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High-pressure phases of vegetable oils (biological aspects)

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Abstract

The article presents the results of the authors' work on pressure-induced phase transformations in the group of vegetable oils. The results of previous and recent studies performed on a number of oils, mainly edibles, are presented. The methodology for generating the pressures necessary to carry out phase transformations in the tested oils and the system for measuring the pressure-volume characteristics are described. Two methods for achieving phase transformations are presented (isobaric method and quasi isochoric method). Research was carried out on less known oils due to the much smaller scale of their production compared to classic edible oils. They are characterized by several parameters that allowed us to assume that the obtained pressure phases would be stable after the pressure was reduced.

These are: hazelnut oil, jojoba oil, and hemp oil. The work presents photographs of the obtained quasi-stable high-pressure phases taken immediately after leaving the pressure chamber. The fatty acid composition of the oils was tested by gaseous chromatography method both before the transformation and after the end of the cycle, without detecting any noticeable changes. The aim of the study, apart from the obvious cognitive ones, was to demonstrate the possibility of studying high-pressure phases from the point of view of food technology - improving the quality (properties) of edible oils.

Key words: vegetable oils, edibles; high pressure, solid phases, phase systems, color.

Introduction

High pressures have found wide and, importantly, prospective applications in the technology of improving the functional properties of edible products. Already, Nobel laureate, P. W. Bridgman, about a century ago, took the first steps in the study of the properties of physico-biological objects under high pressure. In Poland, such research was carried out most extensively at the High Pressure Institute of the

Polish Academy of Sciences (Warsaw) and at the Institute of Physics of the Warsaw University of Technology (Poland). The first phase change of vegetable oil – castor oil – was detected at the Institute of Physics WUT in 1989 [Siegoczyński, Jędrzejewski, Wiśniewski, 1989./1; Wiśniewski et al.1994/2]. The work on castor oil was dictated by the need to control the correct operation of the oil as a pressure transfer medium in high pressure standards – load-piston pressure gauges – over a long period of measurements. The next step was the discovery of the phase transition in triolein [Wiśniewski et al. 2001/,3], which, due to its regular structure, can be treated as a model liquid for the study of phase transitions in triacylglycerols of plant origin.

Further studies confirmed the hypothesis that similar transformations should occur in all oils with a triacylglycerol structure. This led to the initiation of high-pressure studies of various vegetable oils in order to investigate their phase systems. This was confirmed by a study of rapeseed oil, which is widely used in the food industry [Rostocki et al., 2007/4, Wiśniewski, Wilczyńska 2007. /5, The mechanisms of phase production, the transformation pressure and the change in volume during the transformation were studied, as well as the reversibility of the observed changes and their hysteresis. This allows for the interpretation of the properties of high-pressure phases, which is associated with possible improvements of oils as edible or cosmetic products (jojoba and others) [Wiśniewski and Wilczyńska 2006/6, Wiśniewski et al. 2022/7].

The following oils were preliminarily tested: castor, rapeseed, soybean, sunflower, hazelnut, jojoba, walnut, hemp and olive oil. The phases were produced in isothermal-isobaric conditions (basic) and in isothermal-isochoric transformations. An extensive review of papers on the influence of pressure on the physical properties of lipids is presented in the paper [Zulkurnine et al. 2016/8].

Purely physic-chemical tests: basic properties – density, compressibility, structure, chemical composition, colour, rheological, dielectric and organoleptic properties and gas chromatography before and after phase transition were performed. The main direction of high-pressure tests at IBPRS PIB is the determination of phase systems of edible oils after phase transformations at different temperatures with their detection in the form of density changes or state changes. Once the phase transition has been detected (using self-discharging apparatus) [7], the sample is placed under stable conditions and possible tests are performed. Using a more complex apparatus [Wisniewski et al. 2022, 9] than a simple piston-cylinder system, rheological properties, mainly dynamic viscosity, are determined. In particular, the study of atypical phase-forming phenomena determines high values of the isochoric isothermal transformation coefficient of edible oils up to 20 bar/s in the process of producing the high-pressure phase proving the processes of dense packing of complex oil particles.

