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Potential applications of pecan residual biomasses: a review

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ABSTRACT

Considering a large amount of high potential materials coming from the processes to obtaining pecan nut, there are important future perspectives to enable an increase of using pecan materials. For this, structural support and the development of scientific research are needed to reuse the wastes in an environmentally friendly way. Thus, the aim of this scientific research is to present a detailed literature overview regarding the characterization of pecan waste materials, the main applications and technologies used to add value to these materials. The study is fundamentally based on the scientific literature related to obtaining products from pecan wastes and their application in food-related areas. The lack of sufficient data on the proposed theme requires a properly structured approach to provide a clear perspective on the subject and to highlight the current limitations. It is evident that pecan culture has presented a prosperous context with respect to the world and Brazilian production. The scientific literature presented many studies that employ the approach of using remaining pecan materials. Thus, it is clear the range of fields that apply the residuals for the most diverse purposes, which enables them to add value to pecan coproducts.

Keywords: *Carya illinoinensis (Wangenh.) K. Koch; Lignocellulosic materials; Pecan coproducts; Sustainability. Vegetable wastes.*

1. INTRODUCTION

Considered the diversity of nut-producing species, the pecan [*Carya illinoinensis* (Wangenh.) K. Koch] is characterized as one of the largest nut producers. The International Nut and Dried Fruit Council Foundation (INC) identified that, by 2019, the total production was over 140,000 tons worldwide [1]. These results have shown marked growth in pecan cultivation, considering that in 2008/09 harvest the production was just over 60,000 tons. As a trend observed for years, Mexico and the U.S. dominate pecan nut production, accounting for, approximately, 130,000 tons, which correspond to about 90% of global production. These countries are important exporters of pecan nuts, meeting the demand for this product in various regions, such as Europe, China and South Korea.

The increased production of pecan nuts generates a large amount of waste as a consequence of harvesting and industrial processing. Considering only pecan shells, it is estimated that approximately 420,000 tons are produced worldwide every year [2]. Also, up to 50% of the total weight of a pecan nut is accounted to the shell and up to 80% is accounted to shell and husk [3,4].

It is important to assign high attention to the reuse of pecan wastes biomasses, thus exploring the potential of these materials for resulting in higher added value to their coproducts. These materials contain high concentrations of cellulose, hemicelluloses and lignin [5]. Also, a range of applications of pecan coproducts is known, especially in the extraction of compounds of interest for use in different fields of application, such as the biofuel production, pharmaceutical and food industries. Thus, considering the importance of the pecan nut residue and the materials generated from the processes of obtaining pecan nut, the aim of this scientific research is to present a detailed literature overview regarding the characterization of pecan waste materials, the main applications and technologies used to add value to these materials.

2. SCOPE

This review analyzes the existing literature about the importance of the pecan nut in the current panorama. Thus, it is reported the technologies used to process the remaining materials of this species. The main purpose is to expand and to encourage the development of numerous studies on the subject, defining the scenario for this study and helping to identify the most relevant and appropriate points for this research. The work is fundamentally based on the literature related to obtaining materials from pecan wastes and the applicability of these components.

The literature related to waste vegetable materials presents a wide field of study. However, this approach is still scarce considering the pecan culture, which shows the need for more studies about this subject. Therefore, the lack of academic studies on the subject highlights the need to develop properly structured works in order to provide information about the current panorama related to the subject and highlight its main constraints.

Briefly, Section 3 reports the current landscape of pecan culture, focusing on the socio-economic performance of culture at national and international levels. This section provides a historical and economic overview of the culture, providing an economic analysis in Brazil and around the world.

Section 4 explores what the scientific literature addresses the characterization of pecan waste materials. The section begins with studies related to observations pertaining to the husks. Consequently, it describes information about the leaves and stalks.

In conclusion, the section discusses the characteristics of pecan shells.

Section 5 examines the current works that employ the approach of using remaining pecan materials. The objective is to understand the range of fields that apply the residuals for the most diverse purposes, which enables them to add value to the coproducts generated from pecan biomasses.

