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Research of the Process of Supercritical CO_2 Extraction from Sunflower Cake

Abstract. *Sunflower cake is rich both in proteins and polyphenolic compounds, including chlorogenic acid. The kinetics during the extraction of sunflower cake in a supercritical CO_2 environment and using a co-solvent was studied. A high-quality protein concentrate (protein content of 56.2...57.2%) with a neutral smell and color was obtained. Qualitative studies showed a low concentration of chlorogenic acid in the obtained samples. The content of chlorogenic acid in the dry residue was 34 mg/100 g when extracted with pure CO_2 and 14 mg/100 g when extracted with a co-solvent.*

Streszczenie. *Ciasto słonecznikowe jest bogate nie tylko w białka, ale także w związki polifenolowe, w tym kwas chlorogenowy. Badano kinetykę ekstrakcji makuchu słonecznikowego w nadkrytycznym środowisku CO2 i przy użyciu współrozpuszczalnika. Otrzymano wysokiej jakości koncentrat białkowy (zawartość białka 56,2...57,2%) o neutralnym zapachu i barwie. Badania jakościowe wykazały niskie stężenie kwasu chlorogenowego w otrzymanych próbkach. Zawartość kwasu chlorogenowego w suchej pozostałości: po ekstrakcji czystym CO2 – 34 mg/100 g; po ekstrakcji współrozpuszczalnikiem - 14 mg/100 g. (**Badania procesu ekstrakcji nadkrytycznym CO2 z makuchu słonecznikowego**)*

Keywords: CO_2 solvent, extraction, protein concentrate, sunflower cake.
Słowa kluczowe: Rozpuszczalnik O2, ekstrakt, koncentrat białka, cukier słonecznikowy.

Introduction

Population growth in the world and Europe, increasing food demand and the growing trend of non-meat nutrition create conditions for a sustainable demand for vegetable proteins.

In 2013, the world market demand for proteins and amino acids was about 7.8 million tons per year with an expected growth of 5.5-6.0% per year until at least 2025. Vegetable proteins occupy about 14% of the market, and amino acids 25% [1].

In 2014, the global vegetable protein market was estimated at approximately one million tons and $7.7 billion, with an expected growth to $10 billion in 2020. Soybean products dominate with 78% market share [2].

Due to a severe lack of protein in many parts of the world, oilseeds are increasingly used in human nutrition. Most oil seed dishes are rich in health-promoting compounds and are potential sources of plant protein, dietary fiber, and antioxidants [3].

Sunflower seeds are an excellent source of biologically active compounds, including vegetable oils (about 50 wt.%), glycosides, fatty acids, vitamins (E, B1 and B5), alkaloids, minerals and proteins.

According to the classification, cake is a mechanically pressed core with oil content of 7...20%; meal is chemically defatted cake with protein content of up to 40%; concentrate is meal with protein content of 40...80%; isolate is a concentrate with a protein content of more than 80% [4].

Sunflower meal is commonly used as a protein supplement for animals. Long-term studies of sunflower meal have shown that the amino acid composition of meal proteins is superior to other vegetable proteins and can be used in food technologies, which is of great practical interest. Attempts to obtain food protein from sunflower meal have encountered many problems.

Firstly, food purposes have to remove as much sunflower husk as possible, secondly, sunflower meal is rich not only in proteins but also in polyphenolic compounds, including chlorogenic acid, which occupies about 70% of other polyphenols. Some experts classify chlorogenic acid as an anti-nutritional compound [5]. Chlorogenic acid forms complexes with proteins and it is difficult to separate it completely. Chlorogenic acid in an alkaline environment quickly oxidizes and acquires a green color, which is the first obstacle in obtaining food protein [6].

