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Mechanochemically Assisted Hydrolysis of Biopolymers in Food Industry and Feed Production

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Abstract

The works carried out at the ISSCM SB RAS on the mechanochemistry of biopolymers and related applications in plant raw material processing and feed preparation are reviewed. The main features of the cell structure and composition of plant materials essential for mechanochemical processing are considered. The possibility to use mechanochemical hydrolysis to process biopolymers (polysaccharides, proteins, polyphenols) for the production of digestible low-molecular-weight compounds was demonstrated, including the joint mechanochemical processing of the mixtures of powders of plant materials and solid reagents. Biologically active mechanochemical preparations were used in food processing technologies, and as part of the feed to increase the productivity and improve the health of animals.

Keywords: mechanochemistry, plant-based raw material, processing, biopolymer hydrolysis, biological activity

INTRODUCTION

During the recent 25 years, the Institute of Solid State Chemistry and Mechanochemistry SB RAS has been holding the prominent position in studying the mechanochemical reactions of the components of plant-based raw materials. Mechanical technologies under development combine the operations involving mechanical treatment of the plant-based raw material and chemical transformation of the major and minor nutritive components. In some cases, these technologies are characterized by a high degree of resource saving due to the simplicity of implementation, low labor intensity, low energy consumption and environmental safety [1]. Theoretical consideration and experimental investigation of the processes of this kind are strongly hindered by the complex composition and structure of the raw material. The present work focuses on mechanochemical hydrolysis of carbohydrate, protein and polyphenolic biopolymers, used in food industry and fodder production.

The sizes of the majority of plant cells vary from 30 to 100 μm . The cells of different plant organs differ substantially from each other, in particular in the concentrations of biologically active substances (BAS). The concentrations of substances in different parts of plant cells vary even stronger. Some structural features that are most important for specialists in mechanochemistry working on the development of food products and preparations with the high concentrations of BAS for food industry and fodder production are outlined below.

The cell wall composed of cellulose and hemicellulose is the strongest element of a plant cell. With ageing, lignin formed in the cells gets included into the cell walls, so the composite material of cell walls gains increased mechanical strength.

The vital activity products and the metabolites get localized at the outer side of cells in the form of the cell wall, and inside the cytoplasm in the form of vacuoles filled with cellular fluid. These cell parts are separated from each other by

partially permeable lipid membranes, so the extraction of biomass raw materials is usually performed predominantly using organic solvents. The desire to overcome the technological and ecological problems caused by using organic solvents and to eliminate their denaturing action on some BAS is the driving force for the development of alternative mechanochemical methods of extraction and obtaining preparations from plant-based raw materials. Under mechanical action, membranes composed of bimolecular lipid layers are destroyed and make no hindrance for the transport of substances in aqueous solutions. The contents of the internal parts of a cell get mixed with the cell wall polymers and may interact with them.

Under intense mechanical action, the greater part of minor BAS having the complicated structure get denaturated or destroyed. It was discovered in the course of experimental studies that the stability of BAS depending on treatment intensity has a threshold nature [1]. The value of threshold stability depends on the dose of the input mechanical energy, remaining practically constant for specific BAS. This factor is taken into account to determine the conditions of mechanical treatment of plant-based raw material ensuring the stability of BAS would be provided, and the technological gate for mechanical treatment is specified [1]. The stability of BAS in plant raw materials is also dependent on the basic composition of the matrix of the components of plant raw material in which BAS occur after mechanical treatment. The presence of lignin components decreases the stability of some BAS during treatment, for example, this is true for flavonoid quercetin. The ability to enhance the stability of adsorbed quercetin during mechanical treatment varies as the sequence: hemicellulose > amorphous cellulose > crystalline cellulose [2].

Similar effects presumably take place during mechanochemical treatment of the mixtures of preparations of enzymes and biopolymers. The conditions of mechanochemical treatment, first of all, the intensity of mechanical action and process duration, under which the activity of enzymes does not decrease have been determined [3].

