Secondary Material Resources of Oil-Producing Plants

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Abstract—Different ways for utilization of by-products from the production of sunflower, soybean, linseed, and rapeseed oil in Russia are reviewed. Different options of using sunflower press cakes as sorbents, in the production of feedstuffs for animals, in the construction industry, and energy industry are described. Examples of application of oil meal in the food industry and feedstuff production, especially in the production of protein isolates and concentrates, mayonnaise, and enriched bread are described. Prospects for oil meal application in biotechnology are also given.

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Processes for manufacturing of fat and oil products generate large quantities of waste and by-products, the total amount of which in Russia reaches approximately 7 mln t per year. The main type of waste from oil-producing plants is sunflower hulls, while by-products include press cakes and oil meal (schrot).

At present in Russia a stable first place in terms of production and consumption rates is taken by sunflower oil. Its production volume accounts for 93.8 % of the total output of individual types of vegetable oils in the Russian Federation. However, it is possible that in the coming years there will be certain changes in the structure of vegetable oil production towards a reduction in the share of sunflower oil and the proportional growth in the share of soybean, rapeseed, and other types of oil [1]. The growing volumes of oilseeds production and processing bring about a corresponding increase in the volumes of generated secondary material resources, which makes it necessary to develop production facilities to process the waste coming from oil-producing plants.

Sunflower Hulls¹

Sunflower hulls are a stiff plant tissue characterized by a homogeneous physical structure, constant chemical composition, and constant physicomechanical properties. Hulls of high-oleic sunflower varieties contain (% per absolutely dry matter) [2]: 1.63–2.3 of fat; 52.0–57.75 of crude cellulose; 3.75–4.62 of

protein; 38.23–39.55 of nitrogen-free extractives; and 1.97–2.2 of ash.

Sunflower hulls find limited application and are usually taken to landfills. At the same time, hulls can be used as a secondary raw material both at the oilproducing plants and at other production facilities. A traditional way to utilize sunflower hulls is to produce complete feedstuffs for ruminants on the basis of this material. In such feedstuffs sunflower hulls replace barley straw; additions of fat waste increase the oil content of the feedstuffs up to 8% [3].

It is recommended to enrich sunflower hulls with by-products of fat and oil plants, i.e. phosphatide emulsion or soap stocks (sediments formed during vegetable oil refining) [4], containing lipids, and to prepare feed mixtures using sunflower hulls and oil meal in the ratio of 1:2. Feedstuffs containing lipidenriched hulls increase livestock and poultry productivity. The technology for production of pelletized hulls enriched with lipids is described in work [2]. However, application of pelletized sunflower hulls as feedstuffs is limited, as in case of poor milling pieces of sunflower hulls entering the bodies of livestock animals can cause ulcer diseases. In this connection, milling of sunflower hulls into flour with particles of 100–200 µm is proposed for feeding purposes. During milling mechanical degradation of cellulose takes place, which increases the share of digestible carbohydrates and the feeding value of sunflower hulls [5]. One of the options for implementation of this

Technical Specifications 9174-003-55505939-04 and Technical Specifications 9147-468-00334534-2007.

approach is a method to produce press cake flour, consisting of a mixture of ground press cakes (75%) and finely milled hulls (25%) [6]. Specialists of Orenburg State University developed a technology for the production of feed mixtures and feed supplements on the basis of sunflower hulls and wheat bran [7].

After removal of furfural it is possible to grow feeding yeast on pentose-hexose hydrolysates of sunflower hulls [3]. One ton of sunflower hulls can be used to produce 180–190 kg of dry yeast containing 8–9 times more protein than the source sunflower hulls. Prehydrolysis of sunflower hulls with the hydrochloric acid solution under mild conditions results in the formation of a solution of pentose sugars with the yield of up to 20.5% (of the absolutely dry raw material). The method can be used to prepare growth media for edible fungi [8].