The production of proteins from sunflower meal would meet the demand of food industry which is constantly searching for an inexpensive protein source and would be a possible replacement of soy proteins. However, the use of sunflower meal is primarily limited to the low value animal feed. This has been attributed to the presence of polyphenols in sunflower, which reduces the sensory qualities in terms of dark colour and imparts bitter taste and astringency in sunflower meal [7]. Also, the presence of polyphenols lowers the nutritional value of the end product due to interaction with some amino acids such as methionine and lysine. 1–4% polyphenols are present in the sunflower meal with chlorogenic acid being the predominant one. These polyphenols are oxidized by both polyphenol oxidase and the alkaline conditions prevailing during the protein extraction [8].

The production of proteins from sunflower meal would meet the needs of the food industry, which is constantly seeking an inexpensive source of protein and could replace soybean protein. However, the use of sunflower cake is primarily limited to low-value fodder. This is explained by the presence of polyphenols in sunflower, which reduces sensory qualities in terms of dark color and gives sunflower meal a bitter taste and astringency [7]. In addition, the presence of polyphenols reduces the nutritional value of the final product due to the interaction with some amino acids, such as methionine and lysine. Sunflower meal contains 1–4% polyphenols, with predominating chlorogenic acid. These polyphenols are oxidized both by polyphenol oxidase and by alkaline conditions prevailing during protein extraction [8].

Extraction processes in the perfumery, cosmetic, pharmaceutical, and food industries largely depend on solvents, most of which are of petroleum origin.

When extracting, there may arise the following problems: huge energy consumption, significant

consumption of solvents, and low output of the target component.

The authors [9] investigated the influence of the solvent type on the physicochemical characteristics of oil and low-fat meal. The main indicators of the composition and quality of sunflower and rapeseed oil were studied. The quality of the oil and the methods of its use in food products were mostly determined by its fatty acid composition. Analysis of the fatty acid composition of the oil was carried out by gas chromatography in an HP-88 column 100 m* 0.25 mm*0.20 μm.

Solvents for extraction are mainly volatile organic compounds obtained from non-renewable resources, mainly oil-based, harmful to both human health and the environment. One such widely used solvent is n-hexane, a product of the fractional distillation of petroleum mixtures. The main advantage of these solvents is the ease of production and chemical properties. However, hexane is produced from fossil sources and has recently been classified as CMR 3, meaning that it is a Category 2 reprotoxic substance under the European Directives and Regulations on the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH).

The research carried out by the scientists [10] shows that the extraction of rapeseed oil under microwave field conditions has the advantage of using ethyl alcohol as a solvent, since it is polar, non-toxic, and safer (in contrast to hexane).

The possibility of reducing the duration of the extraction process of soybean seeds with ethanol was also studied [11]. A higher output of the target component was obtained, and the amount of tocopherol in the finished product increased.

Therefore, it is necessary to consider alternative solvents, such as liquefied gases or their combination with co-solvents.

Literature review and problem setting

One of the problems that should be solved by innovative extraction methods and technologies is to maximally extract useful products from raw materials [12].

Liquefied gases are selective extractants concerning carotenoids, fatty and essential oils, terpenoids, and other lipophilic compounds. The use of liquefied gases allows the process to be carried out without thermal influence and to preserve thermolabile compounds in their native state, to increase the output of target components.

Liquefied gases including carbon dioxide, propane, butane, liquid ammonia, and freon are promising for extracting components from plant raw materials [13]. Liquefied carbon dioxide can extract essential oils well while fatty oils and other hydrophobic substances are extracted worse.

Freon 11 (CCl_3F), freon 12 (CCl_2F_2) and freon 22 ($CHClF_2$) can extract essential and fatty oils, carotenoids, terpenoids, and other natural substances [13]. Most liquefied gases have the properties of non-polar solvents, although they are hydrophilic compounds themselves. Hydrophilic substances are well extracted by liquefied gases with high dielectric constant (ammonia, methyl chloride, methylene oxide, etc.).

