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# Application and Conversion of Soybean Hulls

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## Abstract

Soybean is one of the most cultivated crops in the world, with a global production of approximately 240 million tons, generating about 18–20 million tons of hulls, the major by-product of soy industry. The chemical composition of soybean hulls depends on the efficiency of the dehulling process, and so, the soybean hulls may contain variable amounts of cellulose (29–51%), hemicelluloses (10–25%), lignin (1–4%), pectins (4–8%), proteins (11–15%), and minor extractives. This chapter provides a review on the composition and structure of soybean hulls, especially in regard to the application and conversion of the compositions. Current applications of soybean hulls are utilizations to animal feed, treatment of wastewater, dietary fiber, and herbal medicine. The conversion of soybean hulls is concerned with ethanol production, bio-oil, polysaccharides, microfibrils, peroxidase, and oligopeptides. On the basis of the relevant findings, we recommend the use of soybean hulls as important source on environment, energy, animal breeding, materials, chemicals, medicine, and food.

**Keywords:** soybean hulls, application, conversion, dietary fiber, polysaccharides

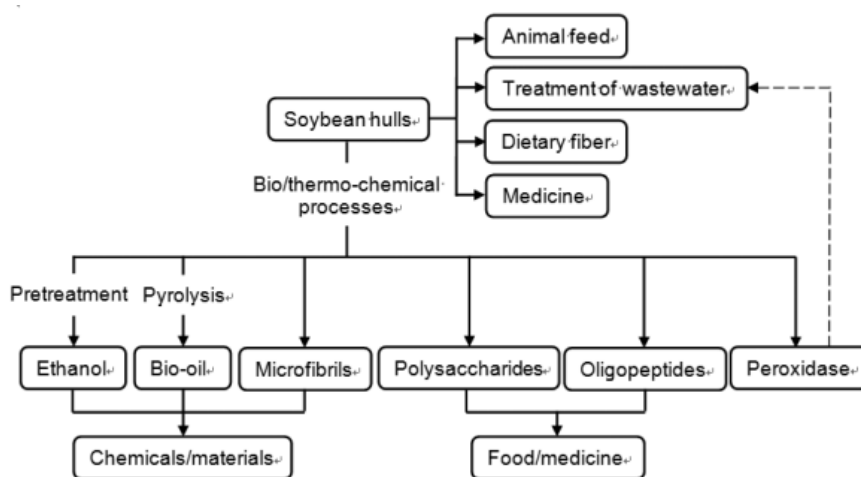
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## 1. Introduction

Soybeans are one of the most worthy crops in the world because of their high protein and oil content, which provides a wide variety of uses [1]. Soybean protein has been used in livestock and aquaculture feeds and is highly digestible, along with many human foods [2–4]. Soybean oil is used as a food and feed ingredient as well as in biodiesel production and cosmetics [5, 6]. Soybean hulls, accounting for a substantial fraction (7–8%) of the total mass of soybean, are the largest amount of by-products in the soybean process industry. In contrast to the oil and proteins, there is a fairly common perception that hull is a “waste” product of soybean processing [7]. It is predicted that the total world soybean production will be 371.3 million tons by 2030 and there will be 29.7–37.1 million tons of soybean hulls available [8].

The chemical composition of soybean hulls depends on the efficiency of the dehulling process, and so, the soybean hulls may contain variable amounts of cellulose (29–51%), hemicelluloses (10–25%), lignin (1–4%), pectins (4–8%), proteins (11–15%), and minor extractives [9–11]. Therefore, soybean hulls are primarily lignocellulose material. However, unlike many other lignocellulosic material such as hardwood or switchgrass, soybean hulls are easy degradable [9, 11]. Chemically, cellulose is a linear polymer of 250 to over 10,000 glucose units linked by  $\beta$ -1,4 glycosidic bonds. Pectin is a polysaccharide consisting of a backbone of  $\alpha$ -1,4 linked galacturonic acid residues usually up to 100 residues in length. The galacturonic acid residues are commonly methylesterified or acetylated, and the backbone may include substitutions of rhamnose and/or branching chains consisting of arabinose and galactose [12]. Hemicellulose is a group of wall polysaccharide that is characterized by being neither cellulose nor pectin and by having  $\beta$ -1,4-linked backbone of glucose, mannose, or xylose [13]. The backbone is frequently decorated with a variety of sugar side chains or acetyl ester groups [14]. The average degree of polymerization of hemicellulose is in the range of 80–200. Lignin is a heterogeneous biopolymer in lignocellulose formed by radical-mediated oxidative coupling of phenyl-propane unit linked together through various types of ether and carbon-carbon bonds [15].

The low lignin content in soybean hulls makes the residues have a very wide variety of application (**Figure 1**). Due to this biomass composition, soybean hulls are widely used as animal feed [16]. In addition, soybean hull is lignocellulosic material containing a small proportion of lignin, as compared with other agro-residues, and has a good potential for saccharification, because lignin is a major hindrance for enzymatic hydrolysis of biomass [17]. Soybean hulls also contain a large amount of dietary fibers (DFs), and have been used as a batter ingredient to decrease the fat contents in cakes and cookies [18]. Moreover, soybean hulls have also been identified as a rich source of peroxidases and as an agro-industrial residue; they are a low-cost alternative for resulting in biocatalyst production [19]. This review summarizes the present knowledge on the composition, application, and conversion of soybean hulls.



