PART 1 CHAPTER 12

Coffee By-Products

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Abstract

Large amounts of coffee by-products are generated in the industrial processing of coffee cherries to obtain the coffee beverage. Approximately 90% of the cherry is discarded during the conversion of the cherry into a tasty, aromatic brew. Coffee waste causes environmental problems worldwide and represents a loss of natural sources of several added value compounds. The present chapter provides a review of the information currently available on coffee by-products including their definition, chemical composition and potential applications. The feasibility of applying the biorefinery concept to achieve a sustainable coffee sector is discussed. Based on the research conducted in this field, we can conclude that coffee is not only for drinking; you can also use it for many beneficial purposes by applying the biorefinery concept. Conversion of by-products into health-promoting products is of particular interest. However, raw materials should be controlled for quality and safety before they are converted into products for human consumption. The safety rules used to test the quality of green beans should also be adopted for other coffee materials. Thus, coffee by-products have a future as co-products and provide an opportunity to increase the competitiveness of the coffee sector.

12.1 Introduction

Large amounts of coffee by-products are generated from the industrial processing of coffee cherries to obtain the coffee beverage.[1–4] Coffee is actually a cherry whose structure is shown in Figure 12.1. Coffee cherries are mainly used to prepare the beverage when they are processed. From farm to cup, coffee processing can be briefly summarized in ten key steps: planting, cherry harvesting, processing (wet and dry methods), drying the beans, milling, exporting, tasting, roasting, grinding and brewing (http://www.ncausa.org/). According to the method used to process the coffee beans (wet or dry method), different solid residues such as skin, pulp, husk, mucilage, parchment, silverskin and spent coffee grounds are obtained.

[Figure 12.1 near here]

The steps from planting to exporting the beans are mainly carried out in coffee producing countries like Brazil, Vietnam or Colombia. While most coffee producing countries are developing countries, coffee consuming countries are usually developed countries with local roasting industries based on green coffee imports. Therefore, two major classes of coffee by-products can be distinguished, those derived from green coffee production (skin, pulp, husks, mucilage and parchment) in producing countries, and those obtained after roasting (silverskin and spent coffee grounds) with a wider distribution.

The sustainability of food production and consumption, defined as the exploration of innovative strategies to increase resource efficiency, providing consumers with healthier products of higher quality and safety while ensuring minimal waste in the food chain, is a research priority.[5] The agro-industrial and food sectors produce large quantities of liquid and solid waste. Since coffee is the second most valuable commodity exported by developing countries,[6] the coffee industry is responsible for the generation of large amounts of waste. Consequently, coffee by-products have attracted great attention because of their abundance and interesting chemical composition.

The study of the coffee by-products generated during the different stages of processing is necessary to decrease the waste produced by this industry. The recovery of coffee by-products is mainly based on their use as a source of energy and biomass. Although these strategies are of interest, they do not consider valuable nutritional compounds that could improve consumers' health and increase the competitiveness and sustainability of coffee production.[7] Interest in the valorization of agronomical by-products into diverse and useful novel products to achieve a global sustainable world has recently been reported in the "Food Waste Recovery" book.[8]

The valorization of agricultural wastes, food processing by-products, wastes and effluents using the biorefinery approach represents the real contribution of many industries to sustainable and competitive development.[9] Biorefineries can be described as integrated biobased industries which use a variety of technologies to make products such as chemicals, biofuels, food and feed ingredients, biomaterials, fibers, heat and power, aimed at maximizing the added value of the three pillars of sustainability (Environment, Economy and Society).[10]

A brief description of these coffee by-products, their chemical composition and their applications is presented in this chapter.

12.2 Definition of Coffee By-Products

The type of by-product generated depends on the process used to obtain the green coffee bean. In the case of wet processing, ripe cherries are depulped to eliminate the outer skin, eliminating most of the pulp fixed to the grains. Then, the coffee beans undergo fermentation processes, are washed to remove the rest of the pulp, dried by sun exposure and peeled to remove the parchment. Here, skin and pulp are recovered in one fraction, and soluble sugars and mucilage are generated in another fraction. Finally, the parchment is obtained.[11] Dry processing involves sun drying the coffee cherries for two or three weeks, and green coffee beans are obtained by simply threshing the dried cherries. At this time, skin, pulp, mucilage and parchment are obtained in a single fraction, along with part of the silverskin.[12] The only by-product of coffee roasting is the silverskin.

12.2.1 Pulp

Coffee pulp is a by-product generated from wet coffee processing, and it represents 29% dry weight of the whole bean.[13] Coffee pulp consists of the outer skin or pericarp and most of the mesocarp (Figure 12.1), which is mechanically removed by pressing the coffee fruit in a depulper.[14] One ton of coffee pulp is obtained per two tons of coffee processed.[15]

12.2.2 Mucilage

The coffee mucilage fraction, also called the pectin layer (Figure 12.2) is located between the pulp and the parchment, and represents 5% dry weight of the berries.[16] It remains adhered to the coffee bean after depulping in wet processing without enzymatic degradation. Since it is highly hydrated, it is an obstacle to further drying the beans. Thus, mucilage must be degraded to facilitate its elimination by washing, before the beans are dried and stored.[17] Wet processing allows the separation and concentration of this fraction.[14]

[Figure 12.2 near here]

12.2.3 Parchment

This yellowish by-product is a strong fibrous endocarp (Figure 12.3) that covers both hemispheres of the coffee seed and separates them from each other. It represents 5.8% dry weight of the berries. In wet processing, the parchment is removed after drying and hulling in separate steps.[18] The latter process allows the parchment to be collected and used separately from other by-products.

