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OIL CROP POMACE AS A POTENTIAL SOURCE OF PROTEIN AND DIETARY FIBER

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Abstract. The oil industry market is promising worldwide, including in the Republic of Moldova. The growth of vegetable oil production has led to the formation of a large amount of waste – oil crop pomace (meal), which is usually discarded or used in small quantities as animal feed and becomes a serious environmental problem. The aim of this work is to analyze and study different kinds of oil crop pomace, which can be used as a functional ingredient in product development due to its beneficial components, dietary fiber, and protein. This review presents the classification of meals, the methods of their production, chemical composition, protein, and dietary fiber extraction methods, also their characteristics are discussed. Harmless extraction methods are preferred as they reduce the number of reagents used, reduce waste, and increase the yield. The review presents physicochemical parameters of protein concentrates, isolates, and dietary fibers, which are actively used for valuable food additives production, used as low-calorie ingredients or texture stabilizers in the formulations of various food products.

Keywords: *extraction, isolates, oilcake, pumpkin seed, rapeseed, soybean, squeeze, sunflower seed.*

Rezumat. Piața industriei uleiului este promițătoare în toată lumea, inclusiv în Republica Moldova. Creșterea producției de uleiuri vegetale duce la formarea unei cantități mari de deșeuri de tip șroturi. Șroturile sunt de obicei aruncate sau folosite în cantități mici ca hrană pentru animale și devin o problemă gravă de mediu. Scopul lucrării este de a analiza și studia tipurile de șroturi care pot fi folosite ca ingrediente funcționale în dezvoltarea produselor alimentare datorită componentelor lor benefice, anume fibrele alimentare și proteinele. Acest studiu prezintă clasificarea șroturilor de oleaginoase, analiza metodelor de producere a acestora, compoziția chimică, metodele de extracție a proteinelor și fibrelor alimentare, precum și caracteristicile acestora. Metodele de extracție inofensive sunt binevenite, deoarece reduc cantitatea de reactivi utilizați, reduc deșeurile și cresc randamentul. Sunt prezentați indicatorii fizico-chimici ai concentratelor proteice, izolatelor și fibrelor alimentare, care sunt utilizate activ pentru producerea aditivilor alimentari valoroși, sunt utilizate ca ingrediente cu conținut scăzut de calorii sau stabilizatori de textură în formulările diferitor produse alimentare.

Cuvinte cheie: *extracție, izolate, șroturi de oleaginoase, semințe de dovleac, rapiță, soia, tescovina, semințe de floarea soarelui.*

1. **Introduction**

 Nowadays, there are more and more problems with the availability of animal proteins because of environmental pollution, climate change, loss of biodiversity, etc. In addition, prices are also rising due to the increased demand for aliments and energy consumption. At the same time, the need to consume high-quality protein does not decrease. In this regard, research into the production of protein from other environmentally friendly sources is widely welcomed. Among them are plant sources rich in proteins with a good amino acid composition, which after extraction can be used in food as food additives. Plant proteins are easily absorbed by the organism, are not toxic, and are quite suitable for use as a substitute for animal protein [1,2].

In addition, there is the problem of utilization of food processing waste, which has an environmental impact. The Food Agriculture Organization reported that each year about 1.3 billion tons of food is lost, which is 1/3 of the global food production. This includes 20% of oilseeds, meat, and dairy products, 30% of cereals, 35% of fish, and 40-50% of fruits and vegetables. Of the total food waste, 54% occurs during cultivation and post-harvest stages, while 46% - during processing, distribution and consumption [3]. Residues after food processing contain precious compounds (pigments, minerals, fibers) that can be used in the food industry and other fields (agriculture, pharmaceutics, cosmetics) [4].

For these reasons, scientists, ecologists, and nutritionists welcome the recycling of food waste to obtain other products suitable for food or everyday use. This fact can also generate additional income for producers and processors. Agro-waste presents oilseed pomace, which remains after the production of vegetable oil. Residues after oil production contain valuable components such as fiber, antioxidants, pigments, and minerals, which after processing can be used in various industrial fields: food, pharmaceutical, agricultural, and cosmetic. This pomace is rich in protein, nitrogenous compounds, and minerals and is mainly used as cattle feed, but with proper processing can be a source of protein suitable for food [5]. Oilseed pomace has been found to increase the weight of young animals [6]. In this regard, oilseed pomace may become a raw material for protein preparations of plant-origin fabrication. Oilseed pomace has great potential to produce various value-added products with high nutritional value [5].

Soybean products remain the leader in processing, but such potential sources of protein as secondary products of melon seeds, flax, nuts, amaranth, and other oilseeds are also studied [5]. The main oilseed crops used for processing and rich in protein are sunflower, pumpkin, flax, rapeseed, soybean, poppy, and hemp.

The work aims to study the characteristics and origin of pomace of different oilseeds, methods of protein and dietary fiber extraction, and their characteristics.

2. Classification and characteristics of the oil crops

Oilseed crops are a large group of plants that include representatives of various families. From the point of view of their national economic importance, they contain 60-80% oil in their seeds or fruits and are one of the varieties of industrial crops [7]. The value of seed as a material for obtaining oil depends on the oil content of the seed, the price of the oil and its applicability, the difficulty of extracting the oil, and the value of the residue from the extraction [8].

The full list of families with high oil content includes more than 30 names. Oils produced from them make up 70% of the total volume of fats consumed in the world. Pomace

obtained during oil production becomes valuable feed for farm animals, but also, with proper processing, can be used for food purposes. The list of oil crops includes *Asteraceae*, *Lamiaceae*, *Umbelliferae*, palm, *Cucurbitaceae*, legumes, olive, *Euphorbiaceae,* and others [7].