Low-molecular-weight BAS, plant metabolites, are initially located in the cellular fluid, where the aqueous solution (the total concentration of the components being ~10 wt %) contains saccharides, organic acids, low-molecular-weight polyphenols, various glycosides, alkaloids, vitamins, pigments, soluble proteins and enzymes. Inorganic compounds are also dissolved in the cel-

lular fluid. Microscopically, inclusions of crystalline or amorphous inorganic substances are also observed in the native and dried raw material. In some cases, inorganic substances, for example, amorphous silicon dioxide in rice husks, account for up to 20 wt % of the dry mass of the plants, forming a separate phase, and their presence has a substantial effect on the results of mechanical treatment.

After drying under the conditions provided by various standards and pharmacopeias, water remains in the plant raw material at a level of 6–12 wt %. Drying of the raw material to the moisture content of < 12 wt % usually requires special equipment and is very expensive.

The liquid contents of the cellular fluid lose approximately 75–85 % of the mass and get distributed in a thin layer over the inner surface of the cell wall. The thickness of this layer is <10 µm. The formation of the crystals of organic contents after drying is not detected by electron microscopy or X-ray diffraction analysis. The organic content is likely to be present in the form of amorphous solid solutions or in the nanocrystalline form. Most kinds of plant-based raw materials contain tissues with a medium lignification degree, with lignin content 10–20 % (dry weight). The dried parts of plants become harder but fragile.

The data obtained by means of electron microscopy show that the regions of lignified and non-lignified cells in the initial plant tissues get grouped. Closer to the surface of the plant taking external action, lignin concentration increases. The particles formed during the destruction, up to 50 µm in size, are mainly the groups of lignified or non-lignified cells. The latter become wrinkled and form layered particles. The shape of cells in lignified particles is conserved till a definite extent of treatment [4]. An increase in the treatment duration or intensity under the conditions of brittle fracture at room temperature or below it causes the fragmentation of cell walls into particles 2–3 µm in size [5]. The studies of this kind have been carried out for the problem of obtaining powdered fuel and biomass refining; these studies mainly deal with cereal straw [6].

An essential but poorly investigated problem in the mechanochemical hydrolysis of biopolymers is the effect of water on the course of the reaction. This problem was considered in the studies of the mechanochemical processing of biopolymers under the shear mechanical action in extruder-type equipment [7]; however, the published data are scarce. This parameter seems to

be essential for the know-how of the corresponding technologies. Calculations show that up to 10 wt % of water would be sufficient to achieve a twofold decrease in the molecular weight of polysaccharides that are usually present in the plant raw material. This condition is met for most types of dried raw plant-based materials. The mixtures of powdered raw materials with high water content are liquid. In this case, mechanical action is not localized at the contact boundaries between particles but is transmitted over the liquid phase. Under these conditions, reaction mechanisms change: reactions usually proceed as a result of quasi-autoclave or cavitation processes [8].

Mechanochemical reactions of acid- or base-catalyzed hydrolysis, oxidative/reductive hydrolysis, or enzymatic hydrolysis are used for the major components of plant raw materials (carbohydrates, proteins, polyphenols), yielding soluble digestible monomers or oligomers. All these reactions are heterophase, their rates are first of all dependent on the size and surface area of particles in the raw material. Mechanical treatment of wheat straw in the devices used for the activation of raw materials reduces particle size to 20 μm and increases the specific surface area to 3.4 m^2/g [9]. Preliminary treatment of the raw material with some reagents (*e.g.* acids) before grinding leads to an increase in the efficiency of grinding. The size of the resulting particles decreases with the same energy consumption for grinding [10].

The reduced particle size also increases the rate of heterogeneous reactions of the plant-based raw material in the gas phase. In particular, mechanochemically obtained particles of plant-based raw materials can be used as dispersed solid fuel for combustion in the torch of vortex power plants [11]. A substantial factor changing the reactivity of the particles is an increase in the defect content in the major crystalline component of the raw material – cellulose [12].

Mills of different types with free or constrained impact are used to carry out mechanochemical processes in the mixtures of solid powders [12]. Many components of plant raw materials get denatured or decompose under intense mechanical action, so special roller-type mills with a limited intensity of pulsed action have been developed [13].