[Figure 12.3 near here]

12.2.4 Husks

Coffee husks are mainly obtained from the dry processing of coffee berries. This coffee by-product is composed of the outer skin, pulp and parchment of the coffee berry.[14] Coffee husks enclose the coffee beans and compromise nearly 45% of the berry.[13] About 0.18 ton of husk are produced from 1 ton of coffee fruits.[19]

Coffee husks are shown in Figure 12.4. Such by-products are generated in coffee producing countries, which separate the coffee beans from the coffee cherry. Since most of these countries are developing, the diversification of agriculture and the coffee industry is particularly interesting from a socio-economic point of view.

[Figure 12.4 near here]

12.2.5 Silverskin

Coffee silverskin (CS) is a thin tegument of the outer layer of the two beans forming the green coffee seed (Figure 12.5) obtained as a by-product of the roasting process [2]. It represents about 4.2 % (w/w) of coffee beans. CS is the only by-product produced in the roasting process, and large amounts of CS are produced by large-scale coffee roasters in consuming countries.[20]

[Figure 12.5 near here]

12.2.6 Spent Coffee Grounds

Spent coffee grounds (SCG) are the residual material obtained during the treatment of coffee powder with hot water to prepare coffee infusion or steam for the instant coffee preparation (Figure 12.6). Almost 50 % of worldwide coffee production is processed for soluble coffee preparation, generating around 6 million tons of SCG per year.[2] On average, one ton of green coffee generates about 650 kg of SCG, and about 2 kg of wet SCG are obtained for each kg of soluble coffee produced.[21]

[Figure 12.6 near here]

12.3 Chemical Composition of Coffee By-Products

Table 12.1 shows an overview of the work previously performed on the chemical characterization of food by-products. More details are provided in the present section of this chapter.

[Table 12.1 near here]

12.3.1 Pulp

Coffee pulp is mainly composed of carbohydrates (44-50%), proteins (10-12%) and fibers (18-21%), and it also contains appreciable amounts of polyphenols (1.48%) and caffeine (1.3%).[11, 22–24]

Four major classes of polyphenols have been described in *C.arabica* fruit pulp: viz., flavan-3-ols, hydroxycinnamic acids, flavonols and anthocyanidins.[25] The composition of phenolic compounds in fresh pulp has been analysed by HPLC, and the obtained profile was chlorogenic acid (5-caffeoylquinic acid, according to IUPAC numbering) (42.2% of total identified phenolic compounds), epicatechin (21.6%), 3,4-dicaffeoylquinic acid, (5.7%), 3,5-dicaffeoylquinic acid (19.3%), 4,5 dicaffeoylquinic acid (4.4%), catechin (2.2%), rutin (2.1%), protocatechuic acid (1.6%) and ferulic acid (1.0%).[26] Additionally, 5-feruloylquinic acid has been identified in coffee pulp.[27] The major anthocyanins present in the pulp derived from wet-processed fruits are cyanidin-3-rutinoside, cyanidin-3-glucoside and aglycone.[14] Several proanthocyanidins (condensed tannins) have also been isolated from coffee pulp. Tannins content has been found to increase throughout the drying process, and yellow coffee varieties are richer in condensed tannins than red varieties.[28] Interestingly, no hydrolysable tannins were obtained in five samples of coffee pulp from different coffee beans.[29]

12.3.2 Mucilage

Mucilage is composed of water (84.2%), protein (8.9%), sugar (4.1%), pectic substances (0.91%) and ash (0.7%).[14] The polysaccharide composition of the alcohol insoluble fraction of mucilage from *Coffea arabica* beans includes pectic substances (30%), cellulose (8%), and neutral noncellulosic polysaccharides (18%). Crude pectins are formed by uronic acids (60%) with a high degree of methyl esterification (62%) and a moderate degree of acetylation (5%).[30,17]

12.3.3 Parchment

Coffee parchment is formed by (α-) cellulose (40–49%), hemicellulose (25–32%), lignin (33–35%) and ash (0.5–1%).[31]

12.3.4 Husks

As mentioned above, coffee husks, which are comprised of the outer skin, pulp and parchment, are the main residues obtained in the dry processing of the coffee berry. They have a high content in carbohydrates (35-85%), soluble fibers (30.8 %), minerals (3-11%) and proteins (5-11%).[23, 32] Coffee husks are also rich in insoluble dietary fiber, containing 24.5% cellulose, 29.7% hemicelluloses and 23.7% lignin.[31] They can also be a source of phytochemicals such as tannins (5-9%) and cyanidins (20%) for the food and pharmaceutical industries.[12, 23, 32] The amount of total polyphenols in coffee husks is 1.22%.[33]

12.3.5 Silverskin

The chemical composition of CS is currently being analyzed by different research groups. CS has a high dietary fiber content (68-80%), which includes about 85% insoluble dietary fiber and 15% soluble dietary fiber.[3, 34] Polysaccharides are also abundant components (60-70 %) in CS. [4, 7, 34, 35] Sugars are polymerized into cellulose and hemicellulose structures which contain glucose, xylose, galactose, mannose and arabinose. The composition of sugars depends on the process used to extract carbohydrates. Some studies have found glucose to be the main monosaccharide in CS [4] while others reported fructose to be the main monosaccharide.[3] Total sugar content varies greatly in this by-product (1.6−12%).[3] Lignin is also a fraction present in a significant amount in CS (30%).[2, 4, 36]

CS contains protein, fat, and ash, at 16.2–19.0%, 1.56–3.28%, and 5-7%, respectively.[7, 34, 35, 37] The ash in CS contains a variety of mineral elements including potassium, calcium, magnesium, sulfur, phosphorus, iron, manganese, boron, and copper among others. Potassium is the most abundant mineral element followed by calcium and magnesium.[4] Caffeine content in CS is lower than in coffee beans. In general, the average caffeine content is 0.8-1.0%.[3, 37]

