Getting Environmentally Friendly and High Added-Value Products from Lignocellulosic Waste

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Abstract

In recent years, alternatives have been sought for the reuse of lignocellulosic waste generated by agricultural and other industries because it is biodegradable and renewable. Lignocellulosic waste can be used for a wide variety of applications, depending on their composition and physical properties. In this chapter, we focus on the different treatments that are used for the extraction of natural cellulose fibers (chemical, physical, biological methods) for more sophisticated applications such as reinforcement in biocomposites. Due to the different morphologies that the cellulose can present, depending from sources, it is possible to obtain cellulose nanocrystals (CNCs), micro- nanofibrillated cellulose (MFC/NFC), and bacterial nanocellulose (BNC) with different applications in the industry. Among the different cellulose nanomaterials highlighted characteristics, we can find improved barrier properties for sound and moisture, the fact that they are environmentally friendly, increased tensile strength and decreased weight. These materials have the ability to replace metallic components, petroleum products, and nonrenewable materials. Potential applications of cellulose nanomaterials are present in the automotive, construction, aerospace industries, etc. Also, this chapter exhibits global market predictions of these new materials or products. In summary, lignocellulosic residues are a rich source of cellulose that can be extracted to obtain products with high value-added and eco-friendly characteristics.

Keywords: lignocellulosic waste, cellulose, lignin, surface treatments, nanomaterials

1. Introduction

The comprehensive use of lignocellulosic waste coincides with the concept of circular economy because these wastes are renewable, abundant in nature, and generated in large volumes. In addition, they are a main source of natural fibers, chemical compounds, and other industrial products. Lignocellulosic residues are used in various applications depending on their composition and physical properties. Generally, lignocellulosic residues are constituted of cellulose, hemicellulose, lignin, pectin, waxes, and ash [1]. One of its main applications is the production of biofuels, where cellulose is subjected to various physical (mechanical, ozonolysis, pyrolysis), chemical

(acid, alkali, organosolv), and biological (commonly used white-rot fungi) pretreatments. However, this review is focused on the different treatments used on the surface of natural fibers in order to improve their compatibility with a polymeric matrix and thus obtain materials with ecological, lightweight, and excellent mechanical properties, called biocomposites. It is important to mention that when carrying out some of these treatments, residues are generated, which can be processed to recover some high value-added compounds (antioxidants, sugars, bioactive phenols, organic acids, polysaccharides, and polyphenolics). Furthermore, the different types of biomaterials that can be obtained from cellulose (MCF, NFC, CNC, BNC) are described. Finally, an investigation of the market size of some of the products derived from lignocellulosic residues was carried out.

2. Biocomposites

The biocomposites are materials formed by a polymer matrix and natural fibers, which act as reinforcements. Among their main advantages, we can highlight the following: low density, low cost, high resistance, and they are eco-friendly as well. However, they have a disadvantage, incompatibility between polymer matrix and natural fibers, because polymers are hydrophobic and natural fibers have a hydrophilic nature. This is reflected in the mechanical performance of biocomposites. Because of this, chemical and physical treatments have been developed to promote interfacial adhesion between polymer and natural fibers, in addition, to improve dimensional stability and water absorption capacity of biocomposites [2]. In comparison to chemical and physical treatments, biological treatments are considered efficient and environmentally friendly processes. In nature, a great variety of microorganisms capable of degrading lignin, cellulose, and hemicellulose are found [3]. Inside these microorganisms, we can find out fungi that have the enzymatic structure necessary to degrade this type of polymers [4]. The main applications of biocomposites are automotive parts (door panel/inserts, seatbacks, spare tyre covers, interior panels, etc.), circuit boards, aerospace industry, building materials, etc.

2.1 Chemical treatment

As mentioned above, the main objective of the chemical treatment is to improve the adhesion between the natural fibers and the polymer matrix, in addition, it is possible to reduce the absorption of moisture, therefore the mechanical properties are improved. Chemical treatments including alkali, silane, acetylation, benzoylation, acrylation, maleated coupling agents, isocyanates, and others are commonly used. *Alkali treatment.* This method changes the surface morphology of the fibers, due to the breaking of the hydrogen bonds causing a roughness surface. The aqueous sodium hydroxide (NaOH) applied to natural fibers promotes the ionization of the hydroxyl group to the alkoxide [5]. It also removes certain quantity of lignin, oils, and waxes from the fiber surface; this treatment depolymerizes the cellulose in such a way that the cellulose crystals are left exposed on the fiber surface, increasing the reaction sites. This type of treatment is widely used with natural fibers that act as a reinforcement in either thermoplastic or thermosets polymers. Vinayaka et al. [6] found that biocomposites containing alkali-treated castor plant fibers have better mechanical properties than those with untreated castor plant fibers. Finally, alkaline processing directly influences the cellulosic fibril, the degree of polymerization, and the extraction of lignin and hemicellulosic compounds [7]. Several studies have been focused on the accurate concentration of NaOH, the temperature, and the time of the treatment over the fibers surface, in order to