2.1. Sunflower

The fat content of modern sunflower varieties reaches 52% of the dry matter weight of the seed. Sunflower oil refers to a semi-drying type and has excellent taste qualities. It is used for consumption, and food preparation and is also used in margarine production, canning, confectionery, etc. The main fatty acids of this product are oleic and linoleic. The linoleic acid content in the sunflower oil reaches 60% of the total fatty acids, oleic acid 30- 35%. Sunflower oil contains vitamins A, D, E, and K, phosphatides, and other beneficial substances. Low-grade sunflower oil is used for soap, paints, linoleum, electrical fittings, and waterproof fabric production [9].

2.2. Rape

The botanical name is *Brassica napus L. ssp. Olivera Metzg*. (winter — *biennis*, spring *annual*). It belongs to the annual herbaceous plants of the Cabbage family (*Brassicaceae*) [10]. Rapeseeds contain from 30 to 50% oil and up to 23% protein. Of all oilseed crops winter rape ranks first in terms of oil content in seeds (45-50%). The seeds of winter forms contain up to 20% protein and 17% carbohydrates. Semi-drying rapeseed oil can be used for food and technical purposes. Spring rapeseeds contain 35-45% oil, 21% protein and 17-18% carbohydrates. The oil is slightly drying and is used for food and technical purposes. Rapeseed oil is important in food, soap, polygraphy, and other industries. The output of pomace from seeds is 56%, and their protein content reaches 38-40% [11], according to other data, up to 45-49%, which is well balanced in the composition of amino acids. The pomace of erucic acid-free varieties serve as good fodder. The pomace of conventional rapeseed varieties contains 6-7% glycosinolates, whereas that of erucic acid-free varieties contains less than 0.5% and can therefore be compared with soybean oilcake. The pomace from the seeds of common varieties can be fed to animals, but in small quantities [12].

2.3. Other oil crops

Styrian oil pumpkin (*Cucurbita pepo var. Styriaca*) has rindless seeds with an oil content of up to 50%. Unlike other varieties of pumpkin, oil pumpkin varieties are cultivated to produce fruit with a large number of seeds and, respectively, a high total oil output. The seeds can be sold to the consumer as whole seeds or can be processed into oil. Pumpkin seed oil is considered beneficial due to its antioxidant properties (higher than olive oil, hemp, and sunflower oil) [9].

Flax seeds contain 30-50% oil, which includes up to 30-60% linolenic acid, 17-35% linoleic acid and 15-20% oleic acid. In terms of biological value, linseed oil takes one of the first places among other edible vegetable oils. In addition, linseed oil has a high specific energy content of 39.4 kJ/g, and the content of high molecular unsaturated fatty acids in the oil determines its ability to dry quickly and its value as a technical oil [10]. Linseeds contain 35-42% of the seed weight of well-drying oil, which is used in the production of paints, varnishes, drying oils, soap, paper, electrical, and other industries, as well as in medicine and perfumery. A small part of linseed oil is used for food purposes. Linseed pomace serves as a good concentrated feed for livestock. It contains 6-12 % fat and up to 30 % digestible protein [9].

Soybean (*Glycine max*) is a legume crop originating from East Asia. Because of its high oil content soya is classified as an oilseed. It is used as oil for consumption and for industrial applications as, for example, biodiesel. Soya accounts for about 60% of the total world production of oilseeds. However, in Europe, soya is considered a legume crop along with beans, lentils, and peas [9]. As a major source of vegetable protein and edible oil, soybean is a very important legume crop in the world. Although soya is produced mainly for its dry seeds, the widespread use of immature seeds, especially in eastern Asia, makes soya an important vegetable crop. The chemical composition of the seeds is as follows: 30-52% protein, 17-27% fats, 6-20% carbohydrates, minerals (potassium, phosphorus, calcium), and vitamins (C, B, E). Soy is recommended for the dietary nutrition of diabetic patients. The protein is characterized by high digestibility (3.5-4 times more than the protein of cereal crops) and water solubility. Among leguminous crops, the composition of essential amino acids is the richest. The main protein of soya seeds is glycinin, which can coagulate when souring. Soy protein contains the amino acids lysine 2.7% (in wheat protein 0.25%), methionine, and tryptophan, which determine the feed value. Soybeans are cultivated for food, fodder, and technical purposes. It is used for food in the form of oil, margarine, soya cheese, milk, flour, confectionery, canned food, and other products. Soybean seeds serve as raw material for the oil industry. Soybean oil is classified as low-drying and is consumed after refining. It is also used in soap making, the varnish industry, the production of glycerine, linoleum, lubricating oils, gelatine, and lecithin. Soybean oil accounts for 38% of global production, while sunflower oil accounts for 17% [7]. For feed purposes, soya is used in the form of pomace, oilcake, and soya flour. The oilcake contains 40 % protein, 1.4 % fat, and 30 % nitrogen-free extractive substances. The pomace is also an additive in baking, pasta making, and confectionery.

Poppy (*Papaver somniferum*) is a source of valuable edible oil. This oil is rich in unsaturated fatty acids, the main component of which is linoleic acid. The oil of the poppy seed is particularly suitable for dish preparation, and raw consumption and is known to be used as a marinade for meat. Poppy seed oil is not so widespread because of the relatively high price of its production in comparison with other oils with similar properties. Nevertheless, poppy seed oil is a very popular ingredient in contemporary diet. Cultivation of the poppy is complicated, due to the small size of the seed and slow growth in the early stages of culture [9].