DEPOLYMERIZATION OF THE DIGESTIBLE PART OF CARBOHYDRATE RAW MATERIAL

Economically efficient and ecologically friendly technology of obtaining glucose from plant-

derived cellulose could provide a substantial reduction of food deficiency in the world or at least ensure a decrease in the amount of food raw material consumed for technical purposes. Processing of plant raw material containing carbohydrates digestible for humans is the basis of food industry and fodder production. Mechanochemical treatment of carbohydrates is used if it is necessary to process poorly digestible raw material or to enhance the process efficiency. For example, the mechanochemical transformation of starchy polysaccharides of cereal grains into glucose syrup is carried out in the liquid phase in rotor installations. The efficiency of hydrolysis increases when glucanases are added into the mixture under treatment [14].

Attention to obtaining glucose solutions and bioethanol from inedible plant raw material springs up every time when the cost of oil exceeds 100 US dollars per barrel. The production of ethanol from food raw materials with increased starch content is 1.5 times more profitable than from inedible raw material because the consumption of enzymes is approximately 100 times lower, so only the production of fuel ethanol from sugarcane has been implemented on a large scale.

Inedible lignocellulose plant raw material has a complicated composition and structure. Polysaccharides incorporated into cell walls may be divided into two major classes differing from each other in the structure and physicochemical characteristics: homopolysaccharide (cellulose) and heteropolysaccharides (hemicelluloses and pectins). In addition, the main cell wall components are lignin and numerous minor components; the content of the latter varies depending on the supramolecular structure. The properties of cellulose obtained from different sources are different and depend on the degree of polymerization and ordering (degree of crystallinity). For herbaceous plants, the polymerization degree is usually not higher than 1500 [15].

Cellulose contains ordered (crystalline) and disordered (amorphous) regions; the degree of crystallinity is 40–60 %. Mechanical treatment of cellulose involves disordering and amorphization of the crystalline regions, rupture of intermolecular hydrogen bonds, rupture of the chains at glycoside bonds, and changes in the molecular weight distribution. All these changes cause modification of the chemical properties of cellulose. Amorphization increases the availability of samples for various reagents and the reactivity of polymers in heterogeneous reactions [16].

Acid hydrolysis of wood was used in the XX century. Several dozen plants in the USSR were pro-

cessing cellulose into the so-called cellulosic ethanol. Acid hydrolysis of cellulose is accompanied by the formation of toxic side products, so it is not used in food industry and fodder production.

Enzymatic hydrolysis of cellulose raw material (first of all cereal straw and husks) and other lignocellulose agricultural wastes is hindered if the content of lignin or the inorganic component (silicon dioxide) in the raw material exceeds 12 wt %. Lignin and amorphous silicon dioxide readily react with the enzymes of protein nature and put the enzymes out of interaction.

Mechanical treatment substantially eliminates the problems related to the presence of lignin. However, in the course of enzymatic hydrolysis, the diffusion of the components in the reacting liquid-phase system is prevented by the formation of a gel-like layer, composed of intermediate oligosaccharide products, on the particles of the solid substrate. In modern technologies, repeated mechanical treatment of a mixture of reactants with water is applied to solve this problem. Glucose yield close to 95 % was achieved after 4–5 cycles of treatment in rotor devices [17].

Cellulose micro- and microfibrils are immersed into plastic gel, which is a complex mixture of polymers where polysaccharides with different molecular weights are prevailing (hemicelluloses and pectin substances). Polysaccharides of hemicellulose do not have crystal structure; their amorphous structure is also conserved after drying of the raw material.

Preliminary mechanical treatment disturbs the ordered fibrous structure and reduces the degree of cellulose and hemicellulose polymerization. This kind of treatment gives rise to a composite with disturbed primary arrangement of macrostructural elements and increased reactivity in heterogeneous enzymatic hydrolysis.

The presence of amorphous regions increases the activity of cellulose in such reactions as acid/base-catalyzed or enzymatic hydrolysis. Among chemical, physicochemical and biological methods of preliminary treatment used in food industry and in the production of fodder, mechanical activation is one of the most efficient methods to enhance the reactivity of a plant-based raw material and its components.

Hydrolysis of the amorphous regions of cellulose proceeds 3–30 times faster than that of crystal regions. A correlation between an increase in the reactivity of lignocellulose material and a decrease in the degree of crystallinity during preliminary treatment is observed [18]. Preliminary treatment may also lead to a reverse effect. Water

causes partial ordering of the amorphous regions of cellulose [19].