**Figure 1.** Application and conversion of soybean hulls.

## 2. Compositions and structure of soybean hulls

### 2.1. Cellulose

Cellulose derived most frequently from wood is widely used in a range of applications including composites, papermaking, food additives, textile, and pharmaceutical industries [20]. More importantly, cellulose is also useful for bio-ethanol production after enzymatic hydrolysis. Cellulose is a linear polymer of anhydroglucose unit linked at the one and four carbon atoms by a  $\beta$ -glycoside bond [21]. This is confirmed by the presence of three hydroxyl groups with various acidity/reactivity, secondary OH at the C-2, secondary OH at the C-3, and primary OH at the C-6 position, and accordingly, by the formation of different strong intermolecular hydrogen bonds [22]. Based on carbon nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra and X-ray diffraction patterns, four major polymorphs of cellulose have been reported and named cellulose I, II, III, and IV [23]. Cellulose I is the most abundant native crystalline form and can be converted into the other polymorphs through a variety of treatments. Cellulose I consists of two phases,  $I_\alpha$  and  $I_\beta$ . Cellulose  $I_\alpha$  has one-chain triclinic structure and cellulose  $I_\beta$  has two-chain monoclinic structure and they differ in hydrogen bonding [24]. The chemical, physical, and biological properties of cellulose depend on its shape properties such as its ease of deformability and its intrinsic form [23]. The noncrystalline cellulose is also important because of higher chemical reactivity of noncrystalline (or amorphous) cellulose.

### 2.2. Hemicellulose

Hemicellulose, next to cellulose, refers to a large group of complex polysaccharide in cell wall of plants [25]. Unlike cellulose, it is a low-molecular-weight polysaccharide, associated in plant cell wall with lignin and cellulose. It forms covalent bonds (mainly  $\alpha$ -benzyl ether linkages) with lignin, hydrogen bonds with cellulose, and ester linkages with hydroxycinnamic acids and acetyl units, which restrict the liberation of hemicellulosic polymers from the cell wall matrix [26]. Large variations in hemicellulose content and chemical structure can occur between various lignocellulosic materials. Many methods have been used to isolate hemicellulosic polymers from plant materials, which include extraction with alkaline, alkali, organic solvent, or twin-screw extrusion and ultrasonication treatments, as well as steam or microwave treatment [26]. For higher lignin content materials, they must be delignified and/or pretreated in some way prior to extraction of hemicelluloses, such as pretreatment by sodium chlorite in acetic acid solution. For soybean hulls, they do not require delignification prior to isolation of hemicelluloses, as compared with other lignocellulosic biomass, because of low content of lignin. The major hemicelluloses in soybean hulls are composed of  $\alpha$ -L-arabinofuranosyl, L-arabino-4-O-methyl-D-glucurono-D-xylan, 4-O-methyl-glucuronic acid and  $\alpha$ -D-galactose units attached with substituted sugars [27, 28]. These hemicelluloses have the potential to be integrated in a wide variety of applications, including thickeners, film-former substances, emulsifiers, binders, and stabilizers in the food, cosmetic, and pharmaceutical industries [29]. In addition, they can be easily hydrolyzed into hexose (mannose, glucose, and galactose) and pentose (arabinose and xylose), and can be transformed into fuel ethanol and other value-added chemicals, including furfural, 5-hydroxymethylfurfural (HMF), xylitol, and levulinic acid (Figure 2) [30].

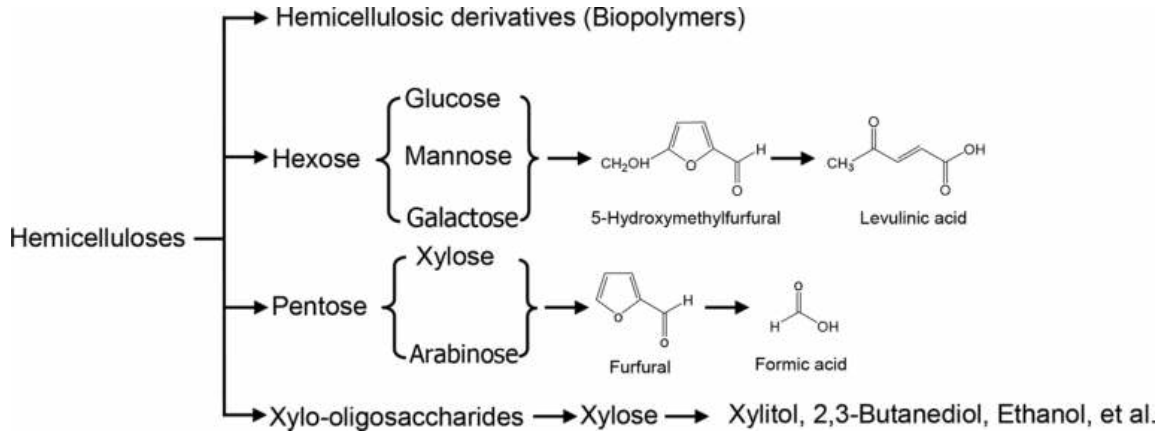


Figure 2. The potential products from hemicelluloses [13].

