INTERNATIONAL JOURNAL OF FOOD TECHNOLOGY AND NUTRITION VOL. 2, NO. 3-4, 2019

UDC: 630*81-027.235:663/664
Review

TREE BARKS AS POTENTIAL SOURCES OF VALUE-ADDED COMPONENTS FOR THE FOOD INDUSTRY

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Abstract

Tree bark is composed of all the tissues external to and surrounding the vascular cambium of the tree and comprises about 13–21% on a dry weight basis. It is liberated as a waste product for the production of forestry industry after debarking process of wood. It is mainly utilized as heat source by direct combustion. However, it's caloric value is much lower than foil. Tree barks are rich sources of several sustainable compounds such as lipophilic and hydrophilic extractives as well as cellulose. lignin and hemicellulose. Although valorizations of bark including production of chemicals and materials, wooden panels, tannin, resins and foams, bio-oils. Research has shown that barks contain valuable compounds such as tannins and cellulose nanowhiskers which can be used in food industry applications at comparable levels with well-established food industry byproducts. Tannins are an integral part of diets and have positive implications for human health. which indicates that bark tannins can be included in food formulations. Cellulose is a common raw material for food packaging while cellulose nanowhiskers can be used as reinforcement agents of biodegradable/nonbiodegradable packaging materials. Therefore. potential valorization fields of tree barks to be utilized in food industry were reviewed in this study.

Keywords: Tree bark, food industry, tannin, cellulose.

1. Introduction

Trees, wood as a raw material to the present day, shelter, since it is used as hand tools and supplies is of great importance (Balaban. 1997). The advancement of technology has led to the development of wood-based industry branches. Taking different shapes of tree material. furniture. their use in the board and timber industry has increased. In the pulp and paper industry, the wood raw material is an indispensable source.

The bark is the second important part of the tree after wood. Depending on the tree species and growing conditions, the amount of bark varies between 10-20%. The crust has been considered as a waste product that has been distressing for a long time and is not used as fuel. Only the bark of some trees (egmegat) was evaluated for tannins. In recent years, bark has become the centre of attention. Structure of the shell. Many studies have been carried out on the evaluation of my wrist (Fengel and Wegener. 1989).

Bark and other wood waste are low-value by-products in the forest industry. They are present in large quantities and are mainly used as fuel. Besides that, bark is a rich source of secondary metabolites and contains several potentially biologically and commercially interesting compounds (Balas and Popa, 2007).

Conventional extraction techniques such as boiling or refluxing used for solvent extraction from natural products longer extraction times and lower yields it needs to be developed due to the use of large amounts of organic solvents and low extraction efficiency (Shirsath and Sonovane, 2012). New techniques for extraction of bioactive compounds from plants in recent years. Ultrasound-assisted extraction (UAE), supercritical liquid extraction (SFE), microwave-assisted extraction (MAE) and accelerated solvent extraction (ASE) (Khoddami, 2013).

2. Other Uses of Tree Bark

2.1. Obtaining tannin from tree bark

Tannins are found in both deciduous trees and coniferous trees. Acacia as an example of trees containing tannin. oak. birch. willow and pine (Obst. 1998). Table 1 shows the amount of water-soluble condensed tannins of various bark (Fengel and Wegener, 1989).

The oil crisis in 1970. phenol triggered the use of natural polyphenols, such as tannin, in place of synthetic phenol in formaldehyde glue (Pizzi, 1983). Tannin obtained from Pinus radiata shells in Şile. is used in the chipboard industry (Roffael and Schäffer, 1998). In addition, two factories in Germany produce chipboard and MDF (Roffael, et al., 2002); In South Africa and Australia, it uses tannformaldehyde glue in the forest products industry, especially in the particleboard industry (Kharazipour, 1996).

In addition to MDF and particle board, tannin formaldehyde glue was used in the construction of plywoods and was left in open air conditions. As a result of the tests, it was determined that the plywood produced was in compliance with European norms (Vázquez, et al., 2002).