A possibility to produce chipboards, highly filled polymer compounds, and various articles on their basis using sunflower hulls as a filler was studied [9]. The resulting materials can be applied for heat insulation purposes in the construction industry and for veneering in the production of furniture [10, 11]. Industrial production of such goods is economically attractive, as the cost of sunflower hulls is 15–20 times lower than the cost of wood chips.

Sunflower hulls can be used for filtration of washing oils at fat and oil plants [12], as well as for manufacturing of sorbents. It was determined that proteins and cellulose contained in sunflower hulls formed a protein-carbohydrate complex capable of binding ions of heavy metals. Such sorbents can be used in water treatment for drinking and technological purposes, as well as in waste water treatment at small-scale local installations [13, 14].

The use of sunflower hulls for manufacturing of biofuels is also promising. Pelletized sunflower hulls possess a high energy content at relatively low volumes. The average calorific capacity of such fuel reaches 16–20 MJ kg⁻¹, which is almost in line with the characteristics of bituminous coal. There are three types of sunflower hulls used for technological purposes: nonpelletized, pelletized, and briquetted [15].

In order to produce solid biofuels from pelletized hulls it is possible to use phosphatide concentrates obtained in the process of sunflower oil hydration as a binding agent [16]. In Russia the development of complete pelletizing lines is performed by Grantekh JV LLC [17, 18].

Soybean Press Cakes and Oil Meal²

Press cakes and oil meal are by-products generated at oil-producing plants. Press cakes are produced as a result of pressing oil seeds for oil, while oil meal is generated due to oil extraction processes.

The value of press cakes and oil meal is related to the high content of protein substances (ranging from 30 to 50% of dry weight) in these products. They contain such amino acids as lysine, methionine, cysteine, tryptophan, arginine, histidine, tyrosine, aspartic acid, glutamic acid etc. [19, 20].

The global consumption of press cakes and oil meal is constantly increasing. This fact contributes to the growing volumes of the world trade in press cakes and oil meal mostly due to the increasing market of soybean oil meal [21]. Due to their high protein content press cakes and oil meal are promising raw materials for manufacturing of vegetable protein products, mainly represented by flour, protein concentrates and isolates, and products of their further processing [22]. The high nutritional value and functional properties of protein products ensure their extensive application in the food industry.

Soybean oil meal contains up to 45-50% of protein rich in essential amino acids. The protein contained in soybean oil meal and products on its basis is superior to many other proteins of plant and animal origin in the content of essential amino acids [22]. The feeding and nutritional values of soybean oil meal proteins depend on the degree of inactivation of proteolytic enzyme inhibitors and lectins. Soybean seeds contain a number of undesirable substances, ruling out a possibility to use oil meal for feeding and nutritional purposes without additional treatment. Such substances include urease, lipase, and lipoxygenase enzymes, as well as such anti-nutrients as trypsin inhibitor, soyin, and saponin [23]. In order to remove these undesirable substances from soybean oil meal it is subjected to wet-heat treatment. The amount of inhibitors to be inactivated in feedstuffs for non-ruminants and poultry should reach at least 80%.

The major part of soybean press cakes and oil meal are used in mixed feed production [3]. Works aimed at increasing the quality of soybean oil meal delivered to fur farms are carried out. Application of oil meal makes it possible to reduce the consumption of meat

State Standard GOST 12220-96, State Standard GOST 27149-95, State Standard GOST 8056-96, and State Standard GOST 8057-95.

and fish used in feed rations for animals. A number of oil-extracting factories are equipped with lines for enrichment of soybean toasted (subjected to wet-heat treatment) oil meal with lipids followed by oil meal pelletization [24], which makes it possible to raise the feeding value, prevent caking, and increase the bulk weight of oil meal.

Soybean press cakes and oil meal find increasing application in the food industry.