The study [13] represented the technology of cryogenic extraction with liquefied freons. Using the equipment to extract lipid fractions from biological raw materials, a freon extract from bay leaves (Laurus nobilis) was experimentally obtained. A low-temperature extraction of lipid fractions from bay leaves was first realized using liquefied freons within the temperature range of –2...–8°C. The difference in composition of these fractions from that of the oils, obtained within the standard temperature ranges of 30...50°C was shown. The dependence of the finished product weight on extraction time as a result of three consecutive cycles of 23 hrs each was demonstrated. Using gas chromatography, 68 components of freon extract were identified, and their quantitative composition and dominant compounds were detected. The content of essential oils and aroma-forming substances, stipulating the number of odor units was specified. These findings may be the basis for novel technological approaches to the separation of lipid fractions, isolated from biological raw materials of plant and animal origin. The device version with a three-stage cryogenic system of freon solvent recovery for effective implementation of the designed technology was described.

The Institute of Technical Thermophysics of the National Academy of Sciences of Ukraine developed an installation [14] for extracting biologically active substances (BAS) from vegetable raw materials with liquefied gases. Freon R12 is used as an extractant. This choice of extractant is explained by the fact that one of the target products of extraction is fatty oils. In addition, the critical dissolution temperature for freon R12 is low enough, which allows working at lower temperatures and pressures in the extraction system.

The principle of operation of the experimental installation for BAR extraction is based on circulating extraction. Extraction from rose hips was carried out at the installation. As a result, rosehip oil was obtained.

However, in some works [13, 14] no tasks were set for extracting oil and chlorogenic acid from sunflower. In addition, it is unclear for freons when they will be canceled or allowed by legislation, how harmful they are to the human body. There are still questions about the scaling of such installations.

Supercritical fluids (SCFs) are a well-proven alternative to traditional methods of extraction with organic solvents [15]. Carbon dioxide (CO_2) is the most widely used supercritical fluid because it is inert, non-toxic, non-flammable, cheap, common, easily removed from the product and has moderate critical properties (supercritical point T_c=31.1 °C, P_c=7.39 MPa).

Researchers [16] compared extracts obtained during marjoram extraction using supercritical CO_2 (50 C/45 MPa) and ethanol extraction in a Soxhlet apparatus. The extraction yields were 9.1 and 3.8%, respectively. The supercritical extract contained 21% essential oil, and the alcoholic extract contained only 9% volatile oil substances.

The researchers [17] also described the ability of butanol to remove colored phenols (chlorogenic and caffeic acids) and oligosaccharides from sunflower meal without noticeable protein denaturation. Further precipitation of the protein extract at pH 5.0 gave a colorless protein isolate (93.5%). The amino acid composition of sunflower meal, concentrate, and isolate was similar. However, butanol is a fire-hazardous and toxic substance, so its use for extraction in the food industry is limited.

The search for new solvents has revived interest in the use of liquefied gases as extraction solvents, such as n-propane, n-butane [18], and dimethyl ether [19]. These gases require relatively low pressure (<1 MPa) to remain in the liquid state. But they are explosive, so their use for extraction in the food industry is limited.

Supercritical CO_2 extraction of chlorogenic acid from sunflower seed kernels using ethanol as a co-solvent was studied [20]. The influence of mode parameters on the process was determined. The kernels were dried (up to 5 wt. %), which could lead to additional energy costs for the extraction process. The authors did not perform preliminary mechanical degreasing. The kernels were crushed to 0.841...0.507 mm, which could make it difficult for the

extractant to pass through the product layer. The task of obtaining a protein concentrate and preserving the native properties of the protein was not set by the researchers.

Some studies [21] were aimed at obtaining sunflower flour with a high protein content and a low content of phenolic compounds. Sunflower meal was defatted using supercritical CO_2 extraction technology. After that, phenolic compounds were extracted using ultrasound with the addition of a water-ethanol mixture as a solvent. But the authors did not consider the possibility of using ethanol as a co-solvent in the process of supercritical extraction.