Hemp are special varieties of *Cannabis sativa L*. used for industrial or medical use. Hemp can be used in a variety of ways: the seeds are used for oil production or can be consumed fresh, the inflorescences can be used for medicinal purposes, and the fibers can be used to make textiles, rope, paper, or building materials. In the case of oil pressing, the remaining pomace is a valuable component of animal feed.

2.4. Production of the oil crops worldwide and in the Republic of Moldova

Wastes of seed processing into oil are named pomace (produced by the oil press method) and oilseed cake (or oilcake) by the extraction method. It is known for its high protein content and often is used as feed for farm animals. Such wastes contain a large number of essential amino acids. The share of waste accounts for up to 35% of the seed weight. 1 kg of the pomace contains 363 g of digestible protein. 1 kg of cake contains 226 g of digestible protein. The fat content in the waste varies from 1 to 7%, and protein from 33 to 35% [12]. According to other data, the pomace contains 8-10% fat, 36-40% protein, and 20% carbohydrates. The oilcake contains 1-3% of fats [13]. In terms of phosphorus and calcium content pomace and oilcake are superior to cereal plants. The output of dried husks reaches 56-60% of the seed weight. 1 kg of flour from dried husks contains 38-43 g of protein [9,14].

Most oilseed crops need to be grown in areas with high temperatures for proper fat accumulation in the seeds. The exceptions are winter types of oilseed rape and turnips, which prefer a relatively cool climate with high humidity and precipitation during the growing season. In contrast, poppy, sunflower, and hemp need warmer climates, especially in summer, for good output of the oil. This explains the reason why sunflower is mainly grown in the southern and south-eastern regions of Europe and rapeseed in temperate regions. Nevertheless, important breeding work is underway to expand the growing ranges of these crops, to develop varieties that also thrive in warmer conditions. Soil conditions have little influence on the geographical distribution of oilseeds. Only very shallow soils are unsuitable for oilseed crops unless they are irrigated. In the mild spring climate can be observed the early growth of oilseed crops (such as mustard, rape, or camelina. Flax can adapt to different climatic conditions, from maritime to continental. There are winter and also spring varieties of flax, allowing farmers to choose the type of crop that better suits the local climate. Oilseed pumpkin, although it grows in almost all regions of Europe, does not thrive in very cold or very warm conditions [15].

The biological features of oilseeds allow their cultivation in a wide range of different climatic and soil conditions. In general, they are well adapted to cultivation in different regions with high or insufficient relative air humidity, and have a significant potential for productivity of high-quality oilseeds [14]. The volume of oilseed production within the European Union in recent years is presented in Figure 1 [16].

Oilseed production in the European Union has been unstable in recent years, with growth until 2022 and then a slight decline. The maximum over the past 7 years was in 2017 and amounted to more than 30 million tons.

World oilseed production in 2022/23 was 629.66 Mt (+2.9% to 2021-2022), including soybeans 370.11 Mt (+2.8%), rapeseed 88.56 Mt (+16.8%) and sunflower 52.46 Mt (-7.7%). Harvested area of oilseeds 303.57 Mha (+2.3%), including soya beans 136.54 Mha (+4.1%), rapeseed 41.84 Mha (+8.8%), and sunflower 27.97 Mha (-2.0%). The main producers of oilseeds are China 68.04 Mt (+9.6%), India 42.29 Mt (-2.1%), and the EU 31.88 Mt (+2.6%) [15].

In the Republic of Moldova, oilseed crops are in great demand and their production is increasing (Figure 2) [17].

Figure 2. Cultivation of some oilseed crops in the Republic of Moldova [17].

Sunflower is the leading crop due to the widespread consumption of refined sunflower oil. Also widely cultivated are rape and soya.

3. The squeeze obtaining

The pomace used in the research is a direct product of the processing of oilseeds during oil production. Oil can be fabricated in two ways: by pressing and by extraction with various solvents, which influence the quality of the pomace. The oil in seeds consists almost exclusively in their kernels, which are surrounded by a dense hard shell, thanks to which the inner parts of the seed are protected from direct access to air. This ensures the relative stability of the seed during preservation, but at the same time makes it difficult to extract oil during processing. Extraction of oil must be preceded by crushing of both the shells and the kernel of the seed, as the oil is contained within the cells [18]. The extraction of most of the oil contained in the seed by pressing can only be achieved under strong pressure, it is very difficult due to its adhesion to the hard parts of the seed and due to the considerable viscosity of fatty oils at ordinary temperatures. Viscosity decreases with increasing temperature; therefore, when pressing heated seed, oil is more easily extracted from it. Heating the crushed seed before pressing has another meaning: if, when the seed is heated, the temperature is raised so that the protein is curdled, the oil obtained from such seed will contain no protein or much less. Heating the seed before pressing, however, has disadvantages. Some substances contained in the seeds, and, probably, the products of the change of these substances from heating, are more easily dissolved in the heated oil, these are the substances that give the oil a yellow or greenish-yellow coloring and a peculiar flavor. Oils obtained by pressing at ordinary temperature are less colored, cleaner, and have a milder and more pleasant taste than oils obtained by pressing heated seed. The same data show that heating of the seed should not be made more than 60-80°C [19].