Likewise, Section 6 provides information on the key-technologies employed for processing nuts within the main context of this study, namely obtaining pecan hydrolyzed materials.

Finally, Section 7 provides an overview of the various applications of pecan biomass and a discussion of its importance. It also presents a brief report on the fragmented literature on the topic and the main future expectations for the research.

3. PECAN FEATURES AND CURRENT PECAN PRODUCTION SCENARIO

Pecan [*Carya illinoinensis* (Wangenh.) K. Koch] is a species belonging to the genus *Carya* of the Juglandaceae family. It is noteworthy that the Juglandaceae family presents several other nut-producing species, standing out the pecan as an important supplier of nuts. The structure of the fruits produced is composed of the pecan, husks, shells and, finally, leaves and stalks, which constitute the residual plant materials (Figure 1).

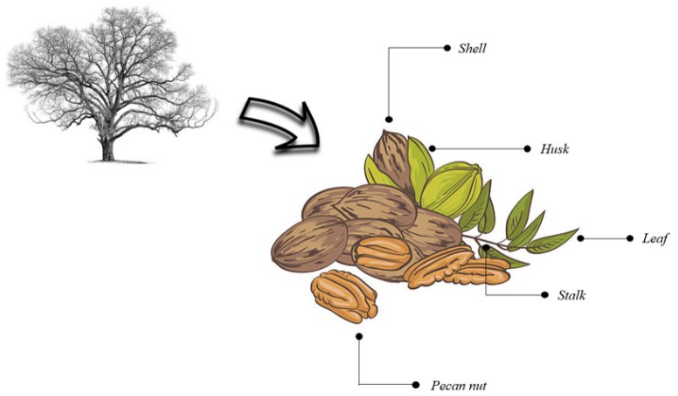

Figure 1. Structural components of pecan trees.

The production status of pecan trees has shown promising results in recent years. According to INC, in 2019 total production exceeded 140,000 tons worldwide [1]. In 2007, this value was close to 60,000 tons. Therefore, it is noteworthy that crop production grows at a rate of approximately 30% annually [1].

The species *Carya illinoinensis* is originated from the Milder Southern U.S. [6]. Mexico (52%) and the U.S. (40%) account for over 90% of pecan nut production. In 2019, these two countries produced approximately 72,000 and 56,000 tons, respectively. In addition, South Africa (7%, 10000 tons) and Australia (1%, 1000 tons), rank as other important leading producers of pecan nuts in the world. However, considering the easy adaptability of the species, its current geographical location covers a significant area around the planet [7,8]. Recently, pecan cultivation presents a globalized panorama, not limited only to the region of origin, but is found in several regions. Countries such as China, Argentina, Uruguay, Peru, Chile and Brazil are also pecan nut producers [9]. Figure 2 presents the current pecan nut production scenario worldwide.

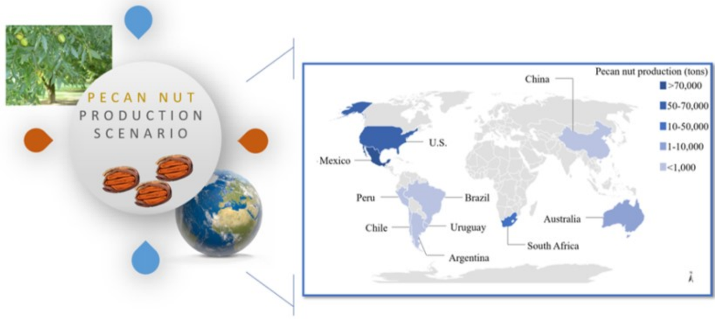

Figure 2. Current pecan nut production worldwide and Brazilian scenarios.

4. RESIDUAL BIOMASSES CHARACTERIZATION

Pecan processing has as its main purpose to obtain the pecan nut. However, coproducts, or plant biomasses, are generated in the midst of this process, such as husks, leaves, stalks and shells. It is estimated that more than 420,000 tons of pecan shells are produced annually worldwide [2].