Table 1. Yield of water-soluble condensed tannins from bark of various tress

Type	Tannin %
Betula alba	10-15
Castenea sativa	8-14
Eucalyptus adstringens	44-54
Eucalyptus wandoo	13-15
Larix decidua	5-20
Larix leptolepis	10-25
Picea abies	5-18
Picea sitchensis	11-37
Pinus densiflora	6
Pinus nigra var. calabrica	13-25
Pinus ponderosa	5-11
Pinus radiata	17-18
Pinus sylvestris	16
Pseudotsuga menziesii	5-25
Quercus robur	12-16
Robinia pseudoacacia	7
Sequoia sempervirens	2-8
Tsuga canadensis	10-11
Tsuga heterophylla	15-16

Due to its acidic and astringent effect, tannins have been widely used in traditional medicine. When tannins are mixed with iron salt, it gives a black color and is therefore used in making ink. In the food industry fruit ripening and many drinks (cocoa, tea and red wine) are added as additives. (Ciesla, 2002).

2.2 Use of Bark in Pharmacology and Medicine

Since ancient times, bark has been considered in the field of pharmacology and medicine. Some tree bark used for this purpose and the purpose of use is as follows:

Willow (Salix spp.) Shells have been used as painkillers and antipyretics for 2000 years. The active ingredient in willow bark is salicin which is a glucoside. Salisin when taken into the body is converted to salicylic acid. The active ingredient of aspirin, which is widely used in salicylic acid, is a component of acetylsalicylic acid. Aspirins used today are derived from synthetic substances. (Ciesla, 2002).

Betulin found in birch bark (15% compared to bark) is used for melanoma tumors (Ciesla, 2002). Inner bark of Ulmusrubra tree is evaluated in medicine in order to eliminate thirst, sore throat and inflammation in the digestive system. (Ciesla, 2002). Quinidine obtained from Cinchona ledgeriana shells. It is used as a sedative or rhythm regulator in heart patients. Quinine obtained from the bark of the same tree. before the discovery of the malaria parasite, it was applied in the treatment of malaria (Kadir, 1998).

Taxus brevifolia Nutt. taxol obtained from the bark has been accepted to be effective against cancer in the world (Kadir, 1998).

2.3 The use of bark against fungus and insects

3-O-Acetyloleanolic acid in Betula nigra shells is used in agricultural control (against colorado potato beetle and Leptinotarsodecemlinoata) (Sakai, 2001).

Harun and Labosky (1985a) in a study of some tree bark (Pinus resinosa. P. Strobus. Carya ovata Mill. Quercus rubra and Acer rubrum) acetone: hexane: water extraction termite (*Reculitermesflavipes*) and brown rot fungus (*Lenzitestrabea*). Accordingly, the best results in termite experiments were Carya ovata and Quercus rubra shell extraction followed by P. strobus extract. In mushroom experiments Carya ovata. Quercus rubra and P. strobus extracts were found to have a significant success in terms of biological resistance.

2.4 Use of Bark for Energy Purposes

One of the uses of the crust in the world is to consider it as fuel. The calorific values of some dry bark in kcal / kg are as follows: Scots pine 4775. spruce 4760. fir 5265. alder 4687. beech 4244. oak 4156. willow 4268. plane tree 4237. aspen 4958 and hybrid poplar 4636 (Bozkurt and Göker, 1981).

3. Potential sources of value-added components from tree bark for food industry

3.1 Chemical Composition of Bark

3.1.1 Lignocellulosic Components

Lignocellulosic biomass formed by bark it consists essentially of 3 polymers: cellulose lignin and hemicellulose. In addition to these polymers, lower amounts of extractives resins, tannins, waxes and inorganic substances (ash). The cellulose network structure formed by cellulose microfibrils and other polymers is given in Figure 1(Alonso, et al., 2012). These polymers depending on the type of lignocellulosic biomass. they are in the form of non-uniform three-dimensional structures of varying degrees and varying relative composition.

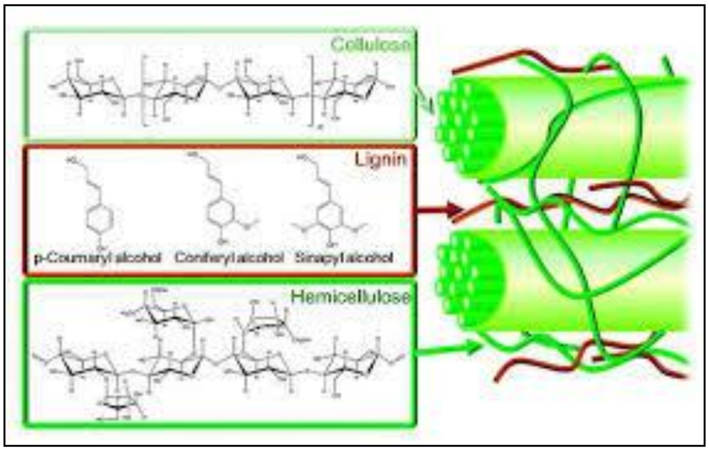

Figure 1. Morphological structure of lignocellulosic biomass formed by cellulose lignin and hemicellulose (Alonso, 2012).