1. Methodology for the production of high-pressure phases.

Classical high-pressure apparatus up to 10 kbar of internal diameter of 20 mm (Fig. 1b) and self-dismantling apparatus [5], diameter of 16 mm, up to a pressure of 4000 bar, used in cases of rapidly disintegrating high-pressure phases of the tested oils (see literature}) were used for the tests. In the existing literature on high-pressure studies, information about phase systems – these very complex organic objects – is highly uncertain. The following are two methods for achieving phase transitions. A sketch of the phase system research procedure on the example of rapeseed oil is as follows (Fig. 1a).. We introduce oil into the clean apparatus without even small amounts of air. Pressure sensors should be resistant to the fact that the oil to be tested solidifies. Strain gauges are more reliable than resistance sensors (manganin, Au Cr or semiconductor). Forcibly displacement of a high-pressure piston results in a decrease in the oil volume, accompanied by an increase in pressure as a reaction. Maintaining a constant temperature of the test system is essential in the interpretation of the observed effects.

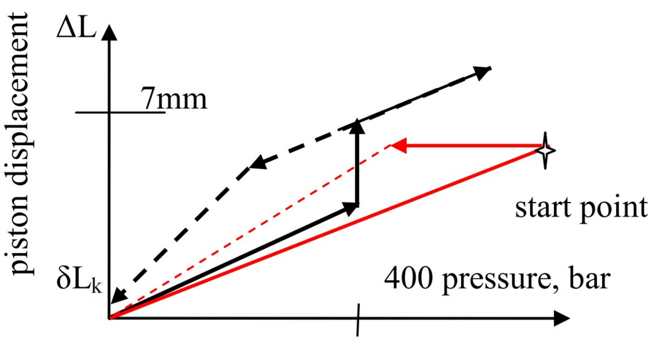

Figure 1a. Illustration of pressure processes producing high-pressure phases of rapeseed oil at a temperature of 25.0±0.5 °C.

The black line describes the determination of the phase transition point, about 390 bar, at T= 25°C. isothermal-isobaric process. A solid line describes a slow process of producing a high- pressure phase, a dashed line describes a slow process of its complete disintegration. In the isothermal-isochoric process, the red line – rapid pressure increases to about 900 bar, temperature 25°C. The red horizontal straight line shows the conformation processes of structures with a high initial pressure drop rate of 4bar/s. Red dot line – a sudden release of pressure to almost zero. The residue δLk - indicates that a certain amount of the high-pressure phase has been preserved. If the apparatus was dismantled slowly the high-pressure phase was not being found. Figure 1b shows a highly simplified diagram of the apparatus used at the stage of long-term formation of a new phase. A typical hydraulic press was used for the operation, with some improvements – digital gauges, piston position detection and others. Due to the observed irregularities, two independent measurement methods were used in the piston displacement measurements: a) with the use of low-deformation press elements and b) the basic - primary method - with the additional use of length standards – Johansson plates (Inventor Carl Edvard).

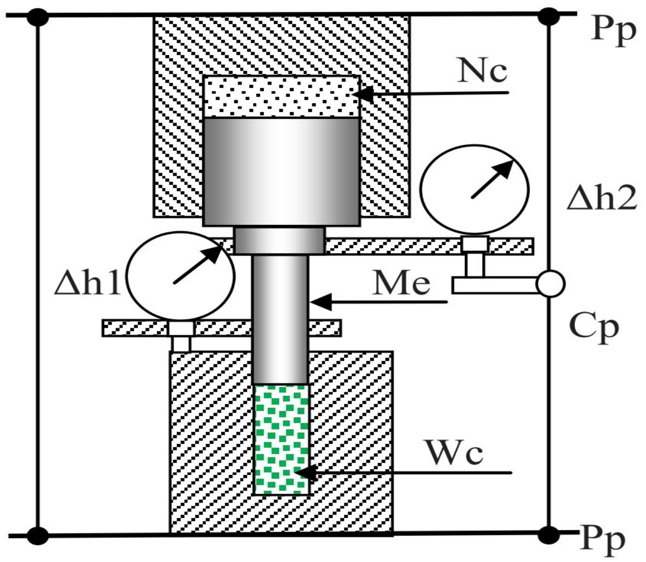

Figure 1b. Diagram of the test system for the long time measuring method: Nc – low pressure (non-active) system, Me –piston of low-friction pressure intensifier, Wc – high pressure active system, Δh1 - direct measurement of piston displacements. Δh2 – complicated measuring of piston displacement, Cp - column of the press, Pp – plate of the press.

