.** Fatty acid composition of research objects.

| №  | Acid name   | Conventional symbol | Sample no. 1 | Sample no. 2 | Sample no. 3 | Sample no. 4 | Sample no. 5 |
|----|-------------|----------------------|--------------|--------------|--------------|--------------|--------------|
| 1  | Myristic    | C14:0                | 0.1          | 0.1          | 0.1          | 0.1          | 0.1          |
| 2  | Palmitic    | C16:0                | 6.4          | 5.8          | 6.1          | 5.8          | 6.8          |
| 3  | Palmitoleic | C 16:1               | 0.1          | 0.1          | 0.1          | 0.1          | 0.1          |
| 4  | Heptadecanoic | C17:0            | 0.1          | 0.1          | 0.1          | 0.1          | 0.1          |
| 5  | Stearic     | C18:0                | 3.4          | 3.8          | 3.9          | 3.6          | 3.9          |
| 6  | Oleic       | C18:1                | 27.7         | 19.2         | 22.6         | 22.4         | 20.5         |
| 7  | Oleic<sup>a</sup> | C18:1           | 0.7          | 0.6          | 0.6          | 0.6          | 0.7          |
| 8  | Linoleic    | C18:2                | 59.9         | 69.0         | 64.9         | 65.7         | 66.6         |
| 9  | Linoleic<sup>b</sup> | C18:2          | 0.2          | 0.1          | 0.1          | -            | -            |
| 10 | Linolenic   | C18:3                | 0.1          | 0.1          | 0.1          | 0.5          | 0.1          |
| 11 | Arachinic   | C20:0                | 0.2          | 0.3          | 0.3          | 0.2          | 0.3          |
| 12 | Gadoleic    | C20:1                | 0.2          | 0.1          | 0.2          | 0.1          | 0.1          |
| 13 | Behenic     | C22:0                | 0.7          | 0.7          | 0.7          | 0.7          | 0.8          |
| 14 | Docosadienoic | C22:2             | 0.1          | 0.1          | 0.1          | 0.1          | 0.1          |
| 15 | Lignoceric  | C24:0                | 0.2          | -            | 0.2          | -            | 0.1          |

<sup>a</sup> undefined octadecenic acid  
<sup>b</sup> undefined octadecadienoic acid

Sample series 5–5.4 contained samples with one main base, to which phosphatides were artificially added in different amounts. The main basis was sample no. 5. Data on the concentration of phosphatides in the studied samples are presented in table 2.

**Table 2.** Concentration of phosphatides in the test samples.

| Sample number | Concentration, g / 100g |
|---------------|-------------------------|
| 1             | 0.005                   |
| 2             | 0.005                   |
| 3             | 0.007                   |
| 5             | 0.018                   |
| 5.4           | 0.041                   |
| 5.3           | 0.105                   |
| 4             | 0.304                   |
| 5.2           | 0.309<sup>a</sup>/0.251<sup>b</sup> |
| 5.1           | 0.968                   |

<sup>a</sup> when measuring specific heat  
<sup>b</sup> when measuring the coefficient of dynamic viscosity
3. Methods of research

3.1. Investigation of the specific heat of oils

The study of thermophysical properties in the temperature range from 0 to 150 °C was carried out using a DSC 204 Phoenix F1 device, a German company Netzsch. This device belongs to the group of differential scanning calorimeters (DSC).

According to ASTM E473, DSC is a method in which the difference in heat flow rate of a substance and a reference is measured as a function of temperature while the sample is subjected to a controlled temperature program.

Specific heat was determined according to the method described in [16]. The data and recommendations of the manufacturer obtained in [17], as well as the accumulated personal experience, made it possible to make some changes to optimize and increase the volume of research within one research cycle.