CS is considered to be a good source of bioactive compounds, particularly chlorogenic acids.[33, 38] The most relevant are 5-caffeoylquinic acids and 3-caffeoylquinic acids with amounts of 1.99 mg/g and 1.48 mg/g, respectively.[38]

The presence of melanoidins has also been reported in CS.[34] Melanoidins are the final product of the Maillard reaction which occurs during the coffee bean roasting process. Coffee melanoidins are formed mainly by polysaccharides, proteins and chlorogenic acid. Conditions during coffee bean roasting give rise to the formation of different types and amounts of melanoidins.[39]

The extraction of bioactive compounds from natural products like CS is increasingly being used to prepare dietary supplements/nutraceuticals, food ingredients and some pharmaceutical products.[40] Due to its chemical composition, CS could be an important source of several bioactive compounds. The extraction yields of bioactive compounds from natural matrices greatly depends on variables such as type of solvent, solvent-to-solid ratio, time, temperature, and pressure, which can be managed to optimize compound extraction.[20, 41] Thus, the compound of interest would determine the conditions needed to achieve maximum extraction yield. The most used methods to obtain CS extracts are water extraction at temperature ranges between 25-100ºC and subcritical water extraction (SWE) with extraction temperatures ranging from 25ºC to 210ºC.[20, 41] Table 11.2 summarizes the chemical composition of the CS extracts obtained using these environmentally friendly technologies.

[Table 12.2 near here]

12.3.6 Spent Coffee Grounds

The macronutrients, fiber and phenolic compounds of SCG are presented in Table 12.1. Polysaccharidesare the main components of SCG derived from instant coffee production (75%). Hemicellulose (39%) and cellulose (12%) are the most abundant polysaccharides in SCG. The hemicellulose sugars composition in SCG is~37.% mannose, 320% galactose, 24.% glucose and 7% arabinose.[4] Some authors have determined the dietary fiber content in SCG reporting 43-54% total dietary fiber, 47-50% insoluble dietary fiber and 6-16% soluble dietary fiber. These values differ from those of our experimental assay which found higher amounts of total dietary fiber (82.8%) and insoluble dietary fiber (82.3%) and lower amounts of soluble dietary fiber (0.43%) (Data not published).

Spent coffee grounds also contain protein, fat and ash (13.6-17.44%, 2.29% and 1.30-1.6%, respectively).[4, 42] With regard to minerals, potassium is the major component, followed by magnesium and phosphorus.[4] Various caffeine concentrations (0.007–0.5%) have been reported depending on the caffeine extraction process and SCG variety.[43, 44] The chemical composition was similar in SCG obtained from the preparation of coffee brews.[7, 45] SCG from different coffeemakers (filtered, French press and espresso) contained between 0.2-0.8% caffeine with the exception of SCG from the regular coffeemaker which did not present this compound.[45]

Different health-related chemicals bound to dietary fiber and proteins such as phenolic compounds, mainly chlorogenic acids, have been reported in SCG from different sources.[7, 45, 46] Monocaffeoylquinic acids (3-CQA, 4-CQA, 5-CQA) and dicaffeoylquinic acids (3,4-diCQA, 3,5-diCQA, 4,5-diCQA) have been identified and quantified in SGC obtained from different brewing processes and coffee species.[7, 45] Total caffeoylquinic acids (CQA) contents ranging from 1.7-0.7% have been found in SGC,[7, 45] and higher levels of total CQA have been found in *Coffea arabica* SGC than in *Coffea canephora* SGC.[45] Furthermore, the amount of total CQA is significantly lower in SCG from 100% torrefacto coffee. Polyphenols may interact with other coffee components in the torrefacto process[7] and CQAs may undergo chemical transformations during coffee processing, leading to reduced amounts of CQAs by transformation into quinolactones and melanoidins.[7]

The amount of coffee melanoidins that remained in SCG after coffee brewing ranged from 15-35%.[7] Coffee melanoidins fractions are diverse and possess different physicochemical properties.[39] Likewise, coffee melanoidins have been hypothesized to become a part of the soluble dietary fiber fraction during the roasting process.[47]

12.4 Applications of Coffee By-Products

Coffee by-products have attracted great attention in the last few years due to the large amounts generated. As these residues are derived from coffee beans, they are expected to have similar properties which could be exploited for different industrial applications. In this sense, some alternatives have been proposed to reuse these coffee wastes.[4, 13, 22] Some of these value-added applications are only in their infancy, while others have already been patented and even used industrially. In this chapter, we will focus on applications related to food, health and derivatives from the application of the biorefinery concept in the coffee sector.

12.4.1 In Foods

The search for new technologies and ingredients with interesting characteristics and potential for incorporation into functional foods has emerged parallel to the environmental problem of water and land pollution caused by the unsafe disposal of coffee by-products in coffee producing countries.[13] The rich chemical composition of coffee and its by-products remains underexploited at the different stages of the value chain.[14] Few applications of coffee by-products have been proposed in foods so far.

12.4.1.1 Coffee Pulp

Several applications have been proposed for coffee pulp. Medeiros *et al.*[48] reported a great potential use of coffee pulp as a substrate of *Ceratocystis fimbriata* 374.83 fungus to produce fruity aroma by solid state fermentation. A total of thirteen compounds were produced from coffee pulp with and without previous thermal treatment. The major compounds obtained were ethyl acetate, ethanol and acetaldehyde, followed by ethyl propionate, propyl acetate, ethyl isobutyrate, butyl acetate, and four compounds remained unidentified. More recently, Bonilla-Hermosa *et al.*[49] studied the production of aroma/flavor compounds that could be interesting for food by applying eight yeast strains to coffee pulp. They detected 35 compounds corresponding to six groups of volatile compounds, higher alcohols, acetates, ethyl esters, aldehydes, terpenes and volatile acids contributing to floral and fruity notes with commercial interest.