2. High-pressure phases of edible oils.

The figure below shows fragments of phase systems, built on the basis of literature data of average freezing points and one or two boundary points of the liquid and solid phases, mainly on the basis of our own measurements. Our main task in this part of the work is to obtain physical high-pressure phases and determine their nature; whether they are waxes, gels, sols or typical polycrystalline systems.

2a. Draft of fragments of phase systems of the studied vegetable oils

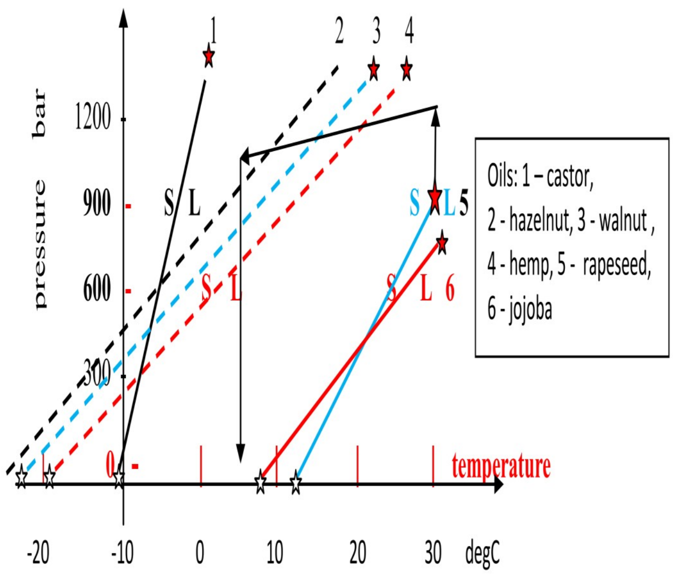

Figure 2. Draft of fragments of phase systems of the studied oils. ☆ – average freezing points, literature data, ★ - own data. S-solid state, L- liquid state

In the case of possible rapid disintegration of the high-pressure phase, the procedure of cooling the high-pressure chamber to a temperature close to the freezing point of the oil in question was used, followed by relatively slow emptying of the chamber. Fig. 2 illustrates this procedure i.e. arrangement of arrows in black. The assumption that there are no changes along the way is justified not by the lack of information about such changes, but by the nature of pressure waveforms from temperature or pressure from time, which do not show any anomalies.

2b. The course of the hazelnut oil experiment

The experiment with hazelnut oil used a typical device: a high pressure chamber with a diameter of 20 mm with a strain gauge pressure sensor and a system for measuring the displacement of a high-pressure piston, built by the authors, with the possibility of making corrections for deformations of the press system. Experiment was provide in a room with a partially stabilized temperature. Used a hydraulic press with a pressing force of 40T, manufactured by the Skarżysko-Kamienna Mechanical Works (history) was equipment with appropriate health and safety safeguards.

The pressure measurement was carried out using two methods: the strain gauge method (red) and the calculation method from the pressure of the hydraulic press with prior adjustment of the system (blue). Pressure conformation time for about 336 hours. (22.12.2022 -05.01.2023). The temperature of the conformation, as variable as the surroundings - in the pavilion in which there is a laboratory built by the authors, was – (19 - 8 - 13) °C .

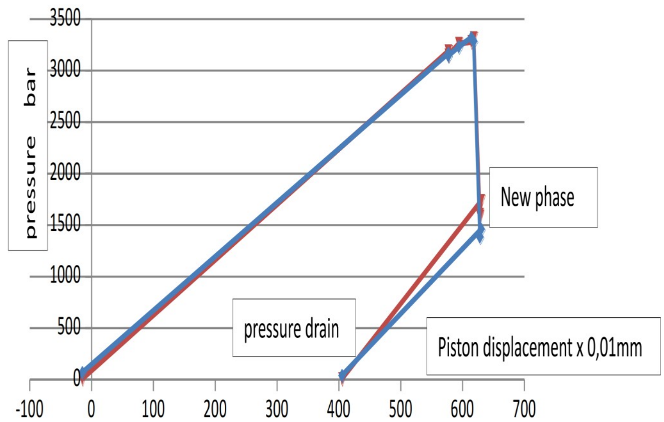

Figure 3. An example of a high-pressure experiment with hazelnut oil. A quick removal of the oil from the apparatus allowed to obtain its solid phase, shown in Fig. 4a.