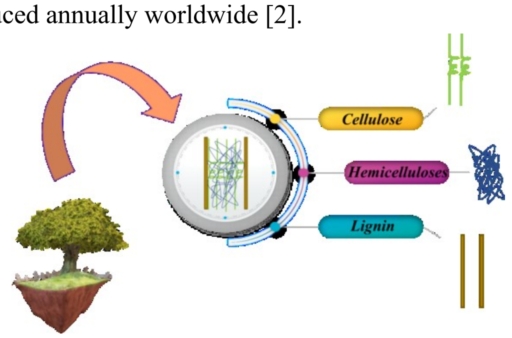

Figure 3. Main constituents of lignocellulosic raw material.

Thus, an analysis of the composition of these materials becomes pertinent when it is intended to verify their potentialities, aiming at adding value and applicability in various fields of study. Also, a perception of the physicochemical properties of pecan lignocellulosic biomasses is essential for the processing of conversion of biomasses to desired products. As presented earlier, these materials are rich in cellulose, hemicelluloses, and lignin (Figure 3). However, there are other compounds of great interest especially using as renewable energy and for the production of bioproducts. Generally, lignocellulosic materials have a mass composition of 35 to 55% cellulose, 20 to 40% hemicelluloses and 10 to 25% lignin, and other elements such as extracts and minerals [10].

Cellulose is an important polymer in the world, being glucose ($C_6H_{12}O_6$) consisting of chains of 1,4-D-glucopyranose units linked in the β1,4 configuration. It is emphasized that the crystalline portion of the cellulose is insoluble and forms the skeletal structure of the cell. On the other hand, hemicelluloses is shorter and complex polysaccharides, containing several chains that are also located with cellulose in the cell wall. Shorter chains of xylose, arabinose, galactose and monosaccharides are attached to the hemicelluloses chains, creating a branched polymer. In contrast to cellulose, hemicelluloses are heterogeneously branched polysaccharides that bind non-covalently to the cellulose surface.

Finally, lignin is characterized as the largest structure of the cell wall. Lignin is composed of three carbon chains attached to six-carbon rings. It is this component that acts on the rigidity of plant cell structure [11].

In general, studies present that lignin and cellulose are abundant constituents in pecan waste materials. The Figure 4 shows some studies that have reported the composition of different parts of the plant, such as shells, husks and branches, with the proportions of the lignocellulosic complex found in the pecan shells (a) [12-15], branches (b) [16] and husks (c) [17].

Also, important bio compounds have been obtained from the exploration of chemical compounds from pecan raw materials. In general, data about these compounds is fragmented and restricted to nuts to a greater extent. However, some studies have been found, where Table 1 presents the parameterization of these components and related studies.

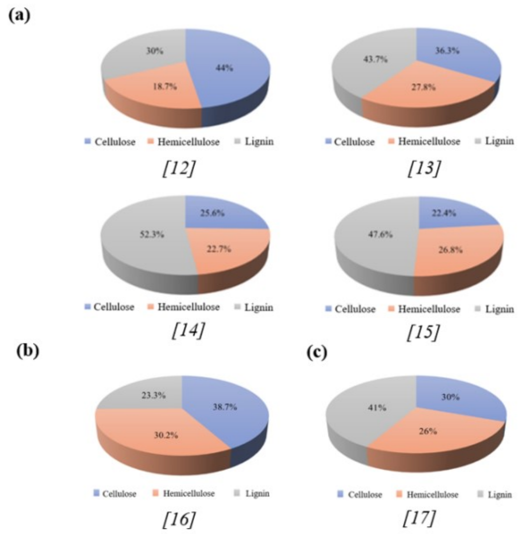

Figure 4. Lignocellulosic composition of pecan shells (a), branches (b) and husks (c).

Table 1. Characterization and applicability of pecan biomasses compounds.