### 2.3. Pectin

Pectin is a complex polysaccharide consisting of D-galacturonic acid linked by  $\alpha$ -1,4 glycosidic linkages [31]. The molecular weight of pectin varies from 50,000 to 150,000 Da depending on the source materials and extraction procedure. Pectin is a highly valuable functional food ingredient and is very important in creating or modifying the texture of jellies, jams, and confectionery, and in low-fat dairy products. Soybean hulls were potentially inexpensive commercial sources of pectin. Soybean hull pectin (SHP) mainly contains galactose, xylose, galacturonic acid, arabinose, glucose, and rhamnose. The chemical composition of the extracted soybean hull pectin has been comparatively investigated with that of commercially soybean hull pectin (CSHP) and citrus pectin (CP) by Yamaguchi et al. (Table 1) [32]. The results showed that SHP had a molecular weight similar to the CSHP and CP. Glucose content in SHP was higher as compared with CSHP and CP, but other sugar contents were

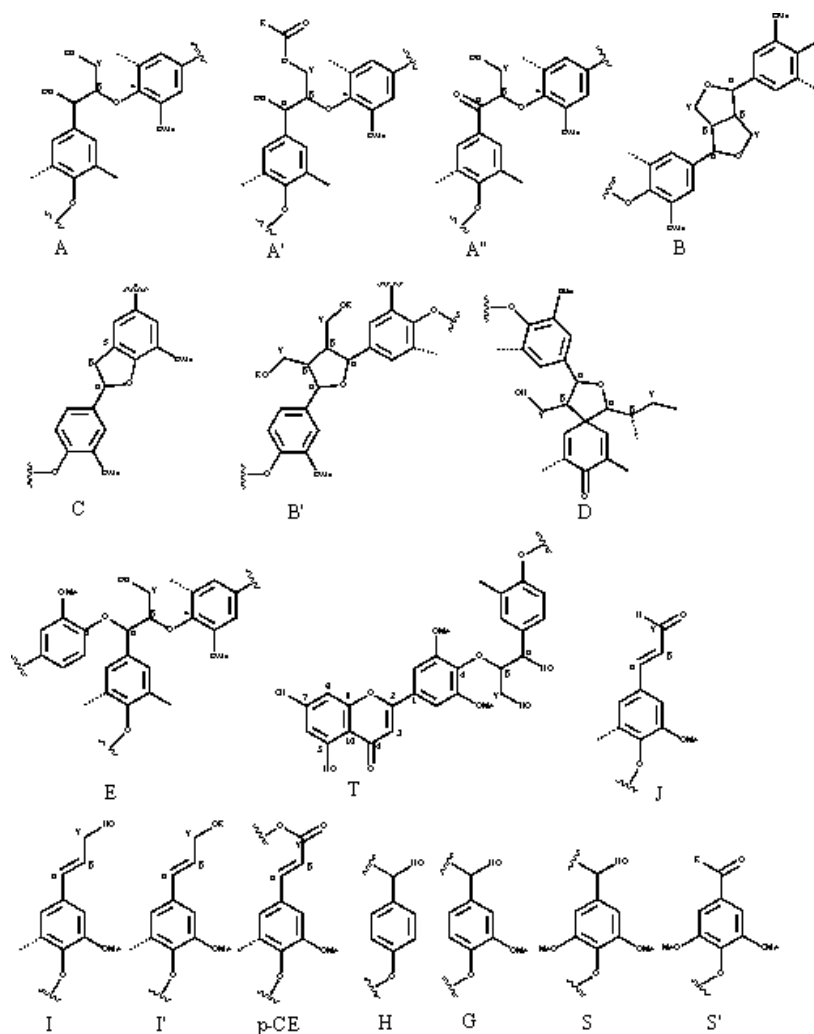
Composition	SHP	CSHP	CP
Galacturonate, % Dry material basis	33.0	18.5	85.8
(% Esterified galacturonate, % Dry material basis)	18.1	0	73.7
Neutral sugar composition, % Dry material basis			
Rhamnose + Fucose	8.0	8.0	25.1
Arabinose	24.2	26.3	15.6
Xylose	2.7	2.5	1.8
Mannose	0	0	0
Galactose	49.8	59.5	49.5
Glucose	15.3	3.7	8

Table 1. Composition of soybean hull pectin (SHP), commercially available soluble soybean hulls pectin (CSHP), and citrus pectin (CP) [32].

similar between SHP and CSHP. The SHP had a similar galacturonan structure to that of CP, but SHP contains more arabinose and glucose, less rhamnose and fucose, and more xylose as compared with CP. The SHP extracted by Yamaguchi et al. [32] showed the degree of esterification of 18.1%, belonging to low methoxyl pectin.