The most abundant component in the lignocellulosic material is cellulose formed by the combination of repeating D-glucose units with β-1.4 glycosidic bonds. H bonds between intracellular and intermolecular glucose units in cellulose, it is tightly linked to glucose (ZHOU et al. 2011). The most abundant polymer after cellulose is hemicellulose in lignocellulosic biomass. Unlike cellulose which is substantially crystalline, hemicelluloses are amorphous. Hemylcelluloses contain 5 (xylose, arabinose) and 6 carbon monosaccharides (mannose, glucose, galactose) and acetylated sugars (Agbor, et al., 2011). Lignin is a 3-dimensional polymer consisting of phenylpropanoid (p-kumaryl alcohol, coniferyl alcohol and sinapyl alcohol) units. Lignin it has a high branching amorphous structure and serves as a cement that holds cellulose microfibrils together (Isikgor and Becer. 2015). The ratios of the lignocelluloses belonging to the bark parts of different tree species are given in Table 1. Table 1. lignin is the most abundant component in tree bark, followed by cellulose. This is usually cellulose and lignin, respectively.

Table 2. Amount of lignocellulosic biomass in various bark and food wastes (%).

Material	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Reference
Yellow Pine	25.4	14.7	44.9	Valentin, et al. 2010
Sweetgum Bark	26.3	29.6	42.0	Istek and Hafızoglu. 2005
Elaeagnus Bark	26.1	28.3	44.2	Akgul and Akça, 2014
Poplar Bark	31.33	25.32	36.04	Akgul, et al. 2013
Carrot pulp	10.01-12.65	-	-	Nawirska and Uklanska, 2008
Apple pulp	3.64-16.10	-	-	Nawirska and Uklanska, 2008

As shown in Table 2 cellulose ratios of tree bark. It contains a higher amount of cellulose compared to fruit pulp which is produced as waste in food industry and especially the fruit juice industry. The cellulose content of the bark and fruit pulp may also vary according to the species. In addition, according to the studies in the literature, it is seen that cellulose amounts of pulp may vary even if they are the same species. The reason for this, variation of plant growing conditions varieties and extraction conditions.

3.2. Extractive

In the composition of trees and bark, there are lignocellulosic substances present at the macromolecular level, as well as extractives soluble in water and other neutral solvents. In the amount of these components there are differences according to the type of tree. These components. although it accounts for only a few percent of the mass of wood, its proportion in the bark is much higher. Especially as the age of the tree grows, the amount of extractive increases (Parham, 1983; Hafizoglu, 1983; Kirci, 2000). Extractives they may be classified as hydrophilic or lipophilic according to the polarity of the solvent. Table 2 lists tree extracts that are soluble in different solvents.

Table 3. Classification of wood extractives and solvents

Lipophilic Extractives	Hydrophilic Extractives
Oils waxes resins Free fatty acids Resin acids Terpenes and terpenoids Fatty alcohols Hydrocarbons	Tannins Dyestuffs flavonoids stilbenes Other phenolic substances carbohydrates Water-soluble polysaccharides alkaloids Inorganic salts

Table 3 shows the amount of extractives in the bark of various tree species.

Table 4. Extractive levels of wood and bark

Type of Tree	Wood	Bark	References
	Extractive (% dry matter)		
Yellow pine	5.0	25.2	Peltonen, 1981; Saarela, et al., 2005; Valentin, et al. 2010
Spruce	2.0	32.1	Bertaudand Holmbom, 2004; Willfor, et al., 2005
Birch	3.8	25.6	Willfor, et al., 2005; Pinto, et al., 2009
Cedar	15.89	23.76	USTA and KARA. 1997
Sweetgum	12.8	istek	Istek and Hafızoğlu. 2005

As shown in Table 4, there are much higher levels of extractives in bark than wood. The level of extractives in the tree bark given in the table varies between 15.9% and 32.1% in dry matter. The main component of bark extracts is the tannins in hydrophilic extracts (FENG et al., 2013). Tannins are a group of water-soluble phenolic metabolites commonly found in plant origin foods that are of relatively high molecular weight and capable of making complex complexes with carbohydrates and proteins (Chavan, et al., 2001).