The use of supercritical CO_2 extraction of products such as sunflower cake is limited. But this method needs further development, as it is low-temperature, non-destructive for proteins, and will allow partial removal of chlorogenic acid from sunflower cake.

The purpose and objectives of the research

The purpose of the study was to investigate the process of supercritical CO_2 extraction and obtain a protein concentrate of neutral taste and color with a low content of polyphenols from sunflower cake.

Objectives:

– determine the effect of operating parameters on the kinetics of the process of supercritical extraction of sunflower cake with pure CO_2 and using a co-solvent (ethanol);

– estimate the content of chlorogenic acid in the dry residue.

Materials and methods

Sunflower seed kernels were pressed using a Dulong ZYJ05 400W press (China). Cold pressing technology was used (product temperature was not higher than 45°C). Biomass in the form of shreddedd cake (particle size of different fractions d_f =1...5 mm) and petals of sunflower cake (petals up to 10 cm) were tested. Extraction was carried out with pure CO_2 and with ethanol (96%) as a co-solvent. Carbon dioxide (CO_2) of 99.9% purity was supplied by GROHE (Germany). The experiments were performed on a laboratory unit of continuous action EXTRATEX (France) with an extractor volume of 25 liters. Experiments were conducted on the basis of Potoky LLC.

Schematic diagram of supercritical CO_2 extraction is shown in Fig. 1.

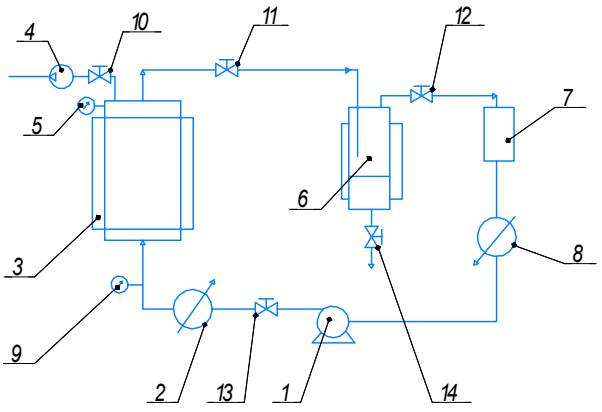


Fig. 1. Schematic diagram of supercritical CO_2 extraction

The installation consists of a compressor 1, heat exchanger 2, extractor 3, vacuum pump 4, pressure gauge 5, receiver 6, filter 7, condenser 8, pressure gauge 9.

The installation also includes shut-off valves (10, 11, 12, 13, 14) and pipelines.

The installation worked as follows. Compressor 1 pumped liquefied CO_2 into heat exchanger 2 to reach the supercritical state. Extractor 3 was filled with biomass. Vacuum system 4 was used at the beginning of the extraction process before the extractant was fed into the extractor. This system includes a vacuum pump 4, a pressure sensor 5, pipeline and shut-off fittings.

In the extractor, the supercritical phase was saturated with soluble compounds from the biomass. Then the mixture of extract and CO_2 went to the separator 6, where the mixture was separated due to the introduction of heat. Gaseous CO_2 was fed to condenser 8, where it turned into a liquid state.

Circulation of the extractant was carried out repeatedly until the raw material was exhausted. A concentrated solution of extractive substances was obtained in the evaporator. CO_2 consumption was monitored using a rotameter (MFG Co. Ltd., Great Britain). The temperature was controlled on the outer surface of the extractor using built-in copper-constantan thermocouples.

An installation including two separators was used to work with the co-solvent (Fig. 2).