It is possible to replace up to 1% of egg powder with raw or roasted soybean oil meal in the formulation of mayonnaise [25]. Partial substitution of egg powder for soybean oil meal at Ussuriisk fat and oil factory made it possible to produce mayonnaise on the basis of the traditional technology. Moreover, in terms of organoleptic indicators such mayonnaise is competitive with Provencal mayonnaise.

A possibility to use finely milled soybean oil meal as an antioxidant for vegetable oils was studied [26]. It is proposed to add soybean oil meal into food products requiring moisture conservation, as it has a high water sorption capacity. There are developed formulations and process flow diagrams for production of chopped meat and fish products containing approximately 12% of soybean oil meal [27].

A method to prepare a thickener, giving a stable viscosity to minced meat croquettes and other similar food articles, was proposed in order to ensure consistent quality of these products under conditions of mass industrial production [28]. It was found that soybean oil meal included into the formulation of sheet wafers instead of wheat flour in the amount of not more than 20% made it possible to produce goods matching the reference products in terms of consumer properties and significantly exceeding them with regard to biological value [29].

Amino acid supplements containing milled soybean press cakes can be used as nutritional supplements or in nutritional therapy [30]. A scheme for production of dry powder baby-food products on the basis of soybean oil meal, skimmed milk powder, and barley malt powder was proposed [31]. A technology for production of milk and vegetable concentrates from defatted soybean flour, soybean oil meal, and milk whey, which can be used to make combined dairy products, was developed [32].

On the modern market of food ingredients soy proteins are represented by isolates, concentrates,

textured products, and various types of soybean flours or grits.

Defatted sovbean flour is obtained through milling and sifting of defatted soybean flakes. Soybean flour contains ~28% of carbohydrates, including 15% of soluble monosaccharides and oligosaccharides and 13% of polysaccharides, which can be extracted in the production of protein concentrates or isolates. In Russia defatted flour is used for manufacturing of textured proteins and in the baking and confectionery industry [33]. Addition of soybean flour into dough during the bread-making processes significantly increases the nutritional properties, improves the appearance, and extends the shelf life of the resulting bread [34]. It is recommended to use soybean flour in the production of various confectionery pastes for candies, caramels, pastilles and jelly products, dragee, halva, and other confectionery products in order to replace the traditional raw materials (sugar, powdered and condensed milk, cocoa powder, and nut-containing materials).

The largest Russian producer of defatted soybean flour and nutritional oil meal (grits) is Irkutsk fat and oil factory OJSC. The enterprise produces defatted soybean flour of different grain-size composition and various degree of heat treatment under Soyanta brand and Soyanta-teks soybean grits, specially intended as raw materials for the domestic production of textured soy proteins. Apart from that, there is a number of companies producing customized defatted soybean flour in the amounts of 50–100 t/month [35].

In recent years there has been active development in manufacturing of soy protein concentrates obtained from soybean flour in the world. The content of proteins in such concentrates amounts to 65–72% depending on the quality of the source raw materials and the production technology. These concentrates are used in soups, high-protein drinks, and sauces in order to give such products certain thickness and to retain water.

Manufacturing of functional protein mixtures and concentrates using domestic and imported ingredients is performed by a number of Russian companies (Tekhnomol Group of Companies, Torgovyi Dom PTI Group of Companies etc.). Construction of new enterprises for processing of soybeans and manufacturing of soy protein concentrates is also envisaged [36].

In application of protein products it is often necessary to give them certain structure through texturing. Depending on the applied technology, the end products can be represented by textured flour and concentrates

obtained using extruders [37] or fibrous isolates produced through spinning [38]. The major areas of their application are the production of meat fillers used in sausage, frankfurter, and chopped meat articles, as well as the imitation of the structure of expensive meat products (e.g. steaks, ham, and chicken meat).

In Russia there is active development in the production of textured proteins on the basis of defatted soybean oil meal. New high-capacity extrusion lines in St. Petersburg and Dzerzhinsk were put into operation. Large Russian producers of textured proteins include Gislav M LLC, Tekhnomol Group of Companies etc. [35].