The technique looks like this:

1. The temperature program contains one stationary segment, a heating segment and a cooling segment to room temperature. The last segment is not used when processing and analyzing the received data.
2. The heating / cooling rate is up to 5 K/min, which allows you to expand the data range for analysis without changing the overall temperature range from 0 to 150 °C.
3. The time of the stationary site and the initial stage remained unchanged.
4. Nitrogen gas was also used as purge and shielding gases at a flow rate of 20 and 50 ml / min, respectively.
5. The calculation of the specific heat of the sample under study is carried out according to the same formula (1) as in [18]:

\[ c_p(T) = \frac{m_{\text{et}}}{m_{\text{обр}}} \cdot \frac{DSC_{\text{обр}} - DSC_{\text{баз}}}{DSC_{\text{эт}} - DSC_{\text{баз}}} \cdot c_p(T) \quad \text{(1)} \]

The change in the technique made it possible to reduce the distortions of the DSC signal curves and heat capacities at the transition points from one temperature segment to another, in comparison with the technique in [17]. As a result, this made it possible to expand the temperature range: from 20 to 6 °C at the beginning, and from 140 to 149 °C at the end.

As in [16], we took the following steps to improve the accuracy and reproducibility of the data obtained from experiment to experiment. Crucibles for research were selected in such a way that the difference in their masses did not exceed 0.2 mg. The crucible mass was 38.6 ± 0.2 mg, while the mass of the studied samples was 20.0 ± 3.5 mg. A sapphire sample provided by the manufacturer of the device was used as a reference sample.

To obtain the dependence of the specific heat capacity of unrefined sunflower oil on temperature, three samples were sequentially taken from each sample, which were examined within one working day, one after another. The studies were carried out with a complete reloading of the sample. Analysis of the data obtained showed that the relative error of the measurement results with a complete reload of the sample does not exceed 0.6%. This indicates the high accuracy of the selected method for measuring the specific heat and the reliability of the data obtained.

Thermometric methods such as DSC provide information on more than physical properties. The research results help to understand the complex processes in the technology of vegetable oils production. For example, the curves obtained with DSC in [18] show two events that characterize the polymerization and decomposition of triglycerides. The heat capacity of unrefined sunflower oil, obtained with the DSC method, showed a good correlation and depended on the composition of fatty acids.

3.2. Research methodology for rheological properties

To study the rheological properties of unrefined sunflower oil, an experimental setup was used, which is a RHEOTEST RN 4.1 SE rotary viscometer in combination with a JULABO F12-MA thermostat.
The measurements were carried out using a cylindrical measuring system. The rotor diameter is 36 mm, the diameter of the stationary measuring cylinder is 38 mm. To measure the rheological properties, 30 ml of liquid was placed in the measuring cylinder. A personal computer was used to transfer and process the results of the experiment. The procedure for preparing the sample and the measuring system before the experiment has features for unrefined sunflower oil. After sufficient temperature control, the dynamic viscosity coefficient was directly measured at a constant shear rate of 20 s⁻¹. This speed was chosen based on the conclusions made in the article [20]. The shear rate of 20 s⁻¹ is close to the transition state from the stationary liquid phase to the new form of the structure of the liquid phase. This makes it possible to reveal the influence of vegetable oils microcomponents on their structural properties. The measurement time at a constant sliding velocity was 600 s. The measurements were carried out at three different temperatures: 40 and 60 °C.

4. Results

4.1. Specific heat
The data obtained as a result of a series of experiments demonstrating the nature of the dependence of the specific heat capacity of unrefined sunflower oil with different content of phosphatides are presented in figure 1. Figure 2 shows the data of the dependence of the specific heat capacity of unrefined sunflower oil 5 with different concentrations of phosphatides. In this case, oil 5 was chosen as the base one, thereby excluding the influence of other components on the change in specific heat capacity. This effect was not taken into account in the study of samples 1–5.

![Figure 1. Dependence of the specific heat capacity on temperature for samples 1–5.](image-url)
When studying the data presented in figures 1 and 2, the effect of the concentration of phosphatides on the specific heat of the samples under study is clearly traced, both in the case of samples with a different primary base, and for samples with one base. The results obtained using this technique correlate well with the data obtained with other methods, which was shown in [18].