Thus, the extraction of oil by pressing can never be complete. For example, in linseed pomace remains between 6.6 and 16.5 % oil. The complete removal of oil from the seeds, as well as from the residue from pressing, from the pomace, is achieved by extraction. In this

method, the pomace is exposed to volatile reagents. In this case, the consequences of the impact of reagents on the pomace are not taken into account, since the goal of this process is to obtain the largest amount of oil [20].

The solvents often used for this process have several main requirements: they must be affordable and available in large quantities in the trade, must dissolve a relatively large amount of oil, and not dissolve other substances contained in the seeds and deteriorate the quality of the oil, must be easily and completely volatile, but at the same time their vapors must easily condense into a liquid. The most often used are the following solvents: carbon sulfide, petroleum volatile oils, and ether. It is believed that petroleum volatile oil has a minimal impact on the quality of the residues from the extraction of oil. Besides, it is the cheapest solvent, doesn't dissolve other substances contained in the seeds and deteriorate the quality of the oil, doesn't change during use, and does not have any harmful effect on the properties of the resulting oil. In all respects ordinary ether is also a convenient solvent: it also mixes with vegetable fatty oils in all proportions, can be easily and completely removed from the oil and the residues, does not undergo any change when used for extraction, has no adverse effect on the oil or the residues, although it dissolves foreign substances. Sulfurous carbon can interact with some of the constituent substances of the seeds and form sulfurous compounds in the residue or the oil. Carbon sulfide is also the most inflammable of the three materials mentioned. The use of common ether would be most convenient for the obtaining of safe oils and residues, but the use of petroleum oils for extraction has become much more widespread because of its cheapness [18,21].

It is obtained safely, and easily clarified by sedimentation and filtration oils and residues in the case of compliance with the following conditions: 1) petroleum oils should be well purified with sulphuric acid and caustic soda so that they contain neither oxygen substances nor hydrocarbons that may be subject to change from the action of air and in general under the conditions of extraction; 2) for extraction should be used only petroleum oils, fully distilled at 100 °C [18].

Both the residue from oil extraction and the oil itself, to completely extract the volatile solvent, should be treated in the end with hot steam, and this steaming should not be carried out for a long time, for the residue to prevent the formation of starch glue, and for the oil to eliminate the decomposition that occurs during the prolonged action of steam on fats [19].

According to the analyses, the residues from extraction contain the following amounts of protein substances: rapeseed residues 28.69% (summer rapeseed), up to 32.7% (winter rapeseed), dried rape residues 35.9-38.65%, linseed residues 31.05-32.0%, hemp residues 33.67-34.45%, poppy residues 31.52-37.0%. The extraction residues contain no more than 2% oil. Thus, comparing extraction residues (oilcake) as feed material with pressed residues (pomace), it is evident that they contain more proteins than pomace, and although they contain almost no fat, they are not inferior to pomace in nutritive value. Extraction residues have the considerable disadvantage that they are friable and therefore more easily adulterated in commerce and less convenient for transport than pomace [21].

4. Squeeze classification

In the oil production process, there is always residual waste - squeeze, which is of high value, primarily for use as animal feed, but can also be used for other purposes. Depending on the type of the initial product - seeds of plant culture, are distinguished sunflower, rapeseed, soybean, peanut, mustard, hemp, corn, and other squeezes.

When processing oil by pressing, pomace is obtained, and when producing oil by extraction, oilcake is obtained. The pomace contains 5-7% of fat, while the oilcake includes less than 2-3%. The study of wheat germ pomace has shown that oilseed pomace retains most of the biologically active substances found in the original seed germ, making it a rich source of proteins, carbohydrates, vitamins, and essential macro- and microelements. This nutrient-dense by-product enhances the nutritional and biological value of food products when utilized as a raw material. Due to its high content of proteins and other essential nutrients, oilseed pomace is an excellent candidate for sustainable food production, contributing to the development of high-quality, plant-based protein supplements and additives in food formulations [19]. Squeezes are also divided into two categories: edible and non-edible. The first category includes soya, rapeseed, linseed, sunflower, and others. It has high nutritional value and is suitable for human and animal food in processed form, as isolate, hydrolysate, protein extract substrate for bioactive compounds, enzymes, pigments, antibiotics, flavors, vitamins, and amino acids. Inedible oilseed cake (castor, mauha, neem, linseed, and karanja) contains toxic compounds. Their composition depends on the way of oil extraction and the composition of the crop [3].

Even though the oilcake as a residue after oil extraction contains many proteins, its purification from the reagents takes a lot of time and resources, and it is not customary to use it for further processing. In contrast, the pomace is a valuable product for further use.

5. **Chemical composition of the pomace**

While the composition of the different pomace is similar, there are also differences. Sunflowers, soya, and cotton pomace contain more protein. Sunflower and soya pomace contains maximum amounts of lysine and methionine. They are a rich source of vitamins B and E, as well as phosphorus and potassium. Soybean and sunflower pomace are ahead of cereal seeds in terms of sodium and calcium content. Rapeseed pomace is not inferior to sunflower pomace in energy value and is ahead of soya pomace in phosphorus, calcium, copper, and magnesium content. In addition, rapeseed pomace is characterized by a significant content of riboflavin, folic acid, thiamine, natural antioxidants, tocopherol (vitamin E), phenolic compounds, and tannins. Soybean pomace, compared to rapeseed pomace, has more lysine, but less cystine and methionine [20].

In traditional technologies of oil production, based on the heating of raw materials, the effect of temperature leads to a decrease in the number of amino acids in the pomace [21]. If seeds of the oil crops are pressed without separating the seed coat, the pomace gets a darker color and a high fiber content [22]. One of the indicators of soya pomace is a low percentage of fiber, the amount of which in 1 kg of the product is 72 g, while in sunflower pomace this indicator reaches 152 g, and in flax pomace - 145 grams [20].