Coffee pulp has also been assayed as a potential source of anthocyanins for application as a natural food colorant.[12, 50] In the wet process, coffee pulp is removed prior to drying, and its color is rapidly degraded by the action of the enzymes liberated or by other oxidizing agents, such as oxygen. As a result, large amounts of natural colorants are wasted. Cyanidin 3-rutinoside was characterized as the dominant anthocyanin, responsible for the colour red. Coffee anthocyanins have also been reported to have multiple biological effects.[50] Therefore, coffee pulp could potentially be used as a colorant and bioactive ingredient in formulated foods. A new interesting ingredient -coffee pulp flour- has been developed from coffee pulp.[51],[51a] Ramirez *et al.*[51] obtained coffee pulp flour with a high fiber and mineral content (18% and 8%, respectively) and low fat (1.6%). This recently developed coffee flour® has been proposed for use in different food formulations such as breads, cookies, muffins, squares, brownies, pastas, sauces and beverages. It possesses 5 times more fiber than whole grain wheat flour, 84% less fat and 42% more fiber than coconut flour and is gluten free. Regarding taste, this product does not have a coffee taste, but rather expresses more floral, citrus and roasted fruit-type notes.[51a] .

Furthermore, coffee pulp has been characterized as source of soluble dietary fibers (SDF) aimed for use in food and pharmaceutical applications.[51b]. Due to its properties as an emulsifier and stabilizer, this extracted coffee dietary fiber is a promising new ingredient for the food and beverage industry.

12.4.1.2 Coffee Mucilage

According to the International Coffee Organization (ICO), coffee mucilage could be used in foods as unrefined pectins, either thermo-reversible soluble gels or nonreversible cross-linked with different mouth feel, antioxidants and flavonoid compounds such as chlorogenic acids and anthocyanin fruit color compounds and colorless pro-anthocyanins. All these compounds have become food additives of special interest for the food industry.[52]

Coffee mucilage has also been proposed for use as honey for human feed.[51] The chemical composition of this honey showed 30-40% moisture, 55º Brix, 4% proteins, 2% fiber and a polyphenols content corresponding to 380 mg gallic acid equivalent/100g. This coffee honey with high sugar content was achieved by means of a vacuum dehydration step at a temperature below 65°C, obtaining a product with minimum nutritional damage by heat, and high digestibility and palatability.

12.4.1.3 Coffee Husk

One of the first applications of coffee husks in the food industry was the production of value-added products such as citric acid.[53] A solid-state fermentation (SSF) system was carried out on coffee husks by employing *Aspergillus niger*. Data indicated that about 1.5 g citric acid was produced per 10g dry coffee husk in the optimized medium with conversion reaching about 80% based on the sugar consumed. It was estimated that a commercial SSF plant could process 5 tons of coffee husk and produce 0.75 tons of citric acid/day, thereby making coffee husks an attractive substrate for the production of citric acid, an additive widely used in juices, candies and sauces.

Coffee husk has been also described as an important source of natural aroma compounds. Soares *et al*.[54, 55] studied the production of fruity flavor by *Ceratocystis fimbriata* grown on steam-treated coffee husk supplemented with glucose, leucine, soybean oil and salt solution. Strong pineapple and banana aroma compounds were formed during fermentation, when different concentrations of glucose (20–46%) were used. Compounds such as acetaldehyde, ethanol, isopropanol, ethyl acetate, ethyl isobutyrate, isobutyl acetate, isoamyl acetate and ethyl-3-hexanoate were also identified. When leucine was added to the medium, total volatile production increased, resulting in a strong banana odor. In this sense, natural flavor from coffee by-products could also be used in the food industry.

12.4.1.4 Coffee Silverskin

CS has been proposed as a natural source of several ingredients such as prebiotic carbohydrates, dietary fiber and antioxidants.[4,13,14, 32,33, 34, 37]

CS was used together with roasted coffee powder, cocoa powder and golden coffee to obtain innovative coffee blends.[56] The new blend was enriched in bioactive compounds such as chlorogenic acids, trigonelline, theobromine and caffeine. It also had a high antioxidant capacity and was favorably appreciated due to its sensory characteristics.

CS has been employed as dietary fiber for the formulation of innovative bakery products, specifically bread.[35] Results showed the feasibility of using the alkaline hydrogen peroxide CS as a food ingredient to reduce caloric density and increase the dietary fiber content of bread. CS has also been used in the formulation of novel biscuits.[57] Biscuit formulations were designed using stevia as a sweetener and CS as a natural colorant and source of dietary fiber. CS improved some of the quality attributes of the biscuits such as moisture, texture, thickness and color. Regarding the processing of chemical contaminants, hydroxymethylfurfural was greatly reduced and no bioaccesible acrylamide was detected in the digests of the new innovative biscuits. The nutritional value of the biscuits was also improved.

12.4.1.5 Spent Coffee Grounds

There is a rising search for new alternatives to add value to this by-product.

Sampaio *et al.*[58] successfully used SCG for the production of a distilled beverage with a coffee aroma. The process was based on the aqueous extraction of aromatic compounds from SCG, supplementation with sugar and the production of ethanol. The novel spirit then produced flavor and volatile compounds. Its organoleptic properties were acceptable and different from those of commercial spirits.

SCG has also had an antimicrobial effect on *S. aureus* and *E. coli*.[7] This antimicrobial activity might be related to the presence of coffee melanoidins in the SCG structure. In fact, the antimicrobial activity of coffee melanoidins extracted from SCG was 2–5 times higher than when assayed alone. Therefore, they could also be used as preservatives in foods at large concentrations. In this sense, other authors have obtained spent coffee extract powder with a high antioxidant capacity after defatting and extract lyophilization.[59] This powder could be used in the food industry as an ingredient or additive with potential preservation and functional properties.