obtain biocomposites able to present satisfactory mechanical properties [8]. *Silane treatment.* According to Xie et al. [9], to effectively couple the natural fibers and polymer matrices, the silane molecule should have bifunctional groups, which may respectively react with the two phases thereby forming a bridge in between them. The general chemical structure of silane coupling agents consists of $R_{(4-n)}$—Si—$(R'X)_n$ (n = 1, 2), where *R* is alkoxy, *X* represents an organofuncionality, and *R'* is an alkyl bridge connecting the silicon atom and the organofuncionality. Silanes can be dissolved in organic solvents or in a water/solvent mixture; this solution can be sprayed on the surface of natural fibers. Silane coupling agents have been found to be efficient improving the compatibility between natural fibers and the polymeric matrix by increasing the tensile strength of the biocomposite. Nishitani et al. [10] studied the effects of silane coupling agents on surface of hemp fiber, and they found that the tribological properties of the biocomposites were improved with the surface treatment by the silane coupling agent. *Acetylation.* Acetylation is a reaction that introduces an acetyl functional group into an organic compound. In natural fibers, the acetyl group reacts with the hydroxyl groups of the fiber and an esterification is generated, which reduces its hydrophilic nature. The advantages of using this method is that it increases the thermal stability as well as the dispersion of the fibers in a polymeric matrix [11]. *Benzoylation.* Benzoylation is an important transformation in organic synthesis [12]. Benzoyl chloride is most often used in fiber treatment. Benzoylation of fiber improves fiber-matrix adhesion, thereby considerably increasing the strength of the composite, decreasing its water absorption, and improving its thermal stability [13]. *Maleated coupling agents.* These agents are mainly used to increase the compatibility between the polymeric matrix and the natural fiber. Generally, maleic anhydride is applied to modify the fiber's surface, and the polypropylene (MAAP) enhances the interfacial bonds, as a result of that the mechanical properties increase (Impact strength, young's modulus, flexural modulus, and hardness) [14]. *Permanganate.* Most of the permanganate treatments are conducted by using potassium permanganate ($KMnO_4$) solution (with acetone) in different concentrations with a soaking duration from 1 to 3 min after alkaline pretreatment [15, 16]. Paul et al. [17] studied the electrical properties of short-sisal fiber-reinforced low-density polyethylene composites using different surface treatments. As a result of permanganate treatment, the hydrophilic nature of the sisal fibers is reduced, and therefore, the water absorption decreases. At higher concentrations of $KMnO_4$, there are possibilities to lead to the degradation of cellulosic fiber by the formation of polar groups. The dielectric constant values increase as the concentration of $KMnO_4$ increases. *Peroxide.* Organic peroxides tend to decompose easily to form free radicals and attack the most available hydrogen in the polymer matrix and natural fibers. Benzoyl peroxide (BP) and dicumyl peroxide (DCP) are used in natural fiber surface modifications [11]. As a result of peroxide treatment, the hydrophilicity of the fiber decreases [17] and the tensile properties increase. *Isocyanate.* The isocyanate functional group (—N=C=O) is highly susceptible to react with the hydroxyl groups of cellulose and lignin in fibers. Joseph and Thomas [18] studied the chemical treatment of the cardanol derivative of toluene diisocyanate (CTDIC) in sisal fiber-LDPE composites. It was demonstrated that CTDIC composites show superior tensile properties than other chemically treated sisal fiber composites due to their better compatibility between sisal fibers and LDPE.