Raw sunflower seeds contain 16-19% protein per dry matter, but protein products are more often obtained from pomace containing about 35-45% protein [23].

Rapeseed pomace obtained by processing rape seeds contains valuable nutritional substances, including 27-41% of protein, containing essential polyunsaturated fatty acids of the omega-3 family, fiber, vitamins such as choline, niacin, riboflavin, folic acid, thiamine, as well as minerals such as calcium, phosphorus, magnesium, copper, manganese, and others [24,25]. Soybean pomace differs from others in its reduced fiber content, but while remaining a good source of energy and protein, it is highly digestible and highly productive. Its main amino acid is methionine. Rapeseed pomace is richer in sulfur amino acids but is comparable

in amino acid balance with soya. Among carbohydrates in rapeseed pomace, pectins (14.5%) and cellulose stand out. It also contains anti-nutritive substances such as tannins, glucosinates, and phytates. Like sunflower pomace, it is low in lysine and high in sulfurcontaining amino acids. Rapeseed pomace contains a lot of fiber, which causes its low digestibility. Pumpkin, flax, and hemp seed extracts have shown 75.09, 65.23, and 409.51 mg/100 g of dry extract amino acids content. When extracted under a nitrogen atmosphere with pure water, a lower content of total amino acids was found: 20.40 (pumpkin), 18.84 (flax), and 219.50 (hemp) mg/100 g dry extract [26,27].

The protein content of different kinds of pomace is presented in Table 1.

Table 1

The highest protein content is characteristic of groundnuts, pumpkin seeds, and soybeans. Also, oil crop pomace is rich in various vitamins and minerals (Table 1). The oil content in sunflower and rapeseeds is more than 40%, 15-25% is found in soybean, and up to 56% in peanuts [27]. Some types of pomaces, such as sunflower pomace, are known to contain phenolic compounds that have antioxidant properties [28].

Among the biologically active substances of flaxseed take place essential polyunsaturated fatty acids (oleic, linoleic), dietary fiber, all essential amino acids, as well as vitamins A, B, D, E, minerals Ca, K, Mg, Na, P, Mn, Fe, Zn [29]. The uniqueness of the healing properties of flaxseed is partly due to the significant content of lignans, which exhibit estrogen-like activity in the human body. Thus, the content of the main representative of lignans in flax seeds - the glycoside secoisolariciresinol is 13.6-32.1 mg/g. Scientists in experiments have also established the anticarcinogenic and powerful antioxidant effect of this lignin [30].

Oilseed pomace is a good source of fiber, rich in non-starch polysaccharides. Their chemical composition can differ based on the oil extraction techniques used [31]. Diets high in fiber bring various health benefits, such as the prevention and management of colorectal cancer, coronary heart disease, constipation, diverticular disease, and diabetes [32,33].

The work on the use of rapeseed pomace for food purposes is presented, where is shown that rapeseed pomace is a useful additive in the diet of athletes. It was found that when the pomace is added to red basic sauce in the amount of 5% there is an increase in the content of macro- and micronutrients, which are directly involved in the processes of muscle contraction and excitability of nerve tissues. When consuming sauce with rapeseed pomace for three months, a decrease in cramps and muscle spasms in track and field athletes was noted due to increased calcium absorption [34,35].

6. **Protein extraction methods**

The development of innovative technologies for pomace processing represents a promising research area. These technologies should focus on producing protein in a way that is waste-free and results in a food-grade product with minimal phenolic content. Existing methods for extracting protein concentrates and production of isolates from sunflower and other crops are well-established. The functional properties of these proteins are influenced by the specific parameters used during the production process [26].

Protein extraction from pomace typically involves using water, alkalis, salt solutions, organic solvents, or acids. Once the protein has transitioned into the liquid phase, it is precipitated at its isoelectric point using hydrochloric acid. The isoelectric point is influenced by the amino acid composition of the proteins by the balance of amine and carboxyl groups. For plant proteins, the isoelectric point generally falls between 4.0 and 4.5 [26].

The other method to obtain protein products from the pomace involves mechanical fractionation, which is commonly used in industrial production. This process includes further technological steps such as grinding and dry fractionation, which help increase the crude protein content while significantly reducing the crude fiber content in specific fractions of protein flour and grits. However, the presence of phenolic compounds causes the protein products to darken, which limits their use in the food industry [26].

For protein isolates and concentrates from oilseed pomace preparation, the most commonly used method is the two-step (extraction-isolation) method patented by Anson and Pader in 1955 [36]. This process begins with the alkaline solubilization of proteins, followed by the removal of insoluble materials, such as starch and fiber, through centrifugation. Afterward, hydrochloric acid is added to the supernatant to precipitate the protein at its isoelectric point (pH 4.0–5.0). The protein is then separated by centrifugation and neutralized [26].

There exist modified methods of protein extraction. Protein extraction can be performed under acidic conditions or in water as outlined by the author Klamczynska [37]. Generally, both acidic and alkaline extraction methods can achieve a high level of purity, often exceeding 90%. Alternatively, instead of using isoelectric point (pHi) precipitation, ultrafiltration can be employed for protein purification. This ultrafiltration method differs from pHi precipitation in that it typically results in proteins with higher solubility and functionality [26].