Coproduct	Observed compounds	Objectives	Reference
Shells	Phenolic compounds (acids, catechin, epicatechin, and others)	Chemical composition study for health application	[18]
	Lipids, proteins, fibers, carbohydrates and tannins	Modeling and kinetic and adsorption studies	[19]
	Phenolic compounds (catechin, and others), tannins and antioxidant extracts	Nutraceutical and food application	[20]
	Phenolic extracts and antioxidants	Antioxidant action for biofuel production	[21]
Leaves	Flavonoids (rutin, kaempferol, and others) and phenolic compounds (acids)	Potential of chemical composition for health application	[22]
	Nutrients (manganese, nitrogen, boron and others)	Nutritional characterization for application in various fields	[23]
Husks	Lipids, proteins, fibers, carbohydrates and tannins	Modeling and kinetic studies	[19]
	Flavonoids, phenols, acids and others	Chemical characterization and antioxidant, antimicrobial and antiproliferative action	[24]

5. RECENT APPROACH AND APLICABILITY OF PECAN RESIDUAL BIOMASSES

This section presents a brief review of studies involving the applicability of pecan wastes for various purposes. It is noted that the current studies about this subject are lacking. However, some studies related to the exploration of the potential of pecan biomass have been reported in the academic field, such as its application in the field of medicine due to its many advantageous properties in disease prevention. The purpose of this section is to enable the use of pecan wastes as materials of wide interest in various fields of study, such as disease prevention and extracts production.

5.1. Disease prevention.

A range of important phenolic compounds is present in plant species. These components are of great nutritional and medicinal concern due to their potent antioxidant capacity. The potential of pecan waste materials in the medical field has recently gained recognition. The use of pecan shells, specifically, has been reported as an efficient alternative in the treatment of various diseases [25].

The shells have a high antioxidant potential due to the high amount of phenolic compounds and fatty acids, which makes pecan as a species of great importance for pharmacological activities [26]. It is estimated that the concentration of these elements can reach 167 mg/ g gallic acid [4]. In this context, studies have shown that aqueous extracts of pecan shells (rich in acids such as gallic, 4-hydroxybenzoic, vanillic, chlorogenic, caelic and ellagic) have the ability to induce breast cancer cell death and increase breast cancer survival time of patients with certain tumors [18, 27]. Also, shell in fresh condition has been used in nutraceutical products against obesity, hypercholesterolemia and as a source for the precaution of metabolic and inflammatory diseases, neurological disorders, gastric ulcers, and cancer [28]. These residues act as antinociceptive and antiedematogenic materials due to the high concentration of rutin, or vitamin P, in its composition [29]. Also, pecan leaves have been reported as antifungal materials, applied as important inhibitors of tuberculosis-causing bacteria activity [26]. Husks have been shown to be special components in antioxidant, anti-proliferative (against lung, colon and cancer diseases) and antimicrobial activities due to the concentration of phenols and flavonoids in their composition [24].

5.2. Antimicrobial and antifungal potential.

Numerous compounds obtained from plants or plant waste biomasses have a high potential to inhibit microbial and fungal activities. The current studies have shown pecan residues as materials with great potential as new sources of fungicides for the control of pathogenic fungi, as well as the application for bacterial inhibition. Due to a significant accumulation of acids and other phenolic compounds of antioxidant function, it was found that pecan shells act as inhibitors of gram-positive bacterial activities, such as *Listeria monocytogenes*, *Staphylococcus aureus*, *Bacillus cereus* and *Vibrio parahaemolyticus* [30]. Also, antimicrobial activity has been investigated against *Staphylococcus aureus*, *Bacillus cereus*, *Listeria monocytogenes*, *Listeria inoccua*, *Salmonella Enteritidis*, *Aeromonas hydrophila* and *Pseudomonas aeruginosa* [31]. Shells have also been reported to have antifungal action, mainly due to the presence of polyphenols, inhibiting the growth of *Pythium* sp., *Colletotrichum truncatum*, *Colletotrichum* sp., *Alternaria alternata*, *Fusarium solticillio*, *Fusarium sambucinum* and *Rhizoctoniasolani*, which are the major causes of diseases in important crops of agricultural interest [32]. In addition, it has been reported that pecan leaves have antimicrobial and antifungal performance, essentially due to the high concentrations of flavonoids, phenolic compounds (gallic acid, catechin, rutin, among others) and tannins in the action against various bacteria and fungi [33].