The initial rate and the yield of enzymatic hydrolysis of the particles of plant-based raw material are affected by the available area for the sorption of enzymes, the degree of crystallinity of cellulose regions and the degree of total disordering of the supramolecular structure of lignocellulose material. Amorphization of cellulose crystallites occurs in proportion to the duration and intensity of mechanical treatment during the first 10 min of activation. Mechanical activation in planetary and roller mills reduces the average size of straw particles from 236 to 21 and 38 μm , respectively, while increasing the specific surface from 2.2 to 3.4 and 2.7 m^2/g , respectively. Wheat straw is crushed easier than microcrystalline cellulose [20].

Cellulose amorphization is observed during grinding in cellulose and cellulose-containing raw materials. Broadening of reflections in the XRD patterns of the mechanically treated raw material samples confirms that crystallite size decreases and the content of the amorphous phase of cellulose increases (the degree of crystallinity rises) with increasing duration of mechanical activation. The average size of crystallites decreases from 2.7 to 1.3 nm [21].

In the case of difficult-to-process plant raw material with higher lignin content (sugarcane) and higher silicon dioxide content (rice husks) than that in wheat straw, the effect of mechanical treatment of the powders simultaneously with enzymatic treatment (cellulase) on the yield of saccharides from subsequent hydrolysis is more pronounced. Under optimal conditions of mechanical activation (10 °C) of cane biomass, the yield of the products of subsequent enzymatic hydrolysis increases by a factor of 1.5 [22]. In the case of the treatment of rice husks, the optimal technological modes of mechanical activation provide an increase in the yield of carbohydrates from hydrolysis by a factor of 7 [22, 23].

Thus, in such different difficult-to-process systems as cane biomass with increased lignin content, rice husks with the high content of amorphous silica, peat with the high content of humic substances, the application of preliminary mechanical activation of the powders of plant-based raw material and the enzyme substantially increases the yield of soluble saccharides during subsequent enzymatic hydrolysis. A hypothesis explaining the observed effects was put forward in the review [1]. It is assumed that mechanical treatment leads to the mechanical distribution of

enzyme molecules over the mass of the plant raw material. The routes to deliver the enzyme to the substrate become substantially shorter compared to those when the substrate is treated with the enzyme solution.

In this case, an essential question is the conservation of enzyme activity during the mechanical treatment of the powdered mixtures of the enzyme and plant substrate. It is known that enzyme activity decreases even if the tertiary structure of the molecule is disordered, which happens under the mechanical action on the molecules of the enzyme protein. Experiments with cellulose substrate demonstrated that the stability of cellulase and other BAS may be conserved and in some cases even increase substantially as a result of mechanical treatment of the mixture of powders [24]. It was discovered that mechanical increases the stability of cellulases adsorbed onto the surface of plant-based raw material particles [25].

The basic predictable area of the application of mechanoenzymatic hydrolysis of lignocellulose raw material is bioethanol production from wheat straw [26–29] and corn straw [16].

DEPOLYMERIZATION OF THE INDIGESTIBLE PART OF CARBOHYDRATE RAW MATERIAL

Numerous polysaccharides that are practically indigestible in human organisms have been detected in plants. The polymers turn out to be biologically unavailable because glucose units in the chain are connected to each other through (1 → 3) bonds, similar to the case of beta-glucans, or the units themselves are “inedible” glucose isomers, as in the case of mannanoligosaccharides. These carbohydrates are not involved in power supply in the human and animal organisms but play a substantial role in other physiological processes, such as adhesion of intestinal microbiota.

The major source of inedible carbohydrates is hemicelluloses, which differ from each other not only by the composition of the main chain but also the degree of polymerization and chain branching, solubility and other physicochemical properties. Hemicellulose content in the plant cell walls may reach 40 wt % [30].

Hemicelluloses and celluloses form a structural matrix through hydrogen bonding. This matrix is further bound to lignin as a result of ester and covalent interactions, forming a lignocellulose complex. Hemicelluloses involve a very broad range of polysaccharides: arabans, xylans, glucans, xyloglucans, mannans, arabinogalactans, glucomannans, galactomannans and polyuronic acids. Hemicel-

luloses of herbaceous plants are represented by pentosans, hexosans (for example, xylose, arabinose, glucose, galactose) and uronic acids. Polysaccharides in hemicelluloses of different plant species differ from each other in the composition of the elementary units of the main and side chains, structure, and branching degree [30].