Brazinha *et al.*[60] proposed a process for obtaining a natural bioactive extract from spent coffee grounds, enriched in caffeine, thereby obtaining a high-value product with known bioactive properties from an abundant material with low value. This extract has a ''natural'' label which could be used in the market segment of energy drinks.

A granted patented application of SCG regards its use as an ingredient with a high level of dietary antioxidant fiber in healthy bakery products.[61] This ingredient could be directly applied in the manufacture of pastry and confectionery foods such as bread, biscuits and breakfast cereals, among others, making it a simple, low-cost method. The developed formulation employed SCG as source of antioxidant fiber in diverse combinations with other basic and/or innovative ingredients like stevia. The resulting formulas were rich in insoluble dietary fiber (3%-7%) and had low acrylamide content. These products might be appropriate for special nutritional needs due to their low glycemic index and energetic value.

Common applications of several of the previously mentioned coffee by-products have been developed. Studies for the cultivation of edible mushrooms have carried out using substrates of coffee cherry husk, coffee parchment, CS, SCG and dried leaves, with and without supplementation of agricultural wastes (wheat bran).[62] Coffee industry wastes were used either individually or in combination for mushroom cultivation. Individual use of the substrates led to low mushroom yields. The highest of these yields was obtained using coffee cherry waste, followed by SCG. Cultivation with a mixture of all coffee wastes yielded maximum mushroom production. Therefore, high mushroom productivity can be reached using coffee by-products.

Furthermore, coffee pulp, coffee husk, CS and SCG contain appreciable amounts of bioactive compounds, mainly chlorogenic acid and antioxidant dietary fiber.[33] Therefore, they represent an exciting opportunity to obtain new functional ingredients for use as natural antioxidant sources, nutraceuticals, and preservatives in an enormous variety of food preparations with high nutritional value.

12.4.2 In Health

12.4.2.1 Coffee Pulp

Coffee pulp, enriched in anthocyanins, contains powerful inhibitors of glucosidase and amylase enzymes. As these enzymes play an important role in the management of glucose metabolism, the use of anthocyanin extracts from coffee pulp has been proposed to improve postprandial blood glucose metabolism.[50]

12.4.2.2 Coffee Silverskin

The highlighted chemical composition of CS suggests that it could be a good source of phenolic compounds, particularly chlorogenic acids.[34, 63, 64] Phenolic compounds have shown potential protective activity against several chronic diseases[65] associated with oxidative stress and inflammation[66, 67]. Chlorogenic acids have shown relatively good bioavailability[68] and present several functions such as antifungal, antibacterial[69,70], anti-inflammatory[71], antioxidant[63], anti-glycative[72], anti-carcinogenic[73] and neuroprotective[74] functions. CS extract is also rich in melanoidins, possessing antioxidant and other health-promoting properties.[7, 20, 34] CS antioxidants have exhibited a powerful antioxidant effect *in vitro*[63, 64] which may be bioavailable for reducing oxidative stress in humans, thereby decreasing the risk of chronic diseases such as cardiovascular diseases, cancer, type 2 diabetes, Alzheimer's and Parkison's disease.[65] Since AGEs (Advanced glycation end products) and carbonyl stress are also associated with the pathogenesis of these diseases, the antiglycative properties of CS extract can also contribute to reducing the risk of such pathologies.[75]

Considering the high fraction of insoluble compounds, especially those enriched in high molecular weight polysaccharides and lignin, CS showed a relevant effect on gut microbiota. The prebiotic activity in CS increased the number of healthy bacteria such as *Lactobacillus spp*. and *Bifidobacterium spp*.[7] Hence, CS could be used as a source of a new functional ingredient with the capacity to promote human health through its potential effect on gut microbiota. Likewise, high molecular weight substances in CS, mainly acidic polysaccharides composed of uronic acid, exhibited a hyaluronidase-inhibiting effect. Hyaluronidase is a mucopolysaccharase related to inflammation by histamine released from mast cells. These results indicate that CS may also be beneficial in inflammatory conditions like allergies.[76]

CGA and coffee melanoidins may also play a role in reducing and controlling body weight, and may therefore be of interest in treating and reducing the risk of obesity.[77] An antioxidant drink based on CS for body fat reduction and weight control has been developed. Health benefits were evaluated *in vitro* and *in vivo* using the animal model *Caenorhabditis elegans*. The resulting beverage contained physiological active concentrations of caffeine and chlorogenic acid to prevent the accumulation of body fat and possessed adequate sensorial properties.[64]

Very recently, CS extracts have also been associated with liporegulatory and glucoregulatory effects. Hence, CS has a great potential for treating metabolic syndrome and diabetes as well as its risk factors. Results were obtained *in vitro* and *in vivo*. The antidiabetic and antiobesity effect of CS extracts may be partially ascribed to the inhibition of α-glucosidase and lipase. Further studies are being carried out to gain knowledge on the mechanism of action of the CS extract in the pathogenesis of these chronic diseases and to determine the contribution of their bioactive components to health-promoting effects.[78]

12.4.2.3 Spent Coffee Grounds

The most important components of spent coffee grounds are polysaccharides, whose thermal hydrolysis may produce mannooligosaccharides (MOS). Previous experiments indicate that MOS obtained from SCG present prebiotics, since they resist digestion, are fermented to short chain fatty acids *in vivo* and promote bifidobacteria growth. Short chain fatty acids inhibited the growth of pathogenic bacteria in the colon by lowering pH, and bifidobacteria are thought to promote intestinal health.[79] Other health effects of MOS were a decrease in blood pressure, elevating the suppressing effect[80] and reducing body fat (especially abdominal fat).[79]

Studies have also found that spent coffee grounds are a good source of hydrophilic antioxidant compounds with antigenotoxic properties. Thus, these by-products could possibly be used to help protecting against oxidative stress-related diseases, such as cancer.[59]

SCG can be a natural source of insoluble dietary antioxidant fiber.[61] This coffee by-product has nutritional characteristics, as insoluble dietary fiber material is indigestible by the enzymes of the gastrointestinal tract producing positive effects on health such as intestinal regulation, increase in the feeling of satiety and slimming. It also has a significant antioxidant capacity. The antioxidant properties of the dietary fiber of SCG have mainly been ascribed to the presence of phenolic compounds associated with coffee in their polymeric structure.