Apart from the food industry, soybean press cakes and oil meal can find application at biotechnological production plants. Thus, e.g. it is possible to use the water-soluble fraction of the protein isolate obtained from soybean oil meal as a growth medium for feeding yeast and cultivated bacteria [39]. A possibility to manufacture nutritional protein products from soybean press cakes through synthesis of proteins by single-celled organisms (bacteria and yeast) cultivated in various non-protein media is considered [40].

Sunflower Press Cakes and Oil Meal³

Sunflower press cakes and oil meal contain protein (38–39%), lipids (up to 1.5% in oil meal and up to 10% in press cakes), phosphorous-containing compounds, vitamins, cellulose etc. The quality of sunflower press cakes and oil meal as sources of concentrated vegetable protein is determined primarily by the nutritional value of this protein. The main protein in sunflower seeds is 11S-globulin containing a lot of glutamic and aspartic acids, as well as arginine (26, 14, and 9.7% of the amino acids total, respectively). On the contrary, the amount of sulfur-containing amino acids is minor. At the same time, the production of nutritional sunflower protein is complicated by the presence of chlorogenic acid (up to 4.17%) and other phenol compounds, causing browning of products during thermal treatment, in sunflower press cakes and oil meal [23].

The major quantity of sunflower press cakes and oil meal is used in mixed feed production. They are included into the composition of protein and vitamin supplements in the amounts of 40–50%. They are added to barley, corn, oats, wheat, and other forage crops. In terms of feed units sunflower oil meal almost matches forage crops and significantly exceeds them

with regard to the protein content: barley, 4.4-fold, oats, 4.2-fold, and corn, 4.6-fold. If it is taken into account that oil meal prices are several times lower than the selling prices for oats, barley, and other crops, the advantages of using sunflower press cakes and oil meal in mixed feed production become evident. A number of oil-extracting factories perform enrichment of sunflower oil meal with lipids followed by pelletization. The most frequently applied enrichment mixtures are soap stock lipids or phosphatide emulsion. Additions of these substances increase the oil meal nutritional value due to its enrichment with triglycerides, phosphatides, tocopherols, and sterols [41]. The subsequent pelletization of the oil meal facilitates its transportation and storage, ensures explosion-proof conditions in the course of these operations, and reduces losses due to the absence of dust.

It was found that sunflower seeds contained two inhibitors of B₁ and B₂ proteolytic enzymes, which had adverse effect on digestibility of proteins by animal organisms, causing hypertrophy of the pancreas, deterioration in digestibility of amino acids, and animal growth retardation. In this connection, for technological processing of sunflower seeds it is necessary to perform inactivation of protein inhibitors [23].

Specialists of Kuban State Agricultural University developed a technology aimed at obtainment of feed protein isolate from sunflower oil meal. The technological process of isolate production is based on the extraction of protein with the alkaline solution, followed by the subsequent separation of the protein extract using gravitational settling and centrifugation methods. The resulting isolate is characterized by a low content of cellulose and a high content of the amino acids that are the most essential for livestock animal and poultry feedstuffs (lysine, methionine, and threonine). The waste (solid oil meal residue and protein-free supernatant) remaining after the protein isolation process can be used as a growth medium for probiotic microorganisms included into the composition of Batsell coenzyme feed supplement [42].

Application of sunflower press cakes and oil meal as nutritional protein sources is also promising. The major area of using nutritional protein is enriching bakery goods, second courses, and other food products with vegetable protein. There is a range of products, formulations, and process flow diagrams for manufacturing of second courses based on chopped meat and meat mass, flour and confectionery goods, suitable for enrichment with proteins extracted from sunflower

³ State Standard GOST 80-96 and State Standard GOST 11246-96.

oil meal. The end products contain all essential amino acids in a favorable ratio and have the optimal composition of minerals. With regard to organoleptic indicators the products under investigation are competitive with the reference samples [43, 44].