The author Ali [38] reports the method based on the use of varying concentrations of ascorbic acid and N-acetylcysteine (0, 20, 40, and 60 mg/100 mL) for the protein solubilization and rigorous pH control, followed by centrifugation, filtration, and freezing of the resulting product. To purify the protein from phenolic compounds, various solvents are used for washing. However, if the washing process is insufficient, phenolic compounds may not be entirely removed. Some organic solvents can denature the protein, reducing its biological value, and they can be difficult to fully eliminate from the final product. Another deficiency of these methods is the high-water consumption, which increases the process cost. When alkaline solutions are used for protein extraction, phenolic compounds are oxidized, forming quinones. Upon heating, these quinones bind to the protein, resulting in dark green and brown compounds that diminish the functional properties of the protein. This poses challenges for the use of these protein products in the food industry. That's why, the main task in producing protein products from pomace is to remove phenolic compounds. Sunflower seeds and their derivatives contain a variety of phenolic compounds, including chlorogenic, isoferulic, and caffeic acids, with an average phenolic content of about 2.5%. Chlorogenic

acid is the most abundant phenolic compound in sunflower seeds, accounting for up to 73%, depending on the growing conditions and variety [11]. Thus, it is recommended to extract chlorogenic acid and other phenolic compounds from raw material before the protein extraction. For this, the milled pomace can undergo a series of washes at acidic pH before the protein extraction [38].

The most efficient solvent for extracting chlorogenic acid is an aqueous ethanol solution with a concentration of 50-96%. This process not only removes phenolic compounds but also eliminates other impurities from the pomace. However, a significant disadvantage is that alcohol extraction in high concentrations leads to protein denaturation. The extent of denaturation can be minimized by carefully selecting the extraction temperature and the concentration of the ethanol solution. The optimal temperature range for extracting chlorogenic acid is 20-70 °C. Adjusting the temperature from 50°C to 70 °C does not significantly increase chlorogenic acid yield while lowering the temperature to 20 °C slows the extraction process. Exceeding 70 °C, however, results in substantial protein denaturation. Residual phenolic compounds that remain associated with the proteins give the final products antioxidant properties without changing their water solubility, but they also impart a dark coloration. Nevertheless, there has been growing interest in recent years in retaining these phenolic compounds or even adding them due to their antioxidant activity and potential health benefits, such as disease prevention and anti-aging effects [39].

For protein isolate preparation the method is based on an underwent to isoelectric precipitation of the resulting after the protein extraction supernatants by adjusting the pH to 4.5, followed by mixing, centrifugation, and freeze-drying using a vacuum pump [39].

To obtain powdered concentrate is often used spray drying, which is advantageous because it avoids overheating the product, thereby preserving its quality, and eliminating the need for additional grinding. It also generally results in high solubility. However, successful spray drying requires careful control of temperature parameters and process conditions. The temperature during drying significantly influences both the solubility and functional properties of the resulting protein. When the process parameters are optimized, it is possible to produce a protein with excellent quality [40].

Thus, the author Shaghinova presents the following process for obtaining protein extract from sunflower seeds (Figure 3) [23].

Figure 3. The method of protein preparation production [23].

Peeled and ground sunflower seed kernel should be defatted in a Soxhlet apparatus by exhaustive extraction with diethyl ether and treated with 80% ethanol solution. After extraction, the mixture should be centrifuged to separate the phenolic extract, and the precipitate should be washed with an alcohol solution. Protein and nitrogen-free extractives can be extracted from the precipitate with 0.1% NaOH solution. This method involves reaching the isoelectric point of sunflower protein for its coagulation to form a precipitate, which can be separated by centrifugation, neutralized, and dried to a powdery state on a laboratory spray dryer. Thus, under laboratory conditions dry powdery protein preparations of light grey color can be obtained from sunflower seeds, which did not darken in the air and contact with water. In this case, the protein preparations had no extraneous odors and had a neutral taste.

There exists a growing need for new green and safe technologies that will reduce the temperature and duration of the extraction process, minimize solvent usage, and improve the quality and yield of extracted proteins [41]. Emerging techniques, such as high-pressure processing, supercritical fluid extraction, microwave-assisted extraction, ultrasound-assisted extraction, cold plasma processing, pulsed electric fields, and radio frequency treatment, are enhancing extraction efficiency and minimizing protein degradation. These methods generally have a lower impact on the environment and are considered safe for human and also animal consumption due to the minimal use of harmful reagents [42]. Furthermore, these methods can improve the nutritional value of proteins, and their functional properties and may even produce bioactive peptides. However, the high energy inputs can cause structural changes in proteins, which may negatively impact their technical functionalities, such as emulsification, solubility, water-holding capacity, gelling, and foaming abilities. Despite these challenges, these technologies can modify the structural properties of allergenic plant proteins, which often have fewer technological applications compared to animal proteins. For example, power ultrasound can be used to adjust the functional, physical, and structural characteristics of protein-based components during extraction and modification [43].

Traditional protein solubilization procedures often incorporate ultrasonication, as it effectively disrupts the cell matrix and enhances extractability. The ultrasonic energy applied to the protein influences changes in its functional properties, including emulsification, solubility, foaming capacity, and hydrophobicity. Emerging technologies have shown significant improvement in the efficiency of protein extraction [44].

During the microwave-assisted extraction the microwave energy creates intense stress on the plant cell walls, leading to more uniform heating, eventual cell wall rupture, and the release of desired components. This method can significantly affect the structural properties and proteins and peptides activity due to the increased dielectric constant of microwaves. Microwave-assisted extraction offers several advantages, including an increased extraction rate, higher reproducibility, uniform heating, reduced solvent and energy consumption, and enhanced functional properties [45].