2c. Illustration of a photograph of oil samples in their high-pressure phases

Figures 4 and 5 show photographs of all the lately obtained high-pressure phases by the authors . The results should be treated as a very beginner. When the appropriate recording apparatus has been obtained, the dynamics of the processes will be recorded.

a)

b)

Figure 4. The high-pressure phase of hazelnut oil – a) and the photo of the high-pressure phase of canola oil –b), just after leaving the high pressure chambers.

On the Figure 5 illustration of conservation effect of solid phase of jojoba oil in temperature of about 6°C. Analysis of shapes of original jojoba elements and it view after very long time let to assert that no main process had place. We can suppose that solid state with sufficient shape strength was property of observed elements.

Approximate scale x2

a)

b)

Figure 5a) condition of the divided wax samples (solid phase of jojoba oil on the beginning of experiment a) and after cooling in a home refrigerator at 6^0C, through a period of 28 months, without noticeable shape and colors changes b). (see also Thomas Parnell pitch drop experiment, Google, 15 02 2021).

The basic question for high-pressure oils phases is as follows - what is the solid state of oils: wax (completely crystallized) or – sole-gel or a natural liquid with a tangled structure, or after conformation, or maybe a liquid solid, quasi liquid? Proper investigation of inside state of an object , not only oleic acid components but real biological objects, will be provided soon.

3. Recent research: hemp oil

Below are shown the first photos from the research on hemp oil conducted by the above mentioned authors in a modest range of biological, physical and chemical research. Figure 7 shown "on face" photos of the free surface of oil in a cylindrical glass vessel in its original state: a) - before the pressure process at room temperature, b) - after the pressure process (slow pressure increase to 4200bar, for a longer period of time to produce a high-pressure phase) and after pouring out the liquid product – suggesting higher viscosity and density and visible thick layer, c) - after 75 hours of storage at 4^{o}C and normal pressure and increased humidity with clearly visible bubble structures and d) - after prolonged aging. Mentioned, after a time of "aging" for about 75 hours at a temperature of 4^{o}C, a bubble structure of the observed free surface of the oil was formed, which is still in the interpretative process. Observation of the surface of the oil after it was further aged for nearly 100 hours did not show any changes, taking on perhaps a slightly darker brown hue.

a)

b)

c)

d)

Figure 6. Illustration of the phenomenon of “bubbling” of the high-pressure phase of hemp oil: a)- photo of the surface of hemp oil before the high -pressure process, b) state of jelly in the volume

poured after a few minutes of the sample from the chamber to the glass vessel, c)-bubble state of the free surface after pouring the oil into the cuvette (4°C preserved), d) –state after a longer (three days) maturation of the oil sample in the refrigerator – clean free surface.

The phenomenon of bubbles in the observed process is explained, in the simplest solution, by the fact that a certain amount of air (up to 0.5 cm^3) from the natural atmosphere is closed (by mistake) in a high-pressure chamber. This corresponds to a 0.02‰ mass fraction of oxygen and nitrogen atoms in 26 g of hemp oil. The particles of the above-mentioned gases are small in relation to the particles of hemp oil, as well as the basic components and other particles being vitamins C, D, E. These are small values and therefore such an intense bubbling effect should not take place. Observations of the bubble structure showed their average time (30 min) stability in the form of a near surface layer and great regularity of their spherical shape and size in the approximate dimension (200-500)μm.

This phenomenon cannot be explained by Henry's law describing the solubility of a gas in a liquid through a free contact surface: p = KC where p - is the partial pressure of a given gas (high under our experimental conditions), C - the concentration of gas in the liquid (probably small), K - Henry's constant. typical for a given liquid-gas system, determined experimentally. A closer look at this phenomenon - shown in Figure 7c - suggests that these are not "bubbles" but small-, micro spherical densely packed objects.

A popular analysis of the composition of fatty acids, by gas chromatography, showed noticeable changes in only two cases - oleic acid 20:1 from 0.5 to 1.2 % and linolenic acid 18:3 n^3 from 18.1 to 17.8%, difficult interpretable. It should not be assumed that there will be any major changes in the properties of the oil as such during and after the pressure process.

Really, in the experiment with the cylindrical research capacitor, the values for its "net" capacitance were obtained: before the pressure tests of 81.26pF, immediately after the high pressure tests of 81.15pF and conductance (electrical conductivity) of 0.01180 μS and 0.01220μS respectively – which corresponds to the high resistivity of the oil of the order of E10 Ωcm and the relative dielectric constant of about μr = 10 (like graphite). Almost unchanged. The good sides are preserved, while the possible but not desirable, but more advanced creatures of life suffer: bacteria, fungal germs or viruses.