Hemicellulose dissolution in alkaline solutions was studied extensively because in paper industry paper quality significantly depends on the completeness of cellulose separation from hemicelluloses. Mechanochemical treatment of hemicelluloses in the initial plant-based raw material leads to changes in the composition of the released polysaccharides. Polymers with lower molecular weight are usually formed. The content of better soluble polysaccharides increases [20]. Unfortunately, a large amount of polysaccharides get into the so-called leach together with polyphenols; they are not separated and remain unused. Polyphenol lignins remain the major environmental pollutant in paper-manufacturing countries. Only an insignificant amount of this kind of waste can be disposed using the known chemical and biological methods. On the other hand, lignins are genetic precursors of humic acids that determine soil fertility [31].

The greatest sources of beta-glucans are cereal crops well growing in Russia: oats, barley and rye. Beta-glucan was discovered in the cell walls of the endosperm and in the outer layer of oats and barley grains. Oats contain beta-glucan at a level of 1.8–7.9 wt %.

A known source of beta-glucans is the cell walls of baker's yeast *Saccharomyces cerevisiae*. Other sources are some fungi species. The content of beta-glucan in wood-decay fungi reaches 10–30 wt %.

Beta-glucans and mannanoligosaccharides are in most cases non-toxic or low-toxic. It is currently believed that the biological activity of beta-glucans is primarily caused by their immunostimulating effect [32].

A new mechanoenzymatic technology of the production of beta-glucan and mannanoligosaccharide preparations from plant-based raw materials (oat grains and bran) and yeast biomass was developed. Instead of the technologies involving liquid phases, mechanical treatment of a mixture of the powders of raw materials and enzymes is used to obtain the preparations [33]. It was demonstrated that the yields of beta-glucans and mannanoligosaccharides can be increased substantially as a result of the process carried out in the solid phase. The technology of obtaining mannanoligo-

saccharides from yeast cell walls is also based on the mechanochemical destruction of cell walls and an increase in the availability of cell wall components, mannanooligosaccharides [34].

Mannanooligosaccharides play a special role as microorganisms substituents for fodder antibiotics. It was demonstrated that the compounds of this type hinder the attachment of pathogenic microorganisms in the gastrointestinal tract of higher animals and prevent the development of diseases. The manufacture of mannanooligosaccharide preparations in fodder production for poultry and cattle breeding according to the mechanochemical technology [35, 36] was introduced at PO Sibbiofarm (Berdsrk). In comparison with antibiotics, these compounds are not cytotoxic but work at a level of fixing bacteria in the gastrointestinal tract, so the results of their application are significantly different from those of usual fodder antibiotics for poultry and calves [37, 38].

As a water-retaining agent, beta-glucan regulates water activity in food, preventing it from drying unfavorable texture changes (most typically, staling). Due to hygroscopicity, the water-retaining agent binds water present in the fresh product and thus prevents or slows down its evaporation into the atmosphere. As a consequence, the state of the initial product (for example, sponge cake or related products) is conserved, and the product stays fresh for a longer time interval [39]. Water-retaining agents are used also to bind undesirable water remaining in the product after the completion of industrial processes [40]. In highly concentrated syrups, the addition of beta-glucans increases the solubility of sucrose, thus slowing down its crystallization. This allows conserving the state of confectionery products, fondants till the use-by date [41].

A method was developed for obtaining beverages from some fruit and vegetables (tomatoes, apples, citrus fruit, melon, bananas, kiwi fruit, avocado, mango, carrots, pumpkin), stable during long-term storage and possessing pleasant taste and odor. These beverages contain glucans formed during the enzymatic hydrolysis of cereals or other crop cultures (oats, wheat, barley, corn, rice, and rye) [42].

MECHANO-CHEMICAL DEPOLYMERIZATION CONTAINED IN PLANT-BASED RAW MATERIAL

Plant proteins occur abundantly in grains, in cotyledons protected with the seed coat composed of the waxy substance cutin. The protein content

in legume seeds is 20–40 wt %. The protective seed coat is removed during food processing.