Another innovative approach is the use of moderate electric field extraction, a potentially reversible permeabilization technique that employs electric fields ranging from 1 to 100 V/cm. Moderate electric field extraction works by inducing internal heating and electroporation, which not only saves time and energy but also improves the properties and yield of the proteins [5].

7. Fiber extraction methods

Dietary fiber refers to a group of carbohydrate polymers, that cannot be digested by enzymes in the human digestive system. This group includes insoluble components such as cellulose, and lignin hemicelluloses, as well as soluble components like pectin, gums, inulin, mucilages, and resistant starch [46].

There exist various methods for dietary fiber extraction, including traditional techniques such as dry and wet processing, chemical, microbial, and enzymatic gravimetric

methods, and innovative extraction techniques using water, ethanol, steam, hydrostatic pressure, ultrasonic treatment, and pulsed electric fields. The extraction method can affect the composition and characteristics of dietary fiber. Among traditional methods, wet processing is considered the most cost-effective and efficient, yielding a purity of 50-90% in the final product. However, using alkali or acid may damage the fiber structure, and enzymatic methods can result in incomplete extraction. Innovative methods offer benefits like a higher recovery rate and lower environmental impact [3].

The extraction of dietary fiber typically involves three stages. The first stage is pretreatment, which focuses on removing microbes without affecting the biological activity of the material. Techniques used at this stage include microfiltration, foam mat, de-watering, and electro-osmotic treatment. The second stage is the extraction process, which can be performed using either classical methods (such as solvent extraction, steam distillation, or maceration) or advanced green methods. These modern methods include extraction with water or ethanol, supercritical fluid extraction, pulsed electric field, mixtures of water/organic solvents with carbon dioxide, enhanced solvent extraction, microwave or ultrasound-assisted extraction, accelerated solvent extraction, enzyme-assisted extraction and high-voltage electric discharge [47].

These innovative methods offer several advantages, such as high-quality extraction, minimal solvent use, selective recovery, shorter extraction times, reduced waste, and lower environmental impact. Additionally, they align with sustainable practices, allowing the use of waste and by-products in line with the circular economy model [47].

However, there are some drawbacks to these methods. For instance, microwaveassisted extraction can have high energy consumption, ultrasonic extraction may present separation challenges, and pulsed electric field technology can be less user-friendly. Traditional methods, while effective, generally require longer extraction times and larger volumes of expensive and toxic, solvents. However, compared to traditional techniques, modern methods offer better efficiency, reproducibility, and control over the extraction process [48].

The final stage of extraction involves purification, which can be achieved through alcohol precipitation, ultrafiltration, or chromatographic techniques [48].

The author Zheng [49] studied how particle size and solvent treatment affect the characteristics of the dietary fiber from the oil pomace. Reduction of particle size influence led to an increase in entrapment, swelling, and water-holding capacities. Cellulase hydrolysis negatively affected the color and oil-holding capacity, but it enhanced porosity, carbohydrate content, swelling, and water-holding capacities. In contrast, acid treatment produced opposite effects [3].

Fiber extraction is known enzymatic gravimetric method, described by the author Sunil [50]. In this procedure, a defatted sample is subjected to digestion of the starches using the phosphate buffer and thermo amylase and digestion of the proteins using pepsin and pancreatin, followed by cooling and filtration. To obtain insoluble dietary fiber the author proposes washing of the retained residue with ethanol and acetone solution, drying, and incineration. For soluble dietary fiber obtaining, the filtrate can be subjected to sedimentation by ethanol, followed by filtration, drying, and incineration.

8. Chemical composition of the oil crop pomace protein and fiber

In other scientific works, physicochemical parameters of protein concentrate from different types of crops were studied [39]. Sunflower pomace is the most accessible for research. The chemical composition of the sunflower pomace and protein concentrates, obtained by different methods is presented in Table 2.

The use of aqueous alcoholic solutions achieved a greater reduction in phenolic compounds compared to sodium sulfite; however, alcohol-based extraction was less effective for extracting components that dissolve more readily in water. Additional steps for removing phenolic compounds using aqueous extraction procedures resulted in protein isolates with higher protein content (76-78% dry basis) and lower phenolic levels, without notable differences in moisture content.

The data from other studies are also known protein 41.4%, ash 11.4%, and moisture contents 6.3%, all based on dry weight [51]. The values of these studies differ due to the use of different batches of sunflower, different degrees of purification, and research errors.

Extraction of phenolic compounds results in higher protein content. The type of reagent and pH affect the physicochemical parameters. For example, when N-acetylcysteine is used, the amount of ash is higher than when ascorbic acid is used. At the same time, as the concentration of the additives increases, the values of the indices also increase. The elimination of phenolic compounds results in an increase in the protein content of the concentrates [38].

According to various sources, protein concentrates contain 30-80% of protein, and protein isolates >90% of protein [47].

Dietary fiber from the pomace consists of both soluble and insoluble components. Both types of fiber contribute to increasing food volume and weight without significantly raising calorie intake, which promotes satiety and reduces appetite. They also help balance the pH in the small intestine, inhibiting harmful bacteria and protecting the digestive system. Insoluble dietary fiber, in particular, has a stronger anti-obesity effect than soluble by promoting lipid absorption and excretion, and it also reduces the risk of type 2 diabetes. These benefits are linked to the swelling and adsorption properties of dietary fiber, which are influenced by its microstructure [52].