## 2.4. Lignin

Lignin is a three-dimensional amorphous biopolymer formed by three major monolignols, that is, p-coumaryl alcohol (H), coniferyl alcohol (G), and sinapyl alcohol (S) of various ratios,



**Figure 3.** Main lignin structures present in bamboo lignin: (A)  $\beta$ -O-4 alkyl-aryl ethers; (A')  $\beta$ -O-4 alkyl-aryl ethers with acylated  $\gamma$ -OH with p-coumaric acid; (A'')  $\alpha$ -oxidized  $\beta$ -O-4 structures; (B) resinols; (B') tetrahydrofuran; (C) phenylcoumarans; (D) spirodienones; (E)  $\alpha$ ,  $\beta$ -diaryl ethers; (T) a likely incorporation of tricin into the lignin polymer through a G-type  $\beta$ -O-4 linkage; (I) p-hydroxycinnamyl alcohol end groups; (I') p-hydroxycinnamyl alcohol end groups acylated at the  $\gamma$ -OH; (J) cinnamyl aldehyde end groups; (p-CE) p-coumarates; (H) p-hydroxyphenyl units; (G) guaiacyl units; (S) syringyl units; (S') oxidized syringyl units bearing a carbonyl at  $\alpha$  [33].

linked together by different types of ether ( $\beta$ -O-4') and carbon-carbon ( $\beta$ '- $\beta$ ' and  $\beta$ '-5') linkages (**Figure 3**). Besides, lignin is covalently linked to hemicellulosic polysaccharides, forming a lignin-hemicellulose network made up of phenyl-glycoside, benzyl-ether, and benzyl-ester bonds [34]. Despite the extensive investigations of lignin, the complex and irregular structure of lignin has not been completely understood up to now. Lignin is considered as the most abundant sources of aromatic compound in nature and can be utilized for adhesives or chemical reagents to replace those derived from oil. For the lignin of soybean hulls, it is not usually utilized as a major value product, due to its lower content. However, the soybean hull is a good resource for lipid production due to its low lignin content and it has been proven in the bioconversion process that soybean hulls can be utilized without any pretreatment [9].

## 2.5. Protein

The chemical composition of soybean hulls depends on the efficiency of the dehulling process. If soybean meal with high protein content is required, the dehulling process is more intense in order to avoid contamination of the meal with pieces of hulls [10]. In general, the soybean hulls may contain 11–15% of proteins. Soybean proteins are commercially and extensively used in food products due to their functional properties, low cost, and high nutritional value. Soybean proteins are composed almost exclusively of two globular protein fractions called 11S (glycinin) and 7S ( $\beta$ -conglycinin) [35].

## 3. Application of soybean hulls

### 3.1. Animal feed

The by-products of agro-industrial may become an economical alternative to corn grain in ruminant diets, especially when the price of corn is high due to the increase of demand from the ethanol industry [36]. Soybean hulls are by-product from the soybean-processing industry, where the soybean is de-hulled leaving a highly digestible, fibrous feed [37]. Due to their compositions, the biomass is widely used as animal feed. Many investigations have demonstrated that there are advantages of using soybean hulls as an energy source for ruminants in replacement of corn, as long as they are supplied together with effective fiber sources to reduce the rate of passage and enable ruminant fermentation [38–40]. For example, the excessive use of starch in equine diets can lead to fermentation of the ingested material by amylolytic bacteria in the large intestine resulting in an increase in lactic acid production and increased production of short-chain fatty acids, which can cause intestinal disorders such as laminitis or colic [41]. However, studies on the inclusion of soybean hulls in equine diets have shown promising a decrease in starch level without compromising the caloric density of the feed [42]. It was suggested that diets with up to 28% soybean hulls can be used as equine feed without negatively affecting digestibility, the selected microbiota or short-chain fatty acids concentrations, and physicochemical characteristics in the feces [38]. Soybean hulls can also be a resource in maintaining sheep meat production without compromising product quality. Investigation has been carried out for the improvement of sheep diets by soybean hulls, which leads to the

improvement of the fatty acid composition of meat and the production of meat with adequate levels of fat which reduce the levels of saturated fatty acids [43]. The investigation found that the inclusion of soybean hulls in the sheep diet increased the total lipid content, conjugated linoleic acid, and omega 3 fatty acids. The increase of unsaturated and polyunsaturated fatty acids ensured greater consumer satisfaction, since the population was increasingly attentive to health. Soybean hulls can also be used replacing ground corn in diets of goats in the early lactation, because they improve the digestibility of the diet and nutrients, do not change the physical and chemical quality or productive performance of the milk, and increase the content of omega 3 fatty acids in the milk [44]. Soybean hulls can replace corn grain to supply about 30% of the dry matter in high-grain content diets without negatively affecting either the digestion of nutrients or fermentation in gastrointestinal tract or the performance of dairy cows [45]. Vinay Kumar [46] investigated the effect of soybean hulls on the physicochemical characteristics, color, texture, and storage stability of chicken meat nuggets. The results showed that the addition of soybean hulls to chicken nuggets improved nutritional value, sustained the desired cooking yield and emulsion stability, and helped in improving instrumental textural and color values. In addition, the inclusion of soybean hulls in the chicken diet increased the storage times of meat.