5.3. Adsorption materials.

Activated carbon adsorption is an important and efficient technique for removing contaminants from waste residues treatments. Although many materials are explored for the production of activated carbon, raw materials are widely used due to their wide availability in the environment and reduced costs, making them attractive options and sources of raw materials for activated carbon production [34].

The potential regarding the use of pecan shells as adsorbent material is significant and more efficient compared to other conventional materials, considering characteristics such as surface area (902 m^2/g), density (0.5 g/m^3), friction capacity (12.8%) and conductivity (331 μS) [35]. Another study was developed based on the adsorptive capacity for Cu^{2+}, Pb^{2+} and Zn^{2+} ions, where the shells showed excellent results in the adsorption of these elements [36].

Furthermore, the activated charcoal of pecan shells treated with sodium dodecyl sulfate was efficient in the removal of methylene blue in aqueous solution, allowing the use of these residues as raw material for cost-effective and sustainable charcoal production [37]. These wastes are also efficient in removing up to 100% of the iron present in contaminated water over a surface area of 1516.5 m^2/g and a volume of 0.7 cm^3/g [38]. Also, experiments referent to the economic evaluation to obtain activated carbons from pecan shells were performed and about 1370 kg of steam-activated and 2964 kg of acid-activated pecan shell carbon could be produced everyday with low costs (U$S 18/h and U$S 2.72/kg) [39].

5.4. Extracts production.

Extracts of pecan residual materials have shown great application potential. Pecan shell extracts, rich in phenolic compounds, were effective in inhibiting cancer cells, decreasing the viability of these cells and preventing the cell cycle. The stimulation of important proteins involved in cell death and cell cycle regulation was the mechanism involved in the observed effects. In addition, it was evidenced that the extracts have the ability to cause DNA damage to tumor cells, indicating that pecan shell extracts can be considered an important alternative to the treatment of some tumors [18].

Studies have also reported that pecan shell extracts have the ability to inhibit the germination of species such as lettuce (*Lactuta sativa* L.) at concentrations higher than 5 kg/m^3, showing that these residues have allelopathic potential and can be employed as natural herbicides [40]. This allelopathic potential was also found when shells were disposed of as mulching, inhibiting weed development in crops of fruit species [41].

Another study involving pecan shell extracts showed that these materials can be used to prevent the degradation in soybean biodiesel production. The addition of these antioxidants is carried out during the soybean biodiesel washing process in an unconventional manner. The concentrations of the extracts that provided the longest induction time for the biodiesel were the ethanol extract of the hull at a concentration of 5 g/L (9.45 h), aqueous extract of the shell at a concentration of 12 g/L (7.40 h) and methanol extract and shell water at a concentration of 12 g/L (7.37 h) [21].

6. TECHNOLOGIES FOR EXTRACTION OF COMPOUNDS OF THE BIOMASSES OF PECAN

A range of processing technologies applied in pecan biomasses is presented in the scientific literature, as well as their main benefits and limitations. Gasification and pyrolysis, compounds extraction and enzymatic/ acid/ alkaline hydrolysis have been employed and are reported in the literature.

An indispensable component in the efficiency of lignocellulose rich material extraction procedures is the technology, or technology integration, adopted for the process. The literature reports several technologies employed in order to add value to these materials. However, other factors should be considered, such as minimal energy exploitation and techniques that do not result in environmental contamination [42]. Numerous chemical solvents and procedures involving high energy consumption have been reported as major concerns related to these processes. In addition, the combination of high costs, minimum yields and/or desirable element losses should be considered with full attention [43]. Developed studies that approach technologies of extraction with pecan residual biomass have been evidenced in the academic-scientific environment. These works present several applications associated with these materials, aiming at obtaining value-added products.