Tannins; gallotanene, ellajitanene, condensed tannin and complex tannin. Of these, gallotanene and ellajitanen are called hydrolysable tannins because they are hydrolyzed to gallic acid and ellagic acid respectively (FENG et al., 2013). Tannin yield of crust; tree type, age, storage period after cutting the tree and is affected by factors such as extraction method (Kelsey, 1989; Vazquez et al., 2001). Generally, more tannins are present in the bark of old trees.

The solutions used in tannin extraction and extraction temperature affect the tannin yield and total phenolic content of the extractant (Makino, et al., 2009). The small particle size of the shell material is also one of the parameters that increases the extraction efficiency.

3.2.1. Tannins

The main group of antioxidant polyphenols found in food and beverages, vegetable-derived tannins have attracted great attention in recent years with the determination of their multifunctional properties on human health. It is abundant in bark, wood, fruit, bark, leaves and roots, as well as in plant tumors. Tannins are defined as yüksek high molecular weight phenolic substances containing enough hydroxyl groups and other suitable chemical groups (such as carboxyl) to form complexes with proteins and other macromolecules under specific conditions (Horvath, 1981). Tannins are divided into 2 broad groups: hydrolyzable tannins and condensed tannins (Proanthocyanidins). At the center of the hydrolyzable tannins is a polyol (D-glucose) and the hydroxyl groups of these carbohydrates are partially or completely esterified with phenolic groups such as gallic acid or ellagic acid (Kumari and Jain, 2012). Weak acids are hydrolyzed by bases, enzymes such as hot water and tannase, and decompose into carbohydrates and phenolic acids as a result of their hydrolysis. The most important sources of hydrolysable tannins are strawberry, pomegranate, raspberry, clove, oat barley, rice, etc. d. Condensed tannins are polyphenolic flavonoids commonly found in trees and shrubs. In addition, tea, coffee, grapes, blueberries, strawberries, apples and cranberries are often consumed by people such as products.

This type of tannin group; Polymer or oligomers of polyhydroxy flavan-3-ol units such as (+) - catechin, (-) - epicatechin. Their core is free of carbohydrates and contains hydrolysis-resistant C-C bonds. Their solubility in aqueous organic solvents depends on their degree of polymerization and chemical structure (Aydin and Ustun, 2007).

The identification of tannins as antibacterial elements has been linked to the inhibition of the digestion of proteins by binding to proteins or digestive enzymes (Mehanso, et al., 1987, Frazier, et al., 2010). In addition to these antibacterial properties, tannins have been shown to possess a range of biological and pharmaceutical activities both in humans and in veterinary medicine. These features include antioxidant, antimicrobial, antiviral, anti-inflammatory, anticancer and antitumor properties (Haslam, et al., 1989, Higdon and Frei, 2003; Okuda, 2005; Nagle, et al., 2006). On the other hand, it has been reported in later studies that tannins lower blood glucose levels and can be used as potential drugs for the treatment of diabetes (Liu, et al., 2001; Muthusamy, et al., 2008).

These properties of tannins, inhibiting or delaying the absorption of glucose by the digestive organs by inhibiting enzymes such as α-amylase and α-glucosidase, which hydrolyze oligosaccharides, polysaccharides or complex carbohydrates, induce β-cells, and induce differentiated effects on adipose cells such as adipose cells. and Jain, 2012). While the majority of the active ingredients of black tea, which are consumed extensively in our country, are tannins, 90% of tannins constitute catechins. In addition, the major component of tannins naturally found in the structure of grapes is epicatechin. Among the hydrolysable tannins, it was found that gallic and elagic acid showed antidiabetic properties by showing insulin-like effect (Waltner-Law, et al., 2002; Kim et al., 2003).

Tree bark contains up to 13% extractives in the total composition, while tannins constitute the majority of the extractives (FENG et al., 2013). Tannins with known medicinal properties are mostly isolated from edible food sources such as cereals and fruits, but tannins from various bark are commercially available and are used for purposes such as adhesives and foaming agents. On the other hand, various studies have been conducted to determine in vitro and in vivo antidiabetic properties of tannins isolated from various bark (Ragavan and Krishnakumari, 2006; Shirwaikar et al., 2006; Gayathri and Kannabiran, 2008; Parthasarathy et al., 2009; Panda et al., 2010; Abdallah et al., 2011).