### 3.2. Treatment of wastewater

Fresh water is a limited and essential natural resource for the development of a series of living organisms in aquatic environments as well as for humans, all of which require its preservation [46]. The quality of the water is being negatively affected by the world's population growth along with accelerated industrial development that generally involves processes requiring a huge consumption of water and the release of wastewaters back into water bodies [46]. Current methods used to treat wastewater include chemical precipitation, oxidation and chemical reduction, filtration, electrochemical treatment, ion exchange, reverse osmosis, evaporation, and adsorption [47, 48]. Among these techniques, adsorption is an economic and efficient method, based on flexible and simple operating conceptions and the use of regenerative adsorbents, for the removal of inorganic or organic pollutants with high efficiency in many cases [48]. Biosorption is the binding of radionuclides and metal ions onto the cellular structure of biological materials, which contain their functional groups and ligands [49]. Biosorbent materials that are lignocellulosic, containing cellulose, hemicelluloses, and lignin, have high adsorption properties due to the ion exchange capabilities [50]. Biosorbent materials have some advantages. For example, they can be regenerated for reuse, can recover the biosorbent material, do not require much energy input, and do not produce a toxic sludge [49, 51]. Much attention has been given to the use of soybean hulls in the remediation of heavy metals [46, 49, 52]. Soybean hulls without the soluble dietary fiber (SDF) present good metal-binding property and can be used as novel biosorbent [53]. The preparation of soybean hulls including pretreatment, drying, modification, activation, and so on was presented to make the preparation process feasible and economical [46, 54, 55]. Generally, adsorption of inorganic or organic pollutants in wastewater by soybean hulls has been limited and the hull modification is desirable to enhance adsorption especially of metal ions. Aparecido N. Módenes [46] investigated the absorption characteristic of the soybean hulls absorbent by

various modification methods for the removal of Cd<sup>2+</sup> and Pb<sup>2+</sup>. The results showed that an increase in the sorption capacity of Pb<sup>2+</sup> ions of around 20% was achieved as compared with the unmodified material and that an insignificant improvement in the sorption capacity of Cd<sup>2+</sup> ions was obtained when the soybean hulls were modified by treating them with strong base (0.1–1.0 M NaOH). Functional groups such as phosphoryl, hydroxyl, and carboxyl could be the activated sites on soybean hulls sorbent, with metal ion uptake on a neutral sorbent surface occurring via an ion exchange process [46]. The addition of surface functional groups by chemical reaction with NaOH could be responsible for the increase in the biosorbent surface area and consequently greater metal sorption capacity as compared with the untreated material [56]. Investigation has demonstrated that soybean hulls work well at removing textile dyes from contaminated water [52]. Results of the investigation indicated that the soybean hulls and rice hulls worked well at removing the Safranin T and Direct Violet 51 dyes from solution. The soybean hull samples were more effective at removing the Remazol Brilliant Blue R dye as compared with rice hull samples.

### 3.3. Dietary fiber

Dietary fiber can be defined as “the edible parts of plants or analogous carbohydrates that are resistant to digestion and absorption in the human small intestine with complete or partial fermentation in the large intestine” [57]. Dietary fiber is a complex component of natural carbohydrate polymer which consists of a variety of nonstarch polysaccharides such as hemicellulose, cellulose, lignin, and pectin [58]. The beneficial role of dietary fiber in health and nutrition has been demonstrated in normal gastrointestinal and physiological functions, including carbohydrate and lipid metabolism, and in the reduction of chronic ailments such as coronary heart disease, diabetes, obesity, and some cancers [59]. Dietary fiber can typically be divided into soluble dietary fiber and insoluble dietary fiber (IDF). SDF includes pectins and some hemicelluloses. Cellulose, lignin, and some hemicelluloses are examples of dietary fiber classified as IDF. Soybean hulls contain the majority of the fibers with a higher level of IDF. Acid-base hydrolysis and autoclaving significantly affect the SDF, IDF, and total DF distribution in soybean hulls [60]. Kumar et al. [61] and Goldnon and Brown [62] reported that 4% addition of soy hull flours had no impact on the cooking yield and texture of chicken nuggets and pork patties, respectively. Investigation by Kumar et al. [63] indicated that 3–5% addition of soybean hull flours slightly improved emulsion stability and water-holding capacity of chicken nuggets. Kim et al. [64] indicated that insoluble fiber from soybean hulls through acid and alkali hydrolysis influenced positive effects on reduction in cooking loss and increase in hardness of meat without any adverse effect on springiness and cohesiveness, and minimized color alteration. The investigation also indicated that acid-base hydrolysis and autoclaving processes in soybean hulls could significantly boost total dietary fiber content, showing the great potential in various food applications due to the functional properties [60].