6.1. Gasification and pyrolysis.

Gasification and pyrolysis are some of the main technologies adopted to add value to the reused pecan biomasses. Gasification is the process of transforming liquid and/or solid materials into a gas mixture, widely used for power generation or biofuel production. The expansion of this practice is a result of the growing concern with the environment and the increase in conventional fuel prices [44]. Pyrolysis is one of the main processes involving gasification and is characterized as the conversion of solid material into a carbon-rich compound and a volatile solid, which will be partially condensed into a liquid fraction [45]. It is of great interest to the systematic impact of gasification and pyrolysis process conditions on production studies and characterization of products generated from these technologies [46]. The literature has reported some studies involving the application of these technologies in remaining pecan materials.

Considering the importance of the product generated from pyrolysis, studies have found suitable conditions of this technique to evaluate the behavior of elements and functional groups present in pecan shells. It was found that in a temperature range between 300 and 500 ºC, changes occurred and the removal of functional groups from the surface of the pyrolysis product generated, as well as a change in the shell structure, and an increase of gaseous products, such as methane, carbon dioxide, and ethane [47]. In addition, other studies have reported the adsorptive capacity of pecan waste materials from the application of pyrolysis. Also, the carbon resulting from the pecan shells pyrolysis technique absorbs a large number of different metals and organic elements present in processing wastewater. Approximately 3000 kg of shell-based products can be produced daily and the results are higher than those found in conventional commercial carbon [38]. Similar results were observed from the pecan husks, characterized as a highly efficient bio sorbent in acid and lead adsorption, with a worship performance of up to 79 mg/g of these substances [17].

6.2. Compounds extraction.

Phenolic compounds are characterized as the main bioactive groups present in plants and include flavonoids, tannins, phenolic acids, among others [48]. Current literature addresses a range of extraction technologies for these compounds in plant species and their wastes materials, such as infusion extraction, ultrasound-assisted extraction, and Soxhlet extraction.

Extraction by infusion is characterized by the contact of vegetable biomass and solvent (normally water) in a given period under boiling conditions. Studies involving pecan shells related to this technique as an extremely efficient method referring to obtaining phenolic compounds, tannins, and antioxidant actions compared to other methodologies such as ethanol extraction and supercritical extraction [30]. Also, it was found that aqueous extracts of pecan shells from the infusion process tests presented inhibitory activities against a variety of pathogenic bacteria of major importance, as well as the potential use of natural conservatives of chemical foods for food industries [31].

Moreover, ultrasound-assisted extraction is an extraction process facilitated by the behavior of mechanical waves under high pressures and temperatures [49]. This technology can be completed quickly and with low consumption of organic solvents, which is extremely advantageous from a sustainable viewpoint [50]. Studies have pointed out the applicability of extraction in the characterization of compounds of pathological interest present in pecan shells.

Finally, Soxhlet extraction is based on the extraction of lipids and other solid-state substances in contact with a solvent at high temperatures [51]. This method has been widely used due to its ease of processing, minimal environmental contamination, strong interaction between samples and solvent, and large-scale application capability [52]. Numerous studies have indicate the application of this technique in pecan waste materials, mainly aiming at characterizing the physicochemical composition and obtaining properties that present activity against pathogens of these residues. Studies have shown that the application of this method and methane as a solvent allowed a detailed analysis of the pecan shell composition, characterizing the phenolic compounds, tannins and lipids present in these materials, as well as a morphological evaluation of their structure [53]. In addition, the obtaining of antioxidant materials from pecan shells by the Soxhlet and methane method as a solvent was effective in inhibiting the activity of a range of bacterial microorganisms [54]. Finally, the use of hexane as a solvent allowed the extraction of important compounds in the shells and pecans, such as polyphenols, acids and antioxidant and antiproliferative substances [55].