Furthermore, SCG exerts a positive effect on beneficial bacteria, increasing the numbers of lactobacillum and bifidobacteria. SCG could also be a good source of prebiotic compounds.[7]

12.4.3 Other Applications

Other feasible applications of coffee by-products are the production of biofuels, composts, animal feed and specific materials such as biosorbents, enzymes, chemicals and cosmetics among others (Figure 12.7) (Table 12.3).

[Table 12.3 near here]

Coffee pulp,[49, 51] coffee mucilage,[51, 81, 82] coffee parchment,[83] coffee husks [52, 84, 85] and SCG [86–93] have been successfully used in the production of biofuels. The conversion of biomass into biofuels can reduce the strategic vulnerability of petroleum-based transportation systems. Bioethanol has received considerable attention over the last few years as a fuel extender and even as a neat liquid fuel.[94]

More attempts have been made to use coffee by-products as substrates in bioprocesses. Recent studies have shown the feasibility of using coffee pulp and husk in the production of enzymes and secondary metabolites by employing different microorganisms such as *Aspergillus oryzae* and *Penicillium sp*. One approach produced enzymes such as tannase from both pulp[95] and husk.[96] Pectinase,[97] α-Amylase,[98] and xylanase[99] were obtained from coffee pulp and protease[100] and endoglucanase[101] from coffee husks. Moreover, Machado *et al.*[102, 103] used solid-state fermentation in coffee husk to produce gibberellic acid, a very potent hormone whose natural occurrence in plants controls their development. In addition, CS has also proved to be an excellent source of nutrients during fructooligosaccharides and β-fructofuranosidase production by *Aspergillus japonicus* under solid-state fermentation conditions. This process is a promising strategy to synthesize these two products at the industrial level.[104]

Recent studies on coffee by-products, specifically coffee pulp, coffee mucilage and CS, and their application in cosmetics have also been carried out.[41, 51, 105] Coffee pulp and mucilage have been described as raw materials for the production of coffee pulp flour and coffee honey, respectively, and may therefore be useful in cosmetics.[51] Del Castillo *et al*.[41] prepared an emulsion by mixing light olive oil in 90% water and 0.4 % powdered CS extract (granted patent). They obtained a solution which had a suitable pH for application to the skin (5.44), a phenolic compound content in the order of 5 times greater than that detected in the base emulsion (10.98 mg of Trolox/100 ml) and a high antioxidant capacity (117.42 mg of Trolox/100 ml of lotion). Rodrigues *et al.*[105] recently showed that CS is a safe source of natural antioxidants with antifungal and antibacterial activity and no cytotoxicity, thereby indicating another potential application in cosmetics.

Several authors have described the usefulness of coffee by-products as activated carbon and biosorbents. Irawaty & Hindarso[106] reported that pyrolysis of coffee pulp impregnated with phosphoric acid produced materials with high adsorption capacity. Coffee parchment proved to be an effective alternative material to remove acetic acid [107] and methylene blue dye in aqueous medium.[108] Moreover, this by-product was proposed as a medium filter to remove suspended solids from the wastewater of coffee shrub cherry pulping.[109] An alternative use of coffee husk is as untreated sorbent for the removal of heavy metal ions from aqueous solutions, as reported by Oliveira *et al.* [110] SGC is also an inexpensive and easily available adsorbent for the removal of cationic dyes in wastewater treatments[111, 112] and a source of activated carbon.[113, 114]

Regarding composting, coffee pulp solids are a good source of humus and organic carbon. Conversion of 350 thousand tons of coffee pulp would yield approximately 87 thousand tons of organic manure.[115] Moreover, coffee husks have proved to be very useful in vermicomposting. The high bacterial growth in earthworms' intestines improves soil fertility and stimulates plant growth making vermicasts good organic manure and potting media.[116, 117]

Animal feed has become an important target of studies on the application of coffee by-products. Coffee pulp [51, 118–120], coffee mucilage[51] and coffee husk[118] can be used for feeding farm animals. Mazzafera [118] correlated the presence of tannins and caffeine in coffee pulp and husk to their lack of palatability and acceptability by animals. These coffee by-products were decaffeinated by microorganisms to use them in animal feed, replacing traditional components such as cereal grains. The possibility of using spent coffee grounds as animal feed for ruminants, pigs, chickens, and rabbits has also been demonstrated by Claude [121] and Givens & Barber [122].

Coffee husk has been used as special environment-friendly material in the production of particle boards [31] due to its high cellulose and hemicellulose content, which is almost comparable to that of wood. Furthermore, coffee parchment and SCG have been used as fillers of polyurethane composites[123], and SCG has been proposed as an additive in the production of ceramic bricks, showing acceptable physical and mechanical performance and low thermal conductivity. [124]

From an agricultural point of view, the possibility of reutilizing spent coffee grounds as an easy and economically feasible soil amendment, represents an exciting opportunity to obtain products of high nutritional value.[125] For instance, low amounts of composted-SCG (up to 15% v/v) produced a relevant increase in essential macro-elements in lettuce, enhancing its quality features.