### 3.4. Medicine

Soybean with black, brown, yellow, and green seed coats possesses antioxidant capacity varying with color because of differences in phenolic levels and composition which is anthocyanins, phenolic acids (chlorogenic and caffeic acids), isoflavones, and proanthocyanidins



[65–67]. Black soybean has been used as an herbal medicine to treat edema and jaundice. It has also been used to treat enuresis by affecting the functions of the spleen and kidney [68]. The hull of the black soybean has been used for the treatment of headache and vertigo, as well as for detoxification and diuresis [68]. Black soybeans were reported to contain anthocyanins and only brown and black soybeans contain proanthocyanins [66, 67]. Investigation showed that black soybean had the highest antioxidant activity as compared with other colored seed coat soybeans [65]. The antioxidant activity of black soybeans is related to their phenolic pigments in the seed coats [69, 70]. *In vitro* anticancer investigation reported that polysaccharides from black soybean may induce differentiation and inhibit proliferation in human leukemic U937 cells [71]. Anthocyanins isolated from black soybean hulls display growth inhibitory effects and strong apoptosis induction effect against human leukemia Molt 4B cells [72]. Animal experiments indicated that the intake of extract from black soybean hulls effectively enhanced memory and learning ability in rats [73]. The extract of the black soybean hulls has also been used as dietary ingredient including pigments and nutraceuticals [68].

## 4. Conversion of soybean hulls

### 4.1. Ethanol production

The National Biofuels Action Plan released in October 2008 states that expanding annual biofuels production to 36 billion gallons by 2022 would be a key component in America's movement toward clean, affordable, and secure energy sources [11]. The interest for ethanol production from renewable resources has increased in the last decade, directly related to environmental and economic concerns over fossil fuels [74]. Currently, ethanol is mainly produced from sugarcane and corn (in the Brazil and USA, respectively), accounting for 66% of worldwide production [75]. However, recently, there has been increasing interest in cellulosic ethanol production, because biomass is an abundant feedstock that is inexpensive and has a high cellulosic content [10, 76]. Lignocellulosic biomass needs to be decomposed into its monomers in order to release fermentable sugars, and which is achieved by using diluted acids or enzymes. The cellulose in the biomass is scarcely affected by the diluted acid hydrolysis, requiring other physicochemical hydrolyses at higher temperatures to result in sugar decomposition, which may lead to metabolic inhibition during fermentation [77]. Lignocellulosic biomass mainly consists of lignin, cellulose, hemicelluloses, and small amounts of extractives. Cellulose structure allows the formation of intermolecular and intramolecular hydrogen bonds, generating organized rigid crystalline regions. The biological role of hemicellulose is the cross-linked interaction with lignin and cellulose, which strengthens the cell wall and embedding of the crystalline cellulose elementary fibrils [78]. The close association between hemicellulose and lignin impedes enzyme access to hemicellulose, which in turn affects accessibility to cellulose [79]. Thus, pretreatment by various technologies is a crucial prerequisite to break down the rigidity of the biomass prior to enzyme hydrolysis process. Soybean hulls are an agricultural residue produced during the processing of soybeans, and the lignocellulosic material contains a small proportion of lignin (1.4–2%) when compared to other biomass. Therefore, soybean hulls are an attractive source of fermentable sugars for cellulosic ethanol

production. Hickert et al. [74] investigated the conversion of pentoses and hexoses liberated from high osmotic pressure soybean hull hydrolysate into ethanol by various immobilized cerevisiae. The soybean hulls were hydrolyzed in a two-step sulfuric acid-enzyme pretreatment, resulting in more than 72% of saccharification. The yields of bioconversion of soybean hulls into ethanol were 38–47%. Physicochemical pretreatments of soybean hulls for hemicellulose removal were essential in order to improve the material digestibility at the enzymatic hydrolysis stage. Cassales et al. [80] investigated various acid concentrations in order to achieve high sugar release and low generation of toxic compounds. Yoo et al. [11] studied the pretreatment of soybean hulls by thermomechanical extrusion. Mielenz et al. [9] reported high yields of ethanol by simultaneous saccharification and fermentation of soybean hulls without pretreatment, because of the low lignin content. However, the time of fermentation was very long (about 9 days). Rojas et al. [10] reported a process for the recovery of proteins from soybean hulls, mainly as oligopeptides, and the production of ethanol from the remaining lignocellulosic fraction. In addition to ethanol production from soybean hulls, Zhang and Hu [81] studied a new application of soybean hulls to be converted to fungal lipids for biodiesel production through solid-state fermentation. The results showed that the total final lipid reached 47.9-mg lipid from a 1-g soybean hull after the conversion, which is 3.3-fold higher as compared with initial lipid reserve in the soybean hulls. The solid-state fermentation is a more cost-effective process because of low-energy expenditure, its low capital cost, less expensive downstream processing, high volumetric productivity, low wastewater output, and less fermentation space needed [82].