A method of obtaining lipid-protein complexes from sunflower press cakes was developed. Such complexes can be used in bread-baking instead of wheat flour. A scheme for preliminary treatment of sunflower press cakes was proposed in order to reduce the content of phenol compounds. Addition of 10% of the product in question to the dough instead of wheat flour resulted in the production of high quality bread containing 25–36% more protein than the standard wheat bread [45].

Sunflower oil meal can be used as an antianemic nutritional supplement within the framework of developing products for special medical purposes [46]. A beneficial effect of enriched bread on hematological parameters and hematogenesis was observed. The formulation of mayonnaise containing protein concentrates produced from sunflower oil meal instead of egg powder was put into production. Such mayonnaise in the form of stable emulsion is characterized by increased nutritional value [47]. It is reported that sunflower press cakes are used for manufacturing of cookies, cheese, and yogurt [48, 49]. It is considered that press cakes containing ~50% of protein can serve as substitutes for casein and gluten. Sunflower oil meal can be used as a partial sugar substitute. In order to improve its processing properties sunflower oil meal is treated with succinic anhydride [50].

Anthocyanins, vegetable dyestuffs, are obtained from sunflower press cakes through extraction with non-aqueous or aqueous organic solvents acidified with mineral acids, which is followed by filtration of the extracts and their concentration in vacuum at low temperatures. The resulting liquid dyeing product is suitable for coloring of food products and can be applied in cosmetic formulations [51]. Advisability of applying modified vegetable sorbents based on sunflower oil meal in refining of vegetable oils is demonstrated [52]. Sunflower press cake extracts can be used for biosynthesis of such antibiotics as penicillin and streptomycin [53, 54] and sunflower oil meal, for production of furfural [55].

Sunflower press cakes and oil meal can also find application for technical purposes. Sunflower press cakes account for 30–46% of the composition of

sealants for radiators with decreased sealing time, increased sealing ability, and corrosion resistance [56].

Linseed Press Cakes and Oil Meal⁴

The chemical composition of linseed oil meal (% to absolutely dry matter): 6 of nitrogen; 36.0 of protein; 3.0 of crude fat; 36.1 of carbohydrates; 9.0–14.0 of cellulose; 45.0–47.0 of nitrogen-free extractives; and 5.5 of ash (total). The amino acid composition of linseed press cakes and oil meal is given in work [3].

Linseed press cakes and oil meal are used in the mixed feed production industry as they are characterized by a very high feeding value. One kg of press cakes and oil meal contains 1.09–1.12 and 0.97–1.04 of feed units, respectively, and 312.8–319.6 g and 324–338.4 g of protein, respectively.

A technology for production of protein concentrates from linseed oil meal was developed [57]; the biological and nutritional values of these concentrates were studied. Biomedical research works revealed a possibility to use the product in question as a nutriational supplement in the production of canned vegetables and meat, meat croquettes, food concentrates, mayonnaise, sauces, and other food products [58]. Formulations of canned vegetables with additions of protein concentrates obtained from linseed oil meal were developed. Combined products can be also added into meat pate [59]. A possibility of manufacturing soy-type sauces from linseed and soybean oil meal through treatment of the oil meal with proteolytic enzyme products was considered. Such sauces contain significant quantities of lysine and other essential amino acids [60]. A method to extract natural polysaccharides, which can be used in the food industry as stabilizers in the production of sauces, meat products and sausages, frozen desserts etc., from linseed press cakes and oil meal was developed [61].

Linseed press cakes can be also applied for technical purposes, e.g. as a component of sealants for car radiators [56].

Rapeseed Press Cakes and Oil Meal⁵

On the average, rapeseed oil meal contains 38% of protein and 12% of cellulose and rapeseed press cakes, 33% and 13%, respectively; the total nutritional value

State Standard GOST 10974-95 and State Standard GOST 10471-96

State Standard GOST 11048-95 and State Standard GOST 30257-95.

reaches 91–111 feed units per 100 kg of the feedstuff [62, 63].