12.5 Safety Concerns of the Use Coffee By-Products as a Natural Source of Compounds

All foods might contain chemical and/or biological contaminants. Numerous processed foods such as French fries, chips, bread, cookies and coffee contain acrylamide, a chemical processing contaminant. The Maillard reaction has been shown to be the main pathway for acrylamide formation. This reaction takes place when precursors are present in raw materials, e.g. reducing sugars such as glucose and fructose, and asparagine, in combination with high temperature and cooking time.[126] Recent studies from García-Serna *et al.*[57] have shown that decreasing the quantity of sugar added to biscuits containing CS and stevia might be a good strategy for obtaining a safe, low sugar product. To date, no other studies have focused on the impact of CS addition on acrylamide content. The addition of CS improved the physical properties and the nutritional value of stevia biscuits, and no bioaccesible acrylamide was detected in the digests of these new innovative biscuits. This indicates that CS could be used as a natural coloring and source of dietary fiber to achieve a healthier, nutritious, and safe quality biscuit.[57]

With regard to the biological contaminants that could be present in coffee, ochratoxin A (OTA) is a mycotoxin produced by *Aspergillus ochraceus* and *Penicillium verrucosum* that tends to bioaccumulate along the food chain. OTA can induce renal toxicity, nephropathy, and immunosuppression, representing a risk for human safety. Therefore, its content in foods should be determined.[127] Coffee is contaminated with OTA when coffee fruits fall onto the soil or during storage. However, Ferraz *et al.*[127] demonstrated that OTA can be destroyed during roasting. Coffee is considered a secondary source of OTA in the human diet. Even when the coffee beverage is prepared from highly contaminated green beans, the coffee transforming process is able to reduce the amount of OTA that presents a risk for human health[37]. Research carried out by Toschi *et al*.[3] suggests that CS could be safe a source of bioactive compounds (such as fiber and polyphenols) which could be used as ingredients in the pharmaceutical/cosmetic industries or in the development of functional foods. However, as in other food ingredients, it is very important to establish rigorous quality controls and develop a suitable procedure to reduce OTA.

Heavy metals are widely dispersed in the environment and can be found in varying concentrations in human food. Food contamination is a serious problem, as heavy metals exert a harmful influence on many tissues. Metals disturb ionic balance and mineral regulation, induce oxidative damage to cell structures, produce injury to DNA and induce cancer transformations.[128] Nędzarek *et al.*[129] studied Mn, Co, Ni, Cr, and Ag levels in coffee. Such levels were shown to be too low to influence human health. However, some coffees had high levels of Pb, which might be harmful if accumulated in the body. This indicates that such products need to be controlled for metal contamination.

The management of by-products is a key step to ensure the safety of these products. Proper management of collecting coffee by-products, cooling/freezing the material, drying or thermal stabilization and/or addition of chemical preservatives can provide solutions in the case of coffee by-products.

12.6 Conclusions

Coffee is not only for drinking; you can also use it for many beneficial purposes by applying the biorefinery concept (Figure 8.7). Coffee waste biorefinery is possible.

[Figure 11.7 near here]

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12.7 References

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Table Captions

Table 12.1 Chemical composition and antioxidant capacity of coffee by-products (% w/w dry matter).

Table 12.2 Chemical composition and antioxidant capacity of coffee silverskin extracts (% w/w dry matter).

Table 12.3 Updated summary of proposed applications of different coffee by-products other than in food and health.

Figure Captions

Figure 12.1 Transversal section of a ripe coffee cherry, showing its anatomic parts. Courtesy of Joey Gleason, Marigold Coffee, Portland, Oregon, USA.

Figure 12.2 Ripped open coffee cherry, showing coffee pulp and mucilage. Courtesy of Andres Belalcazar, Pectcof B.V. Wageningen University, Netherlands (A). Coffee beans in parchment coated by mucilage. Courtesy of Sweet Maria's Coffee, Inc., West Oakland, California, USA (B).

Figure 12.3 Image of dried coffee fruits, skin and husks obtained from dry berries.

Figure 12.4 Image of parchment covered coffee beans, fragmented parchment and green coffee beans.

Figure 12.5 Coffee silverskin, the only by-product obtained during roasting.

Figure 12.6 Spent coffee grounds from the instant coffee brewing process.

Figure 12.7 Application of the biorefinery concept in the coffee industry.

Table 21.1

Components	*Pulp*	*Husks*	*Mucilage*	*Parchment*	*CS*	*SCG*
Proteins	10-12[11, 24]	5-11[23, 32]	3.4-8.9[16],	-	16–19[4, 34]	13-17[4, 7, 42]
Fats	2.5[11]	-	-	-	2.2–3.8[4, 34]	1.6-2.3[4, 7]
Carbohydrates	44-50[11, 24]	35-85[23, 32]	4.1-7.8[16],	-	62-65[34, 35]	71-75[7, 42]
Moisture	12.6[11]	-	84.2[18]	-	2.6-10.3[3, 35]	-
Ash	8[11]	3-10[23, 32]	0.7[18]	0.5-1[31]	5-7[4, 34]	1.3-1.5[4, 7, 42]
TDF	18-60[11, 33]	43[33]	-	-	68-80[3, 34]	54-60[4, 7]
SDF	18[33]	17-30.8[23],	0.91[18]	-	8-14[3, 34]	6-16[4, 7]
IDF	10[33]	26[33]	-	-	46-80[3, 34]	47-50[4, 7]
Glucan	-	-	-	-	17.8[36]	-
Xylan	-	-	8.9-11.2[16]	-	4.7[36]	-
Arabian	-	-	14.7-52.5[16]	-	2[36]	1.7[42]
Galactan	-	-	-	-	3.8[36]	13.8[42]
Mannan	-	-	0.8-1.4[16]	-	2.6[36]	21.2[42]
Cellulose	17.7[11]	19-43[31, 32]	8.9-9.1[16]	40-49[31]	23.8[4]	8.6[42]
Hemicellulose	2.3[11]	7-45[31, 32]	-	25-32[31]	16.7[4]	36.7[42]
Lignin	17.5[11]	9-30[31, 32]	-	33-35[31]	28.6-30.2[4, 36]	24[4]
Caffeine	1.3[11, 24]	-	-	-	0.8-1[3, 38]	0.2-0.8[44, 45]
Tanins	1.8-8.56[11]	5-9.3[23, 32]	-	-	-	-
Flavonoids	0.6[25]	20[12]	-	-	-	-
CQAs	1.2-2.5[11, 25, 33]	2.5[33]	-	-	0.6-3[33, 38]	0.3-1.4[7, 44, 45]
3-CQA	-	-	-	-	0.15[7, 38]	0.063-0.14[7],
4-CQA	-	-	-	-	0.08-0.10[7, 38]	0.097-0.25[7],
5-CQA	-	-	-	-	0.20-0.22[7, 38]	0.12-0.34[7, 45]
TPC	1-3.79[25, 33]	1.2[33]	-	-	0.7-1.7[3, 7, 38]	1-17[7, 44, 45]
ABTS	-	-	-	-	19.2-598[7, 34]	387[7]
FRAP	-	-	-	-	654[7]	387[7]
ORAC	-	-	-	-	-	1821-2594[44]
DPPH (%)	65-69[33]	50-65[33]	-	-	65-70[33]	61-89[33, 44]
Melanoidins	-	-	-	-	-	15[7]
Ochratoxin A	-	-	-	-	<4ppb[34]	-