4.2. Rheological properties

Based on the results of measuring the dynamic viscosity, graphical dependences of the dynamic viscosity of unrefined sunflower oil on the concentration of phosphatides at various temperatures were obtained. They are presented in figures 3 and 4.

**Figure 2.** Dependence of specific heat capacity on temperature for samples 5–5.4.

**Figure 3.** Dependence of the dynamic viscosity on the concentration of phosphatides for a temperature of 40 °C.

**Figure 4.** Dependence of the dynamic viscosity on the concentration of phosphatides for a temperature of 60 °C.
Despite the small amount of experimental data, we can observe a nonlinear increase in the coefficient of dynamic viscosity depending on the concentration of phosphatides. The approximating function is constructed very conditionally, solely for a visual representation of the nature of the dependence.

5. Conclusion
Analyzing the experimental data for samples with different main bases (samples 1–5), it can be seen that the heat capacity curve for sample 4 lies higher than the curves for samples 1–3. The difference in numerical values between samples no. 4 and no. 1–3 is about 5%. A similar increase can be traced between sample no. 4 and no. 5, but in this case it averages 3%.

According to the data obtained, the maximum concentration of phosphatides among all the samples of unrefined sunflower oil studied in this work is possessed by sample no. 4 (304 mg / 100 g), and the smallest sample no. 1 (5 mg / 100 g), no. 2 (7 mg / 100 d) and no. 3 (5 mg / 100 g). The concentration of phosphatides in samples no. 2 and no. 5 is 7 mg / 100 g and 18 mg / 100 g, respectively. Data for samples 5–5.4 were considered separately.

The dependences of the values of the specific heat capacity of unrefined sunflower oil no. 5 at temperatures from 6 to 65 °C, with different concentrations of phosphatides (table 2), shown in Figure 2, show an increase in the values of specific heat by an average of 5% for samples with the highest concentration of phosphatides. At the same time, this indicator decreases to an average of 2.5% at temperatures from 70 to 149 °C.

As a result, after mathematical processing, equation (2) for the dependence of the specific heat capacity of unrefined sunflower oil on the temperature and concentration of phosphatides was obtained:

$$c_p = 0.0215 \ln c + 0.0027 t + 1.7597$$

(2)

Figure 5 shows a graph of the dependence of the specific heat capacity of unrefined sunflower oil on concentration at temperatures of 20, 40, 60, 80, 100 and 120 °C, built according to equation (2).

![Figure 5](image)

**Figure 5.** Dependence of the specific heat capacity on the concentration of phosphatides at different temperatures.

To clarify the obtained dependences, it is planned to conduct similar studies within the concentration of phosphatides in sunflower oil from 5 to 200 mg / 100 g, since in this range the greatest nonlinear increase in heat capacity is observed, which may be associated with the formation of a three-dimensional structure of the substance. With a further increase in concentration, the dependence becomes linear, and the slope of the straight line on the graph tends to zero.
The obtained results of the effect of the concentration of phosphatides on the specific heat capacity of unrefined sunflower oil, together with the data obtained in [18], are a good starting point for further investigation of the effect of various components that make up the oils.

The study of the rheological properties of unrefined sunflower oil, in particular the dependence of the dynamic viscosity on the concentration of phosphatides at various temperatures, was carried out to demonstrate the correlation of rheological and thermophysical properties. These measurements are more likely a confirmation of the results obtained in thermophysical experiments than an independent full-fledged study. The study of rheological properties is a topic for a separate work and is associated with more complex mechanisms of interaction of all components of unrefined sunflower oil.

The accumulation of such data and their subsequent analysis will ultimately make it possible to obtain the equation of the liquid state of sunflower oil. In the future, it can be used to solve the problems of optimizing the processes of heat and mass transfer and heat transfer in technologies for the production and processing of oilseeds.

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