#### 4.2. Bio-oil

Lignocellulosic biomass can be converted into useful form of energy using biochemical and thermochemical processes, but thermochemical conversion technology finds its dominance due to high efficient conversion to gas, liquid, and solid products under thermal conditions [83]. The liquid product called bio-oil is a complex mixture of water and organic chemicals, which are alcohols, aldehydes, acids, ketones, esters, heterocyclic derivatives, and phenolic compounds [84]. There are two typical thermochemical processes to produce liquid product with high yield: pyrolysis and liquefaction. During the pyrolysis processes, the biomass feedstock is heated in the absence of air to a high temperature (400–1000°C), resulting in the formation of bio-oils and gaseous products. Another important method to convert the biomass into liquid fuel is liquefaction in solvents (such as acetone, ethanol, water, or their mixtures) by heat. By the method, biomass can be decomposed into liquid at a mild temperature and a high pressure as compared with the pyrolysis process [85]. Oliveira et al. [86] studied soybean hull bio-oil produced by fast pyrolysis. The main components of the bio-oil were analyzed by gas chromatography/mass spectrometry (GC/MS). The results indicated that the soybean hull bio-oil can be used as an alternative source of chemical products with higher added value. As a result of the decomposition of cellulose, hemicellulose, and lignin, the soybean hull can be transformed into products having various molecular structures. The soybean hull bio-oil was proved to be a complex mixture of a variety of organic compounds (more than 60 compounds were identified) [86]. For the aqueous phase of the soybean hull bio-oil (acid extraction), the main compounds were pyridine (17.06%), acetic acid (9.12%), phenol (16.94%), pyrrole (5.14%),

and acetamide (5.73%). The high acidity presented in the aqueous phase of soybean hull bio-oil is probably because of the thermal degradation of hemicelluloses, which produces acids as the final product of reactions involving the removal of acetyl groups [87]. Cellulose can be decomposed into levoglucosan at first, and then the levoglucosan can be generated by depolymerization reactions, which produce small quantities of acids, such as propionic acid and acetic acid, as well as furans (furfural, furfuraldehydes, and pyrans) [88]. In the organic phase, the main compounds identified in soybean hull bio-oil were phenol (14.88%), 4-methylphenol (12.55%), and 2-methylphenol (7.59%) [86]. The phenol compounds and derivatives were obviously due to the decomposition products from lignin (and maybe hemicellulose and cellulose). Those phenolic compounds can be separated from soybean hull bio-oil by using vapor distillation, reverse osmosis membranes, and solvent extraction [89–91].

### 4.3. Polysaccharides

Polysaccharides are species of macromolecular substance existing widely in organisms. It has been reported that plant polysaccharides or their derivatives have strong antioxidant activities and can be explored as novel potential antioxidants [92]. Some of the polysaccharides have been targeted as important candidates for the development of effective and nontoxic medicines with strong free radical-scavenging and antioxidant activities [93]. The insoluble carbohydrate fraction in soybean hulls contains 50% hemicelluloses, 30% pectins, and 20% celluloses [94]. Therefore, the soybean hulls are potentially commercial source of polysaccharides. Liu et al. [27] studied the extraction of soybean hull polysaccharides by hot-compressed water in a batch system. The results showed that a moderate temperature (160°C) and short extraction time (60 min) were suitable for the preparation of soybean hull polysaccharides. In the sugar composition of the polysaccharide products, arabinose constituted 35.6–46.9%. Nagata et al. [95] investigated the effects of soybean hull polysaccharides on serum immunoglobulin concentration and production of NO and interleukin-1 $\beta$  from peritoneal macrophages. The soybean hull polysaccharides consisted of arabinose, galactose, xylose, glucose, and rhamnose, and the molecular weight was 500,000. The investigation demonstrated that soybean hull polysaccharides enhanced humoral immunity and activation of macrophages, thereby leading to the augmentation of immune responses in rats.

### 4.4. Microfibrils

Microfibrillated cellulose developed for the first time in the early 1980s by Turbak and coauthors can be obtained through mechanical treatments such as refining and high-pressure homogenization [96]. Microfibrillar cellulose is a bio-based material with interesting intrinsic properties that make it attractive in many applications. It is characterized by a high specific surface area, flexibility, and crystallinity, and contains a large amount of hydroxyl groups [97], all of which influence its interactions in liquid dispersions or in solid films. Merci et al. [98] produced the microfibrillar cellulose from soybean hulls by using a simple method based on reactive extrusion. The reported microfibrillar cellulose produced from soybean hulls was composed of short and rod-shaped fibers, and had a cellulose content of 83.79% and crystallinity index of 70%. Miranda et al. [99] studied the kinetics of degradation process of cellulose extracted from soybean hulls and compared its behavior to commercial microcrystalline