An attempt to measure the density, in the absence of hydrometers on the market, forced the authors to perform tests on the buoyancy in the tested liquids (including pure water) of a hollow object made of duralumin rod to an average density of 0.780 g/cm^3.

An experiment with swimming this object in hemp oil after a high-pressure experiment showed a density slightly higher than the average density of the object, i.e. approx. 0.820 g/cm^3- Figure 7. The oil and frontal levels of the gauge are different, the latter slightly higher. It can be assumed that the high-pressure phase has a higher density and is a fluid. An explanation for this phenomenon is ongoing. The densities of the oils were evaluated using a sensor made of duralumin with a density of 2.81 g/cm3. Average sensor density 0.780 +- 0.05 g/cm^3). The density of rapeseed oil was 0.886 g/cm^3, hemp 0.840 g/cm^3 and its density after the high-pressure process was estimated at 0.906 g/cm^3. i.e. its significant enlargement (while maintaining the character of the liquid).

Density measurements using a picknometer calibrated with pure water gave the following results: water 0.972 g/cm^3, hemp oil in factory condition 0.893 g/cm^3 and after high-pressure experiments 0.906 g/cm^3. Which is only a 1.5% increase in density. When assessing the accuracy of our measurements at 1%, we can only talk about certain tendencies. Literature data on the density of other oils: jojoba (hohoba) 0.55 - 0.75 g/cm^3. coconut 0.92 – 0.93 g/cm^3, castor 0.947 – 0.970 g/cm^3, palm 0.91 – 0.92 g/cm^3, olive oil 0.91 g/cm^3, walnut 0.926 – 0.927 g/cm^3, linseed oil 0.92 – 0.94 g/cm^3. Comparative organoleptic tests of hemp oil samples boil down to the assumption of a stronger increase in dynamic viscosity.

Figure 7. Photograph of the process of determining the density of oil using swimming standard of density

Figure 8, shows a schematic sequence of the first step of obtaining the solid phase of hemp oil (stage 1 - creating a pressure guaranteeing a phase change of about 5000 bar. Stage 2 -leaving the system in a constant volume, constant temperature for a very long time (1 - 2 weeks) was to make sure that the phase transition was complete. The observation of a monotonic decrease in pressure – at about half p_{max} (with a guarantee of no leakage) and the stopping of this process justified us to assume the fact that the oil has moved to a new phase (stage 3). Stages 3 and 4 – repetition of stage 1. Stage 5 a reduced temperature only to 6^{o}C (the freezing point of hemp oil in the range of -15, -20^{o}C). In stage 6 , the high-pressure chamber was relatively quick opened and pouring (sic) the oil into a cooled glass container. In each case, no classical solid phase or solid-like phase was observed.

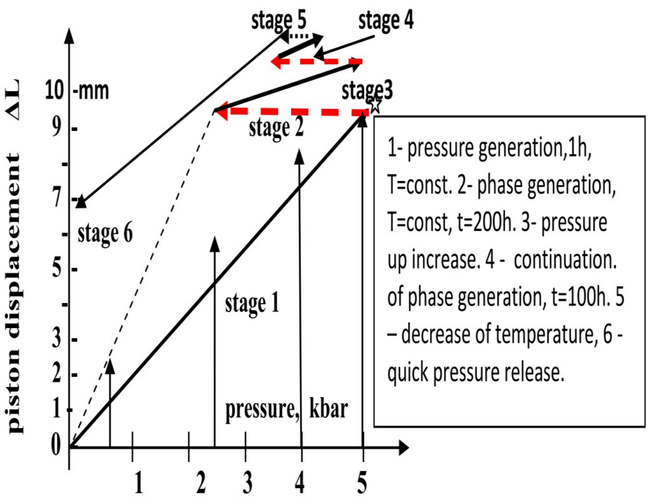

Figure 8. Diagram of the experiment with hemp oil. Characteristic for this kind of experiment is character of stage 2 and 4 being practical parallel to the pressure axis.