2.2 Physical treatment

There are different types of physical treatments used to modify only the surface of natural fibers without changing their chemical composition. Physical treatments promote the separation of the fiber bundle into individual fibrils and thus increase the

surface area of the fibers and the compatibility with the polymer matrix. According to Ahmed et al. [11], these physical treatments can be classified as follows: mechanical treatment (stretching, calendaring, or rolling), solvent extraction treatment, and electric discharge (plasma treatment, corona treatment, ionized air treatment, thermal treatment, steam explosion, electron radiation, dielectric barrier, and ultraviolet). The *mechanical treatments* promote the interactions between the natural fibers and the polymeric matrix by increasing the surface area of the fibers and decreasing the density and stiffness; therefore, a better distribution of the fibers in the polymer matrix is achieved [19]. *Solvent extraction* can increase the surface area and remove soluble impurities for natural fibers and fillers. Hence, fibers with high cellulose content are obtained. However, this treatment is not widely used because it generates dangerous stems that pollute the environment [20]. *Electric discharge* improve the compatibility between the hydrophilic fiber and the polymer matrix through roughness of the natural fiber surface and structure [21]. Plasma treatment does not need the use of chemicals, which makes it environmentally friendly and cheaper as well. Fazeli et al. [22] modified cellulose fibers by using plasma treatment for the development of biocomposites using a thermoplastic starch matrix (TPS), obtaining a biocomposite with acceptable mechanical properties due to a good interfacial interaction between cellulose fibers and TPS, verified by scanning electron microscope (STEM). Corona treatment changes the surface of natural fibers (surface energy can decrease or increase and free radicals can be produced) by using different types of gases and cold plasma [23]. The steam explosion and alkaline extraction treatments are the most efficient for the removal of hemicellulose fibers. Ultraviolet rays treatment oxidizes the surface of the natural fibers and improves the mechanical properties due to a good interfacial adhesion between natural fibers and the polymer matrix [24].

2.3 Biological pretreatment

Biological pretreatment is based in the extracellular enzymes released by microorganisms in which enzymes degrade the noncellulosic components of the fiber surface. Biological pretreatment of fiber offers relevant advantages, such as low chemical and energy use that make it eco-friendly [25]. A great variety of microorganisms exists in nature, they are able to hydrolyze lignin, being the fungi the most studied [3]. Basidiomycetes white-rot fungi are responsible for lignin degradation in nature; they can break down not only lignin but also hemicellulose and cellulose. It has been reported that these microorganisms degrade lignin in a selective way that is able to offer potential biotechnological application [26]. However, recent studies have shown that many bacteria are able to break down lignin [27]. Likewise, enzymes have an enormous potential to be used for lignin valorization.

2.3.1 Fungal lignin degradation

The breaking down of lignin by fungi has been reported mainly for white-rot fungi due to their highly efficient enzymatic system. White-rot fungi are able to degrade lignin in such an efficiently and selectively way that gives them utility in the industry. These fungi have been applied by different industries such as paper, biofuels, and biorefinery for delignifying biomass [28]. According to the selected strain, it is possible to obtain 20–100% for lignin removal. Black liquor from a pulp and paper mill, treated with the fungi *Pleurotus ostreatus,* reduced 70% its lignin content [29]. Sugarcane bagasse treated with *Lentinula edodes* and *P. ostreatus* presented, after the treatment, 87 and 85% of lignin, respectively [30]. Biological pretreatment of bamboo culms with *Punctularia* sp. Strain TUFC20056 showed more than 50% on lignin degradation [31]. High ligninolytic capabilities have

been found in the fungi *Polyporus brumalis* using wheat straw as substrate [32]. The fungal lignin degradation is based in an oxidative system. The oxidative and ligninolytic system is based in extracellular enzymes, which break down lignins and open phenyl rings; these enzymes are divided into two families: polyphenol oxidases (laccases) and lignin-modifying heme-containing peroxidases (LMPs); this second family comprises: lignin peroxidases (LiP), manganese peroxidases (MnP), and versatile peroxidases (VP) [33].

Laccases use molecular oxygen to oxidize aromatic and nonaromatic compounds, such as phenols, arylamines, anilines, thiols, and lignins [34]. The oxidation leads to the constitution of free radicals that act as intermediate for the enzymatic reactions. Likewise, these mediators can react with others high redox potential compounds and mediate nonenzymatic reactions [26]. White-Rot fungi are mainly reported to produce laccases such as, *Phlebia radiata*, *P. ostreatus,* and *Trametes versicolor* [35]. Although this enzyme is generally found in fungi, it has been found in bacteria as well, such as *Streptomyces lavendulae*, *S. cyaneus*, and *Marinomonas mediterranea* [36]. Laccases present an enormous potential because they work efficiently on a broad range of substrates with applications on paper industries, biosensors (identifying morphine or codeine), food industries, textile industries, soil bioremediation, and in the production of polymers [37].