Superscript numbers correspond to the cited literature

TDF: Total Dietary Fiber

SF: Soluble Dietary Fiber

ISF: Insoluble Dietary Fiber

TPC: Total Phenolic Compounds

ABTS, FRAP and ORAC units: µmol TEAC/g

Table 12.2

Compounds	*Water*[63], [64] *(100˚C, 10min)*		*SWE*[20] *(210˚C,1.5 MPa)*	*SWE*[41] *(200˚C,10.3MPa)*
	ACSE	*RCSE*		
Proteins	5.36	0.99	53.5	-
Carbohydrates	5.44	13.43	22.8	-
Caffeine	3.02	3.39	1.4	0.38
Melanoidins	17.26	23.94	-	-
TDF	28.69	36.21	-	-
SDF	24.01	26.80	-	-
IDF	4.67	9.41	-	-
CGAs	1.12	6.85	-	0.027
TPC	3.10[a]	3.54[a]	12.4[b]	0.46
ORAC	1194	1513	2321	109.9[c]
DPPH	219.9	231.3	323	-
ABTS	85.20	225.8	-	103.7[c]
FRAP	829.8	640.1	-	-

Superscript numbers correspond to the cited literature

ACSE: *Coffea arabica* L Silverskin Extract (Arabica Silverskin Extract)

RCSE: *Coffea canephora* Pierre var.robusta Silverskin Extract (Robusta Silverskin extract)

SWE: Subcritical Water Extraction

TDF: Total Dietary Fiber

SF: Soluble Dietary Fiber

ISF: Insoluble Dietary Fiber

TPC: Total Phenolic Compounds

[a] g CGA/100 g CS extract

[b]g GA/100 g CS extract

[c] µmol CGA/g CS extract

ORAC, DPPH, ABTS and FRAP units: µmol TEAC/g CS extract

Table 11.3

Coffee by-product	*Applications*	*References*
Pulp		
	Biofuel	Bonilla-Hermosa *et al.* [49], Ramirez *et al.* [51]
	Tannase	Bhoite *et al.* [95]
	α-amylase	Murthy *et al.* [98]
	Pectinase	Murthy and Madhava Naidu [97]
	Xylanase	Murthy and Madhava Naidu [99]
	Cosmetics	Ramirez *et al.* [51]
	Biosorbents	Irawaty *et al.* [106]
	Compost	Nogueira *et al.* [115]
	Animal feed	Ramirez *et al.* [51], Mazzafera [118], Nurfeta[119], Pedraza-Beltran *et al.*[120]
Mucilage		
	Biofuel	Ramirez *et al.* [51], Pérez-Sariñana *et al.* [81], [82]
	Cosmetics	Ramirez *et al.* [51]
	Livestock feed	Ramirez *et al.* [51]
	Thickening Agent	Avallone et al. [16]
Parchment		
	Bioenergy	Luana Elis de Ramos *et al.* [83]
	Biosorbent	Hernández *et al.*[107], Brum et al. [108], de Matos *et al.*[109]
	Composite materials	Funabashi *et al.*[123]
Husk		
	Biofuels	Gouvea *et al.* [32], Rathinavelu and Graziosi [52], Saenger *et al.* [84], Jayachandra et al. [85]
	Tannase	Battestin and Macedo [96]
	Protease	Murthy and Madhava Naidu [100]
	Endoglucanase	Navya *et al.* [101]
	Gibberellic acid	Machado *et al.* [102], [103]
	Biosorbents	Oliveira *et al.* [110]

	Compost	Sathianarayana & Khan[116], Adi and Noor [117]
	Particle board	Bekalo and Reinhardt [31]
Silverskin		
	Fructooligosaccharides and β-furctofuranosidase	Mussatto and Teixeira [104]
	Cosmetic ingredient	del Castillo *et al.* [41], Rodrigues *et al.* [105]
Spent coffee grounds		
	Biofuels	Silva *et al.* [86], Sendzikiene *et al.*[87], Machado [88], Sampaio [89], *Kondamudi et al.*[90], Rocha *et al.* [91], Couto *et al.* [92], Burton *et al.* [93]
	Biosorbents	Hirata *et al.* [111], Franca *et al.* [112], Nakamura *et al.* [113], Namane *et al.* [114]
	Animal feed	Claude [121], Givens and Barber [122]
	Ceramic manufacturing	Sena da Fonseca *et al.* [124]
	Composite materials	Funabashi *et al.* [123]

Superscript numbers correspond to the cited literature