The amino acid composition of proteins contained in rapeseed press cakes and oil meal and their various fractions speaks for a high biological value of these products. Rapeseed proteins are well-balanced in terms of essential amino acids. With regard to the content of lysine, the main essential amino acid, they are close to soybean proteins. Moreover, the biological value of rapeseed protein amounts to 86%. In general, with regard to essential amino acids (33.0–35.2%) rapeseed proteins exceed sunflower proteins and can compete with soybean proteins [64, 65].

Approximately 2 t of rapeseed press cakes and oil meal is generated as a result of production of 1 t of rapeseed oil [66]. The most feasible way to process rapeseed is to use the pressing-extraction scheme, according to which rapeseed press cakes with the oil content of 17–20% are obtained at first, and rapeseed oil meal with the oil content of maximum 3% is generated as a result of the subsequent oil extraction [64].

Due to the unstable structure of rapeseed press cakes and oil meal they are manufactured in the form of pellets, which makes it possible to reduce caking, avoid spontaneous heating, and increase the bulk weight of the pelletized product (by a factor of 1.7–1.8). Pelletization of rapeseed press cakes and oil meal in compliance with the optimal processing patterns has no significant influence on the quality and feeding value of these products, which is confirmed by the results of studies on the amino acid and fractional compositions of the protein complex. Moreover, inactivation of redox and hydrolyzing enzymes of the lipid fraction of rapeseed press cakes and oil meal in the pelletizing process contributes to improved quality and stability of press cakes and oil meal during storage [64].

Unlike other oil seeds, rape seeds contain erucic acid and thioglycosides, which reduce the nutritional and feeding values of rapeseed-processing products. The content of anti-nutrients in rapeseed press cakes and oil meal can be reduced in the process of thermal treatment, under the influence of microorganisms, or by chemical means. But all these techniques are inefficient and economically unviable. Moreover, the treatment reduces the protein quality. Therefore, all efforts of the Russian plant breeders were focused on the creation of double-quality rapeseed varieties (00-type), not only containing no erucic acid but also characterized by a low glycosinolate content. Rapeseed

is considered high-quality when the glycoside content does not exceed 20 mcM per 1 g on air-dry basis [75].

The major area of application of rapeseed press cakes and oil meal is in rations for livestock animals and poultry [67]. The share of rapeseed press cakes in feedstuffs can be as follows: up to 15% for milking cows and young cattle (older than one year), up to 10% for fattening cattle and pigs, and up to 5% for poultry; the share of rapeseed oil meal can reach 10% in feedstuffs for milking cows and 5% for young fattening pigs and laying chicken [68-71]. In order to increase the oil meal energy value it is possible to add 1.5% of soap stock obtained in the process of canola oil refining. Mixed feeds for broiler chicken with additions of rapeseed oil meal proteins have the same impact on the productivity of chicken and the quality of meat as mixed feeds containing soybean oil meal. Rapeseed oil meal is recommended to be included into the formulations of mixed feeds for cattle in the amounts of 5-25% [72, 73].

Rapeseed press cakes and oil meal are valuable sources of protein, which are promising for obtainment of food-quality protein products. Schemes for production of protein-lipid enriching agents from rapeseed press cakes and oil meal, possessing a high biological value, were developed [74, 75]. The resulting products are characterized by high lipid-emulsifying, water-retaining, and foaming abilities, which makes it possible to use them as functional components of various food products [76]. It is proposed to use protein products obtained from rapeseed press cakes in the formulations of wheat flour goods and mixed rye-wheat bread in order to enrich these products with protein and optimize their amino acid composition [77, 78].

Technologies for production of biofuels from rapeseed oil are intensively developing, which in turn causes a drastic increase in rapeseed oil production [79, 80].

Thus, almost all types of waste and by-products generated by oil-producing plants can be used for manufacturing of feedstuffs and food products, as well as for technical purposes. However, the existing possibilities are not fully utilized as yet.

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