Proteins are among the major components of food and fodder. Compared to saccharide chemistry, there are much more studies focused on protein chemistry, which mainly deal with the genetics and biological chemistry. The position of mechanochemistry in food chemistry is the production of food for healthy nutrition. Gastrointestinal disorders, food intolerance and allergic response are connected with the consumption of low-quality protein products. The methods allowing one to reduce the molecular weight of proteins and manufacture products containing relatively low-molecular-weight proteins (peptides and simple amino acids) from plant-based raw materials are of interest for sports nutrition and starter diets. An alternative method, which involves seed sprouting in order to increase the amount of bioavailable substances, is very time-consuming, so in some cases enzymatic treatment of leguminous plants is economically sound.

The application of mechanoenzymatic approach to the treatment of protein-containing raw material involving proteases was successful, too [43]. The treatment of pea powder in mixture with proteases allows one to bring the content of water-soluble proteins in the powder product to 70 wt % [44]. As a result of hydrolysis, a large amount of soluble proteins with a molecular weight below 50 kDa is formed, which makes these powder components suitable for starter diet. The amount of free amino groups and free amino acids in the extracts of the products of mechanochemical processing increases [45].

Similar approaches are also applicable for treating other legumes [46]. Using mechanochemical approaches can also be promising for the treating the green parts of protein-containing plants (trefoil, lucerne, sainfoins, amaranth, and goat's rue), especially those containing deficient amino acids.

MECHANO-CHEMICAL DEPOLYMERIZATION OF THE POLYPHENOL PART OF PLANT-BASED RAW MATERIAL

Polymeric polyphenols hold a special position among biopolymers. They are accumulated in the natural environment in several hundred million tons forming the deposits of brown coal and peat. Polyphenol substances – humic acids – possess unique ability to get adsorbed on the surface of mineral particles and to retain nutrients for plants in the upper layer of soil, which determines soil

fertility. Lignin from cell walls is transformed into humic acids under the conditions of oxidation by atmospheric oxygen.

Lignin renders mechanical strength to cell walls, participates in the transport of water and nutrients. It is not assimilated in humans and animals; it is valuable first of all as a food-borne adsorbent. From the viewpoint of chemical food technology, lignin acts as an inhibitor in the majority of chemical transformations, for example, it adsorbs enzymes onto its surface during enzymatic hydrolysis.

Lignin is a high-molecular-weight aromatic heteropolymer composed mainly of phenylpropane structural monomers: guaiacylpropane, syringylpropane, *p*-phenylpropane. Lignin of herbaceous plants and cereals contains all kinds of phenylpropane units. Lignin content in plants depends on the kind of raw material, growth period *etc.*, for example, for herbaceous plants it varies within a broad range from 5 to 40 wt % [15]. Investigation of lignin is hindered due to some reasons: the complex structure of its macromolecules (diversity of bonds and functional groups), the presence of different types of bonds with other components of cell walls and easy oxidation when isolated in the individual form. Depending on the method of extraction from the plant-based raw material and the method used to determine molecular weight, the molecular weight of lignin varies within the range of 1–10 kDa, which approximately corresponds to the degree of polymerization of 5–60 monomer units.

High-molecular-weight amorphous polymers, in particular, lignin, undergo dynamic phase transitions at different temperatures. In the glass-like state, the vibrational motion of atoms occurs around the equilibrium position, therefore, the motion of polymer chains is almost absent. When in highly elastic state, the units undergo rotational vibrations, and the polymer chain may bend. The polymer passes from highly elastic to viscous-flow state, when macromolecules become able to move as a whole.

The separation of the phases of lignin and polysaccharides within the cell wall during mechanochemical treatment was discovered [47]. The processes of this kind might be employed to develop the technologies for separating the phases of polysaccharides and lignin using the dry method without lignin dissolution.

Mechanochemical depolymerization of wood-derived lignin is widely used in paper industry. Enormous amount of wastes is formed during al-

kaline dissolution followed by deposition. The utilization of those wastes is not carried out on the industrial scale.

Under natural conditions, plant lignins are transformed into humic substances, which are the main components of peat. These are high-molecular-weight heteropolymeric compounds containing the regions of polyphenol humic acids, the regions of polysaccharides, a small amount of proteins and hydrocarbons. Humic acids are insoluble in water. To use their biological activity, it is necessary to destroy the structure of the compounds, increase the contents of hydrophilic hydroxyl and acid groups in polyphenols, and transfer the acids into the soluble salt form. To achieve these purposes, mechanochemical interaction of peat and humic acids with alkalis and enzymes is used [48].