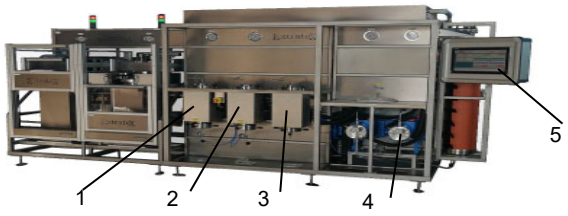


Fig. 2. Experimental plant: 1 – extractor, 2 – separator, 3 – separator for co-solvent, 4 – compressor, 5 – control unit

During the experiment with the co-solvent, the two separators were operating at the same temperature and pressure (6 MPa, 50 °C). The extract was mainly collected in the first one, which was a mixture of oil and ethanol. In two hours, the pressure in the first separator was increased to 12 MPa and the temperature was maintained at 50°C. The goal was to maintain the supercritical state in the first separator but under milder conditions in order to precipitate the lipids and try to keep the ethanol very soluble in the supercritical phase. The second separator was maintained in gaseous conditions for the final recovery of ethanol.

Table 1. Conditions of experimental studies

N	Product	Initial oil content, %	Final oil content, %	Initial protein content , %	Final protein content, %	Temperature, °C	Pressure, MPa	Consumption CO_2, g/min
1	Shred-ded cake	7,5	1.6	53.2	56.7	50	30	50
2			2.4		56.2			200
3			1.5		57.2			500
1	Petals		1.6		57	70	60	833
2			1.8		56.8	50		

According to the color of the dry residue, the extraction appeared to be completed after the first hour. The use of a co-solvent makes it difficult to estimate the extraction output by weighing the extract, so the kinetics of the process was not investigated in this case.

Experiments without co-solvent were performed in the following range (Table 1).

The amount of extract in percent was calculated as the ratio of the mass of the raw material to the mass of the obtained extract multiplied by 100%. The sample was weighed on a laboratory electronic scale (ER-Plus-06, Technobalance, Ukraine).

The crude protein content in the dry residue after extraction was determined by the Kjeldahl method, and the oil content by the Soxhlet method.

The content of chlorogenic acid in the dry residue was determined using high-performance liquid chromatography.

Results of studies of the supercritical extraction process

Results of studies of the kinetics of the process

The dependence of the amount of extract on the duration of the process for the crushed cake is presented in Fig. 3.

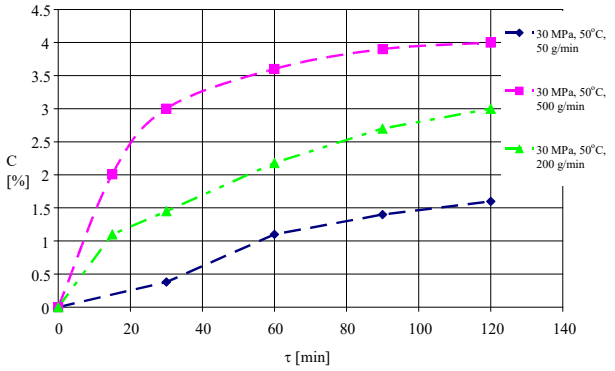


Fig. 3. Kinetics of supercritical CO_2 extraction of crushed sunflower cake

An increase in the consumption of the extractant leads to a significant increase in the extraction rate. Thus, a 10-fold increase in extractant consumption leads to a 2.5-fold increase in the amount of the final extract. The solubility of sunflower cake compounds under the selected conditions demonstrates the effectiveness of the process.

The dependence of the amount of extract on the duration of the process for raw materials in the form of petals is presented in Fig. 4.

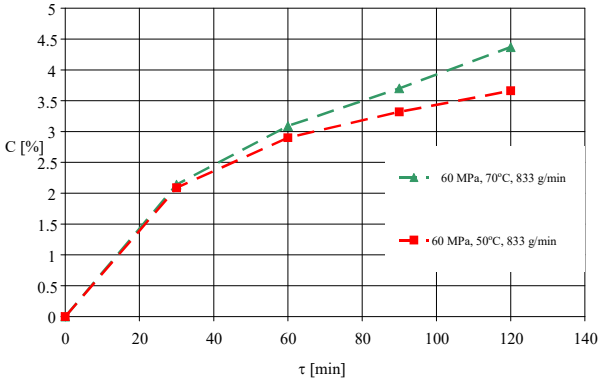


Fig. 4. Kinetics of supercritical CO_2 extraction of cake in petals

An increase in temperature by 20 °C practically does not lead to an increase in the speed of the process. The speed of extraction under equal conditions for petals and crushed cake practically does not differ (Fig. 3, 4).