cellulose under inert environment. The results indicated that kinetic degradation behavior of soybean hull cellulose was more similar to commercial microcrystalline cellulose. However, the activation energy value of commercial microcrystalline cellulose was higher as compared with soybean hull cellulose. Ferrer et al. [7] isolated cellulosic microfibrils (SMF) and brick-like microparticles (SMP) from soybean hulls by combining mechanical and chemical pretreatments. The SMF and SMP chemical compositions included residual polysaccharides and lignin that endow such biologically derived materials with properties typical of nanocellulosics. As compared with those of micro- and nanofibrillated cellulose obtained from fully bleached wood fibers, the SMF and SMP exhibited enhanced crystallinity and thermal stability. In addition, a strong shear-thinning behavior was observed for aqueous dispersions of SMF and SMP, revealing that cellulose microstructures are of interest for rheology modification, coatings, and films. These SMF and SMP extracted from soybean hulls have been used in films and also combined with wood-based micro- and nanofibrillar cellulose in hybrid systems [100]. The hybrid films displayed similar strength and barrier performance to those of neat nanofibrillar cellulose films, thus offering an option for reduced cost while keeping a performance from synergistic contributions of the components. Furthermore, dense films with low porosity, a characteristic essential for barrier properties, can be easily produced by replacing up to 75% of micro- and nanofibrillar cellulose with SMF or SMP.

#### 4.5. Peroxidase

The extraction of enzymes from agro-industrial residues is an alternative for reducing costs in biocatalyst production. Soybean hull peroxidase (SHP, E.C. 1.11.1.7) is a glycoprotein that belongs to plant peroxidase superfamily that also includes horseradish (HRP), peanut, and barley peroxidases [101]. Because of the high thermostability, broad pH stability, and cheap source for production from soybean hulls [102], SHP is a more promising biocatalyst for industrial use as compared with the widely used HRP. SHP was previously used for the removal of aqueous phenols from wastewaters in stirred membrane reactor, as a bromination catalyst, for luminal oxidation, for the synthesis of polyaniline, and in organic solvents [103–106]. Then, higher-value commodities such as diagnosis tests and therapeutics would require more costly alternatives such as purified or recombinant peroxidases. Soybean hull peroxidase has a ferriprotoporphyrin IX prosthetic group located at the active site. The catalytic mechanism follows a peroxidase ping-pong mechanism involving the two-electron transfer from hydrogen peroxide to the heme, creating an oxidized form of the enzyme, “compound I.” Successive one-electron reductions return the enzyme to its native or reduced state via an intermediate oxidized form of the enzyme, “compound II” [107]. As compared with free enzymes, immobilized enzymes offer more advantages, such as enhanced stability against various denaturing conditions, easier product and enzyme recovery, higher catalytic activity, continuous operation of enzymatic processes, reusability, and reduced susceptibility to microbial contamination [108, 109]. Chagas et al. [110] extracted peroxidase from soybean hulls and immobilized the enzymes on chitosan beads cross-linked with glutaraldehyde. The immobilized enzyme showed a potential of 50% in the oxidation of caffeic acid after four consecutive cycles.

#### 4.6. Oligopeptides

Soybean oligopeptides produced by proteolysis or microbial fermentation techniques followed by purification protocols are widely used in the food industry. The soybean hulls

may contain 11–15% of proteins, and the proteins can be transferred into oligopeptides by various techniques. Most commercial productions of oligopeptides use batch hydrolysis, which depends on various factors such as protein denaturation, hydrolysis temperature, and protease specificity [111]. The hydrolysate of protein is a complex mixture of peptides with various lengths. Molecular size of the peptides has a major effect on functional properties. In general, smaller peptides with less than six amino acids have the greatest impact on cell growth and production [112]. Rojas et al. [10] published the results concerning the recovery of proteins from soybean hulls by hydrolysis, mainly as oligopeptides, and subsequent ethanol production from the remaining lignocellulosic fraction. The results indicated that soybean hulls might be a promising feedstock for the production of a high-value protein hydrolysate composed mainly of low-molecular-weight oligopeptides.

## 5. Conclusion

Soybean hulls are a major by-product in the soybean-processing industry, and have a variable chemical composition of cellulose (29–51%), hemicellulose (10–25%), lignin (1–4%), pectin (4–8%), proteins (11–15%), and minor extractives. The low lignin content in soybean hulls makes the residues have a very wide variety of applications. Due to their compositions, the soybean hulls are widely used as animal feed and have demonstrated the advantages of using as an energy source for ruminants in replacement of corn. Adsorption of inorganic or organic pollutants in wastewater by soybean hulls has been limited and the hull modification is desirable to enhance adsorption, especially of metal ions. The soybean hulls are potentially commercial source of ethanol production, dietary fiber, microfibrils, polysaccharides, and pectin. Soybean hulls can be converted into useful form of energy such as bio-oil by thermochemical processes. The extraction of peroxidase from soybean hulls is an alternative for reducing costs in biocatalyst production. The peroxidase has been used for the removal of aqueous phenols from wastewaters in stirred membrane reactor, as a bromination catalyst, for luminal oxidation, for the synthesis of polyaniline, and in organic solvents. The protein content in soybean hulls has produced a high-value protein hydrolysate composed mainly of low-molecular-weight oligopeptides.

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