LMPs belong to class II peroxidases, named plant, and fungal peroxidases, which contain protoporphyrin IX as a prosthetic group [38]. LiP enzymes oxidize different phenolic aromatic compounds and nonphenolic lignin compounds due to the fact that they are not very specific to their substrates [39]. LiP enzymes have been found only in a few white-rot fungi such as the genera: *Bjerkandera*, *Phanerochaete*, *Phlebia*, and *Trametes* [40–42]. The most common peroxidases found in white-rot fungi and other litter-decomposing fungi are the glycoproteins MnP [43]. The MnP glycoproteins catalyze the oxidation of Mn (II) to Mn (III), which is released in complex with oxalate or others chelators [44]. MnP enzymes are found in white-rot wood and litter-decomposing fungi such as *Dichomitus squalens*, *Agaricus bisporus*, and *Agrocybe praecox* [45]. VP enzymes present molecular similarities to LiP and MnP, oxidizing substrates as LiP and Mn^{2+} with a similar catalytic site to MnP [38]. VP enzyme has been found in white-rot fungal in the genera *Pleurotus* and *Bjerkandera* [46]. A variety of low molecular weight aromatic compounds are obtained from fungal lignin degradation, such as, guaiacol, coniferyl alcohol, p-coumarate, ferulate, protocatechuate, p-hydroxybenzoate, and vanillate [47]. The resulting liquor can be used by bacteria that can metabolize lignin-derived aromatics compounds [48].

2.3.2 Bacterial lignin degradation

It has been reported that bacteria are able to degrade lignin through a complex of enzymes, such as extracellular peroxidases, Dye-decolorizing peroxidases (DyPs), and laccases. Among the reported bacterial genus, we found *Rhodococcus*, *Pseudomonas*, *Streptomyces, Novosphingobium*, and *Bacillus* [49]. The bacteria *S. viridosporus* and *N. autotrophica* were able to degrade lignin through extracellular peroxidases, whereas *P. putida*, *Rhodococcus RHA1*, and *Rhodococcus* sp. were active in hydrogen peroxide absence suggesting the presence of extracellular laccases [50]. DyP peroxidases are able to oxidize lignin, aromatic dye, and other phenolic compounds [51]. In spite of finding at first the DyP peroxidases in fungi, recent studies have shown that these enzymes are prominent in bacteria [52]. Bioinformatic analysis showed that *R. jostii* sp. presents two peroxidases members of the DyP peroxidase family, and the deletion mutant gene assay in these genes showed reduced lignin degradation [53]. Bacterial laccases have showed high tolerance to temperature, salt, and acid/alkaline conditions, which make them valuable in the industry,

being the first bacterial laccases identified in *Azospirillum lipoferum* [54]. Many soil bacteria, actinobacteria, and α-, β-, and γ-proteobacteria have shown bacterial laccase genes [55]. A higher laccase production was reached by the bacteria *Streptomyces* sp. KS1025A compared with white-rot fungi in reduced time [56].

2.3.3 Lignin-derived aromatic compounds breaking down by microorganisms

Low molecular weight aromatic compounds are obtained after fungal lignin depolymerization, such as guaiacol, coniferyl alcohol, p-coumarate, ferulate, protocatechuate, p-hydroxybenzoate, and vanillate [57]. Bacteria have the enzymatic machinery to metabolize-derived aromatic compounds that could allow the generation of value-added products such as flavors, polymer building blocks, and energy storage compounds (**Figure 1**). *R. opacus* DSM 1068 and PD630 strains were able to convert lignin into triacylglycerols under nitrogen-limiting conditions [58].