As a result of mechanochemical treatment, polysaccharides of peat change: their molecular weight decreases, the number of hydroxyl groups increases. The composition of water-soluble polysaccharides is represented by carbohydrates: glucose, galactose, rhamnose, xylose, arabinose and fructose [49]. Mechanochemical treatment of peat under oxidative conditions, for example in the presence of persulphates, not only increases the amount of oxygen-containing functional groups by a factor of two but also decreases the degree of their aromaticity [50].

The maximal antioxidant activity connected with the increased concentration of phenolic hydroxyl groups is observed for mechanochemical products from sphagnum peat [51].

Mechanochemical activation of peat increases the yield of humic acids after extraction. The changes in the composition of functional groups in humic acids alter the properties of these acids and enhance the ion exchange properties of the products [52, 53]. Mechanical activation and an increase in the amount of acid functional groups improve the adsorption properties of humic acids and the materials containing humic acids. The molecular weight of humic acids decreases through the rupture of bonds in the peripheral part of macromolecules. The size of the molecules of humic acids obtained mechanochemically is 18 nm [54].

Chelating (complex-forming) ability of mechanochemically prepared humic acids is believed to be connected with the formation of pairs located closely to each other in the aromatic ring: phenoxyl–phenoxyl and phenoxyl–carboxyl ones, binding the ions of heavy metals [55]. The chelating ability of polyphenols may be used to make readily assimilable complexes of micronutrients, for

example, silicon [56], and develop new prophylactic antiviral preparations [57].

Antioxidant properties of the preparations of humic acids obtained mechanochemically are determined by the presence of hydroxyl and carboxyl groups; their content increases from 6.9 to 9.5 and from 2.5 to 6.0 mol/g, respectively. Modification of humic acids with the help of solid-phase reactions with peroxide substances [58] demonstrates the possibility of obtaining humic acids with the composition going beyond the composition range of natural acids in the O/C parameter. An increase in the amount of oxygen-containing functional groups is a promising direction of making new humic acids with improved properties.

For fodder purposes, alkaline depolymerization of peat is used. This process results in the isolation of the polyphenol component of peat and its use as humic acid preparations. Traditional areas of the use of humic preparations are soil recovery and enhancement of the productivity of agricultural crops; area broadening proceeds due to the application of these preparations as growth-stimulating means for cattle breeding, in particular for male calves [59].

CONCLUSION

Cellulose present in plant-derived wastes, and cereal straw in particular, are refined by mechanical activation of raw material powders in the presence of enzymes (cellulase) by approximately 25 %. Subsequent mechanical treatment of hydrolysis product in the liquid phase in rotor-type devices provides further transformation of cellulose into glucose. The efficiency of using the resulting glucose to produce bioethanol as an alternative fuel and the possibility to use these processes in industry are determined by the current market value of hydrocarbons. The currently developed methods for separating the plant-based raw material into cellulose and hemicellulose open up prospects for biotechnological production and manufacturing powdered lignin fuel for combustion in the torch of vortex power plants.

Mechanochemical hydrolysis of inassimilable polymers incorporated in cell walls of some kinds of plant-based raw materials is promising for application in food industry and in the production of fodder. For example, beta-glucans of oats are used in functional nutrition to enhance the immune protection of humans and animals, and as a component improving the technological and con-

sumer characteristics of food products prepared from the raw material after mechanoenzymatic treatment. Beta-glucans and mannanoligosaccharides from the yeast cell walls are an alternative to fodder antibiotics.

Mechanochemical treatment of protein raw material increases the solubility of the resulting product, decreases the molecular weight of proteins in the product, gives rise to free amino acids, and increases the digestibility of the product. Using the mechanoenzymatically treated leguminous powder improves the consumer characteristics of a number of food products: soups, beverages, bakery and confectionery products.

Polyphenol components of plant cell walls, transformed into humic acids during the formation of peat and coal, are used in fodder production for sanitation and enhancement of the productivity of animals. Mechanochemical technologies significantly increase the efficiency of amino acid extraction from the raw material. Mechanochemical modification of humic acids through the introduction of additional hydroxyl and carboxylic groups improves the quality of humic products.

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