6.3. Hydrolytic process.

Hydrolysis reactions consist of breaking the chemical bonds of substance molecules by the action of water. Chemical materials of different natures (acid and alkaline substances) have been used as solvents in hydrolytic processes, as well as the use of microorganisms (enzymatic biotechnology) capable of hydrolyzing the components of the lignocellulosic matrix. In the current literature, the procedures involving pecan raw materials and the hydrolysis technique as a technology for extracting compounds have been widely portrayed aiming at obtaining walnut oils and compounds [56-60].

Regarding the pecan remaining materials, some studies have reported that the use of substances such as sodium citrate and cellulase and certain conditions in the enzymatic hydrolysis process is effective in obtaining compounds present in the shells, which can be used to produce biofuels [61]. Moreover, hydrolyzed pecan shells solutions subjected to acid/ alkaline hydrolysys (acetone: water, 70:30, v/v) were detected with high concentrations of phenolic compounds of high antioxidant capacity (up to 633 mg CAE/ g) as ellagic acid, gallic acid, and others [62]. In addition, pecan shell hydrolysis by supercritical conditions also resulted in high concentrations of phenolic compounds of high antioxidant capacity, as well as acting as potential antimicrobial materials, inhibiting the development of *Vibrio parahaemolyticus*, *Staphylococcus aureus*, *Listeria monocytogenes* and *Bacillus cereus* [30].

7. GENERAL BACKGROUND AND EXPECTATIONS

Considering the information presented in this review, it is clear that pecan culture has presented a prosperous status with respect to the world and national production. However, as a result of this scenario, there is a large number of waste materials generated and disposed of in the environment. As previously presented, some authors report that up to 80% (25 to 30%, husk; 49%, shell) of the pecan corresponds to the coproducts produced by the plants. These materials, coming from harvesting processes and industrial processing, remain in nature and can cause serious environmental problems. In common for the husks coproducts, leaves and stalks and shells, high contents of lignocellulosic material are evidenced. This context refers to the various applications of these wastes as renewable sources for biofuel production, energy sources and bioproducts generation.

Recently there has been a major concern about the environment. This situation is due to the alarming situation of population growth experienced in recent years and, consequently, the increased production of food and waste generated from it. Thus, the application of vegetable wastes stands out as an important alternative to be employed in relation to other products in food-related areas. Considering the concept of biorefinery as a sustainable technology, these materials have been applied in a range of studies for various purposes, such as synthesis of polymers, organic fertilizers, human and animal feed and industrial purposes, with pharmaceutical and biotechnological aptitude.

This scenario highlights the expansion of studies that use the approach of reusing these materials, which is characterized as a very optimistic perspective. From an investigation of the modern literature about the applicability of pecan waste materials and the technologies employed for the purpose of exploration and value addition of these coproducts, it is clear that several procedures have been used to extract compounds and elements of interest for various purposes. Furthermore, it is noteworthy that many companies have been using environmentally advantageous techniques for large-scale reuse of plant residues, such as ReGrained®, located in San Francisco, U.S.; Renmatix, Inc®, in Montreal, Canada; AINIA® in Valencia, Spain; and Bio-on® in Bologna, Italy. Also, it is important to note that there are academic-scientific organizations that address the same context, such as The Ohio Bioproducts Innovation Center (OBIC), located at The Ohio State University in Ohio, U.S.

In view of this context, it is evident that many alternatives have been portrayed as promising techniques regarding the processing of these coproducts. Nowadays, about 1/3 of the food produced in the world is wasted. This scenario occurs at the same time as more than 1 billion people suffer from food shortages. Pecan residues constitute only a small portion of this problem. However, as evidenced earlier, more than half the weight of pecan is waste material and a coproduct of great potential. Thus, it is necessary to increase the use of pecan coproducts in large proportions and for multiple purposes. This review presented the main applications of pecan waste reported in the current literature, pointing out the potential use of these materials.

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Author contribution and ethical statements

The authors contributed equally to the achievement of this Review. The authors inform that there are no conflicts of interest.