3.2.2. Cellulose and Cellulose Nanocrystals

Cellulose, hemicelluloses and lignin, which are lignocellulosic substances, are the main components of wood and bark. Of these, cellulose; It is a low cost, non-toxic and biodegradable biopolymer and also exhibits interesting functional properties due to its molecular structure (Peng, et al., 2011; Santana-Meridas, et al., 2012). The physical, chemical and biological properties of natural cellulose have enabled it to be used in paper, food, pharmaceutical and cosmetic fields. In recent years, micro- and nano-scale structures of cellulose have attracted attention due to their mechanical, chemical, optical and rheological properties (Peng, et al., 2011).

"Nano-cellulose-type" refers to cellulosic materials in the nano range generally refers to at least one dimension. Cellulose nanocrystals (CNC) are rod-shaped particles obtained by processing cellulose micro fibrils, having a width of 5-70 nm and a length between 100 nm and several microns. SNKs consist of 100% cellulose and show high crystallinity (between 54-88%) (Moon, et al., 2011). Due to the limited crystalline regions, cellulose exhibits much lower flexibility than microfibrils (Brinchi, et al., 2013). Large variations in size, morphology and crystallinity are related to the source of the cellulosic material and the conditions under which it is obtained (HABIBI et al., 2010). Table 4 shows the differences between cellulose microfibrils and CNCs.

Table 5. Size differences between cellulose microfibrils and nanocrystals (Klemm, et al., 2011).

Cellulose type	Average Diameter	Length
Cellulose microfibrils	5-60 nm	Several microns
Cellulose nanocrystals	5-70 nm	100-250 nm (vegetable origin); 100 nm-several microns (algae, bacterial origin)

Nanoscale cellulose (cellulose nanocrystalline - CNC); high specific force and modulus, high surface area and unique optical properties have been found to have advantages such as (Peng, et al., 2011). In addition, studies have shown that CNC does not have any toxicity (Brincghi, et al., 2013). Like natural cellulose, CNC also has modifiable surface properties due to reactive -OH groups on its surface. The biodegradability of CNC with various nanoparticles was compared according to OECD standards and was found to biodegrade faster than commonly used nanoparticles such as fullerenes and carbon nanotubes and cellulose of the macro scale (Kummerer, et al., 2011).

CNC can be obtained from cellulosic sources such as plants, animals (shirted), bacteria and algae, and in principle from all cellulose-containing materials. However, wood is the cheapest and most common source of cellulose due to its high cellulose content and its ubiquity in nature (Brinchi, et al., 2013).

Table 6. Polymers in which cellulose nanocrystals are added as fillers.

Polymer matrix	References
Polylactic acid	Oksman et al. 2006; Pandey et al. 2012; Fortunati et al. 2012; Sullivan et al. 2015
Starch	Cao et al. 2008; Savadekar and Mhaske, 2012; Da Silva et al. 2012; Slavutsky and Bertuzzi, 2014
xylan	Saxena et al. 2009; Saxena et al. 2010
chitosan	Khan et al. 2012; De Mesquita et al. 2010; De Mesquita et al. 2012; Pereda et al. 2014a
Soy protein	Gonzales and İgarzabal, 2015; ZHANG et al. 2016
Polyvinyl alcohol	El-Miri Vd., 2015
polythene	De Menezes, 2009; Sapkota et al. 2014; Sapkota et al. 2017
Polyurethane	Wang et al. 2010

Conclusion

Food industry processes result in significant amounts and types of waste. These wastes, if not evaluated in any way, are released to the environment and cause great environmental pollution. Examples of such waste include fruit pulp, cold press oil wastes, whey after fruit juice production. These wastes also contain highly valuable and nutritionally important components such as pectin, antioxidants, phenolics, dietary fibres. When the literature is examined, it is seen that there are many studies on these wastes and there are applications in the food industry to evaluate these wastes.

When the forest industry is considered, many of the trees considered as wood are cut from the trunk of the wood or cut to a great extent as waste, or used as fuel or as raw material in relatively different branches of industry (biofuel production, tanning etc.). Looking at the bark composition, it has been found that it contains valuable ingredients which can be of great importance in food science and technology. When compared with fruit/vegetable pulps considered as food waste, it was thought that tree bark contains higher levels of cellulose and tannin and can be used as a different industrial branch waste which may be used for the food industry.

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