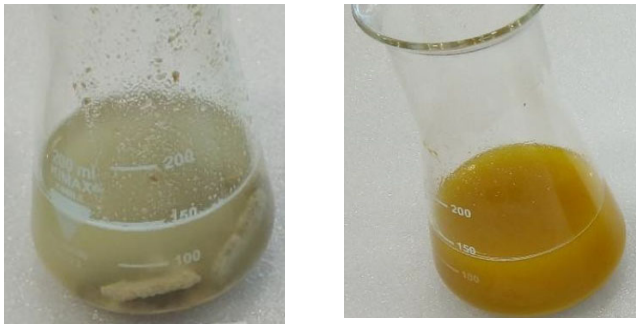
Evaluation of the content of chlorogenic acid in the dry residue

Qualitative analysis of the obtained samples shows that most of the polyphenols (chlorogenic acid) have passed into the extract. The extract is a yellow-green liquid (Fig. 5a), dry residue is well-bleached (Fig. 5b, c). In fact, the dry residue is a sunflower protein concentrate.

a) b) c)

Fig. 5. Products obtained during CO_2 extraction of sunflower cake: a) extract; b) dry residue from crushed raw materials; c) dry residue (petals)

To assess the presence of chlorogenic acid (which can turn the protein concentrate green after oxidation), samples of the dry residue were mixed with water to which sodium hydroxide solution was added and was aged for one hour.



a) b)

Fig. 6. Qualitative assessment of the content of chlorogenic acid in the protein concentrate: a) a solution of the concentrate with water; b) concentrate solution after aging in an alkaline environment

The mixture of the concentrate and alkali solution does not turn green within an hour (pH 9), which indicates a low concentration of chlorogenic acid.

The content of chlorogenic acid in the dry residue was 34 mg/100 g when extracted with pure CO2 and 14 mg/100 g when extracted with a co-solvent.

Discussion of the extraction process results

Experiments show high solubility of polyphenols using CO_2 and a co-solvent at 60 MPa/50°C. Qualitatively, this can be assessed by the color of the extract (Fig. 5a). The results can be explained by the fact that during supercritical extraction, CO_2 acts as a non-polar solvent and washes oil away well, while ethanol, in turn, acts as a polar solvent and effectively removes polyphenols.

The extract at 60 MPa/70°C is a yellow emulsion and the residue is well bleached. A higher temperature does not increase solubility, but it is a dangerous parameter that can damage the final product.

The protein content in the concentrate increases by 3.5-4%, compared to the raw material (Table 1), which is due to the extraction of oil and polyphenols by the extractant.

Conclusions

A high-quality protein concentrate (protein content 56.2...57.2%) with a neutral smell and color was obtained. The use of low-temperature extraction modes makes it possible to preserve the native properties of the protein. In contrast to experiments [21], preliminary mechanical

degreasing of raw materials was carried out, which allows obtaining high-quality cold-pressed oil. In addition, a larger size of particles enables to avoid additional hydraulic resistances in the system.

The kinetics during the extraction of sunflower cake in a supercritical CO_2 environment was studied. The influence of mode parameters, pressure, temperature, and extractant consumption on the speed of the process was determined. Thus, increasing the consumption of the extractant (at a pressure of 30 MPa) by 10 times leads to an increase in the amount of the final extract by 2.5 times.

Qualitative studies show a low concentration of chlorogenic acid in the obtained samples. The mixture of the concentrate solution and alkali does not turn green within an hour (pH 9).

Chlorogenic acid content in the dry residue is 34 mg/100 g when extracted with pure CO_2 and 14 mg/100g when extracted with a co-solvent.

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