Summary

The paper presents photographs of obtained of high -pressure phases of some oils be useful for further different basic investigations. Of particular interest is a photograph showing a high pressure product of hemp oil, which can be called the liquid high-pressure phase of the oil [Tefelski 2013, 10]. This phase can be compared to the phase of water at low temperatures (liquid - entangled phase). The study of biological, physical and chemical properties of living creatures is at the beginning of its development. However, the increasing applications of high pressures in food processing technology and the methodology of food preservation allow us to hope for the development of such research at many world Laboratories (see Neil Widlak, Richard Hartel, Suresh Narine 2001/11 and Kaneko F., Yano J., Sato K.1998/12. „Diversity in the fatty-acid conformation and chain packing of cis-unsaturated lipids", Curr. Opin. Struct. Biol. (1998) August, 8 (4), p. 246. The method of obtaining oil samples using pressures up to 10 kbar, at temperatures from -30^{o}C to +75^{o}C, after any acting time of maximum pressure, has been mastered. It is possible to observe basic parameters, mainly physical parameters and biological aspects particularly, in the Institute of Agricultural and Food Biotechnology, National Research Institute in Poland. Interesting and connected with published here materials are described in literature (13-16) especial classical data by [Gad H.A. 15] connected with jojoba oil.

Acknowledgement

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We would like to thank Thomas Gola, MD, PhD, the owner of the outstanding Dr Gola company, Mińsk Mazowiecki Oil Mill, Poland, UE, for - no cost - providing us with high□quality oils for our scientific research.

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Something about properties of hemp oil

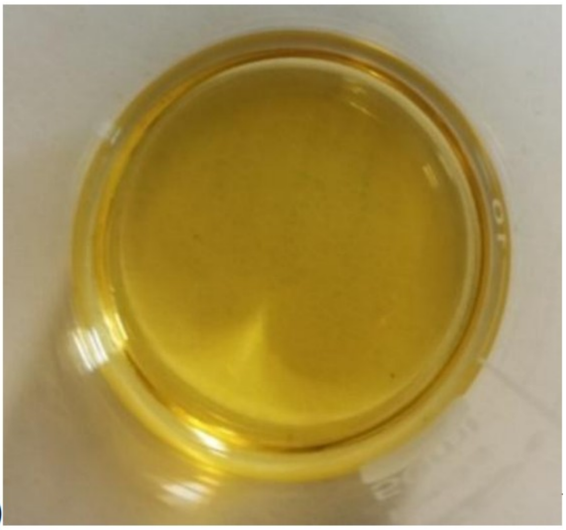
Hemp oil is a versatile product that owes its unique health properties to the optimal proportion of omega-3 to omega-6 acid, which make up as much as 75-80% of its composition. Most of the composition of hemp oil consists of EFAs (Essential Fatty Acids), including: linoleic acid (52-62%), alpha-linolenic acid (12-23%) and gamma-linolenic acid (3-4%). A characteristic feature that is responsible for the properties of hemp oil is the ideal ratio of omega-6 to omega-3 acids of 3:1, which is an exemplary condition for lipid metabolism (i.e. the transformation of unsaturated fatty acids into compounds necessary for the body).

In addition to n-6 and n-3 acids, hemp oil also contains: amino acids, plant sterols, phospholipids, carotene, vitamins (A, E, K and B) and minerals (calcium 20, zinc 30, phosphorus 15, magnesium 12, potassium 19, sulfur 16, iron 26) with antioxidant, anti□inflammatory, analgesic, antibacterial, regenerative and immune stimulating properties.

ADDENDUM

In conclusion (see photos bellow) we would like to mention the fact that the appearance of hemp oil has changed by changing the color of a sample subjected to high-pressure treatment, placed in a glass vessel for a period of several months, under normal ambient conditions in our laboratory, i.e. at changing temperatures – minimum 10deg C, maximum 20deg C and typical relative humidity. We observe a brighter yellow color, increased transparency and lack of irregularities. It can be assumed that there were some positive changes, such as greater homogeneity, in the case of a system of reduced number of scattering centers (e.g. related to bacteria).

Work in the field of "edible oils" inevitably causes interest in the studied oils also in the field of health and cosmetics. The latter use of oils in the information department (advertising) is of great interest in the cosmetics business. One of the authors (90+) who has the greatest problems in the field of hair health, having encountered relevant information, e.g. about the properties of hemp or jojoba oil, (mainly using their after post pressure states) follows the relevant recommendations, admitting that with positive results (see photo - Krakow 2013, Falenty, Poland , UE, 2023).

a) 

b) 

c) 

Stills: a) transparent hemp oil after long detention after a pressure process, b) from the Congress of Polish Physicists, Krakow 2013, c) from the IBPRS and PSPO Conference, Falenty near Warsaw, 2023.