9. Application area

Protein extracted from oil crop pomace has bioactive properties that can be enhanced by chemical or enzymatic hydrolysis with the aim of protein hydrolysate production. For example, author Girgih [53] reported higher angiotensin-converting enzyme inhibitory activity and antioxidant activity of pomace hydrolysates.

Protein isolates are known for emulsifier properties as they have high emulsifying activity and moisture retention capacity. Protein hydrolysates increase the output of culinary products due to moisture retention capacity and also improve the organoleptic characteristics of meat products. Enzymatic hydrolysates can be applied in the production of meat flavorings. For example, the addition of canola protein concentrate to sausages improves their aroma, flavor, and texture, which was confirmed by tasting [54].

Oilseed pomace is a functional product and is actively used in the production of valuable food additives. Protein extracts from the pomace can be used in many applications as additives. Carbohydrate-rich pomace, such as pumpkin pomace, is used as an additive for meat and dairy products. Pomace rich in proteins and fibre can be added to confectionery and bakery products [55].

There is a known study in which the author uses pomace of sunflower, coconut, pumpkin, and flax to create a food additive in the form of tablets to which flavorings can be added for better taste [56].

Bioactive peptides, specific fragments of proteins, exhibit biological activity and have a positive impact on health. Among this is demonstrated hypocholesterolemic, antioxidant, immuno-modulatory, and antithrombotic activity. The controlled cleavage of soybean protein hydrolysate, followed by hydrolysis with microbial protease, produces peptides with enhanced functionality, such as improved iron-chelating activity and better surface-active properties [57].

Protein isolates are used as a functional ingredient in many food products such as protein bars and shakes, meat substitutes, frozen desserts, cheese substitutes, and proteinenriched pasta. Protein isolates have gelling properties, solubility, and surface-active properties and are also used as food additives. Other beneficial properties and uses of proteins are presented in Table 3.

Table 3

The author Petraru [3] reports on the antioxidant properties of rapeseed bioactive peptides, blood pressure regulation capacity, and bile acid-binding capacity. At a concentration of 30-50 mg/L it inhibits thrombosis activity up to 90%. However, the production of food additives from some types of pomaces (for example, rapeseed pomace) requires considerable expenses associated with the use of enzyme preparations and other reagents, creation of optimal conditions for biochemical processes, drying, grinding of the obtained products, in addition, creation of conditions for the development of microbiological processes in wet media, which is an additional risk factor about the safety of end products. The wide application of the methods of protein preparations obtained in practice is restrained by the complexity of the management of these processes and the insufficient output of proteins due to their strong connection with other components and denaturation in the process of oil extraction.

The addition of 10% sesame protein concentrate to snacks improves their sensory properties, increases protein content, and reduces carbohydrate content [58]. Antithrombotic activity has been identified in peanut peptides, which will improve the health benefits of the products to which it is added [59].

Dietary fiber extracted from the wastes can serve as a functional ingredient, and supplement in both food and pharmaceutical industries. The functionality and effects of dietary fiber vary based on its physicochemical properties. For instance, dietary fiber with high water-holding capacity can promote satiety, while fibers with strong binding activities can protect against damage to the epithelial cells. Dietary fiber offers numerous health benefits, such as lowering the risk of cancer, coronary heart disease, diabetes, and obesity [60].

In the food industry, dietary fiber is valued for improving organoleptic, nutritional, and textural qualities. It enhances water and oil-holding capacity, emulsification, and reduces syneresis. Additionally, it helps extend shelf life and boosts oxidative stability [60]. Utilizing

fiber from by-products is essential for sustainable production, as it provides health benefits, is environmentally friendly, low-cost, and supports a zero-waste circular economy [3].

10. Conclusions

Oilseed pomace, which is a waste product of the oil mill industry, is rich in various substances. Therefore, this product is valuable for the food industry. The processing of the pomace will provide valuable products that can be used as food additives as sources of protein of vegetable origin and fiber.

There are 2 general methods of oil production: pressing and extraction. A comparison of all available data concerning the press and extraction methods in large-scale production leads to the following conclusions: 1) the extraction method makes it possible to obtain a larger quantity of oil of much better quality; 2) the cost of the device and the cost of oil production in the extraction method is less than in the press method; 3) the press factories do not present any special danger in fire terms, the oil-extraction ones are very dangerous. Despite this, the method of oil production directly affects the quality and properties of the pomace. Therefore, the most favorable methods are those that do not involve the use of chemical reagents. Pressing is one such method of oil production. The pomace obtained after the mechanical way of oil production contains exceptional levels of protein and some amounts of fiber.

The article mainly focused on sunflower, pumpkin, flax, rape, and soya pomace. The most protein-rich pomace was pumpkin (55-56%), soya (50-50%), and sunflower (37%) pomace.

Protein extraction from the pomace is widespread and there are known several methods for obtaining protein concentrate and isolate. These technologies should prioritize producing protein in a waste-free manner, ensuring the final product is food-grade and contains minimal phenolic compounds. The presented extraction methods show good results in terms of protein yields and are up to 90%.

Green technologies that have a minimal impact on the environment are becoming increasingly popular. These include high-pressure processing, supercritical fluid extraction, microwave-assisted extraction, ultrasound-assisted extraction, cold plasma processing, pulsed electric fields, and radio frequency treatment. The use of aqueous alcoholic solutions gives better results in protein output and extraction of phenolic compounds results in higher protein content.

Extraction of fiber from pomace is less common due to its lower content, but it is also known to be used. The most common method is solvent extraction. The resulting products are widely used in the food industry as additives with beneficial properties for the organism.

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