P. paucimobilis is able to metabolize β-aryl ether lignin dimer compounds to yield vanillic acid [59]. In the catecholic compounds production, *O*-demethylation is an essential process with ring cleavage catalyzed by dioxygenase [60]. *Sphingobium* is a bacterial genus characterized for the catabolism of lignin-derived aromatic compounds sp. being able to produce protocatechuate/gallate and 3-*O*-methylgallate [61]. While *Ralstonia eutropha* strain H16 was able to synthesize the biopolyester
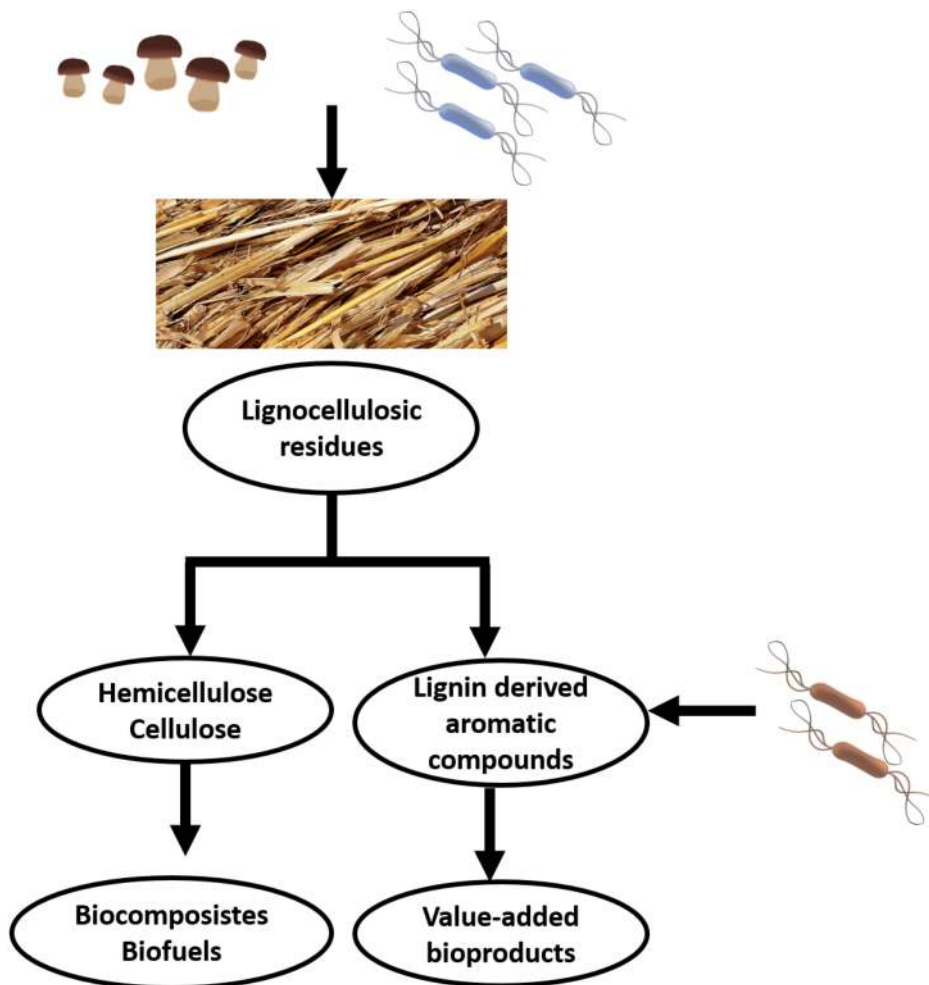

Figure 1.
Biorefinery based on microbial pretreatment in lignocellulosic residues.

polyhydroxyalkanoate (PHA) from lignin derivates [62], *Pandorea* sp. ISTKB converts lignin and its derivates into a value-added product PHA [63].

Fungal and bacterial lignin degraders (BLD) depolymerize the lignocellulosic residues, thus obtaining hemicellulose and cellulose that can be used to produce biocomposites or biofuels and lignin-derived aromatic compounds which can be transformed by bacteria to value-added bioproducts.

2.3.4 Challenges in microbial lignin degradation

Biological lignin degradation process does not involve high temperatures and pressures and does not generate any undesirable products. However, it is a time-consuming process, and there is not an accurate control on it [64]. Long time is necessary to achieve microbial lignin degradation that can range from 10 to 100 days, which is not suitable for commercial applications [28]. Several efforts have been made to engineer microorganisms in order to be more efficient to metabolize lignin-derived compounds with remarkable biotechnological applications, such as pretreatment of lignocellulosics, pulping and bleaching in the paper industry, and decolorization in the textile industry [49]. *Yarrowia lipolytica* was transformed with laccases genes from *Pycnoporus cinnabarinus* offering an efficient model for the engineering of laccases with industrial applications [65]. A dye-decolorizing peroxidase from *P. putida* MET94 strain was engineered to enhance 100-fold the catalytic efficiency when oxidizing phenolic lignin model substrates [66]. On the other hand, multi-copy recombinant *Pichia pastoris* strain expressed lignin peroxidase from *P. chrysosporium* reaching a maximum activity after 12 h induction [67]. Systems among ligninolytic microorganisms and enzymes demonstrate an enormous potential to enhance the lignin degradation [68].

2.3.5 Purified enzymes

The application of enzymes is an attractive alternative due to its shortened time, improved yield, and simple processing [69]. The most common enzymes used to break down lignin are peroxidase and laccase, catalyzing lignin oxidation. Among the most studied peroxidases are lignin peroxidases and manganese-dependent peroxidases. These enzymes degrade lignin randomly converting the phenolic group to free radicals, which lead to lignin depolymerization [70]. Fungal peroxidase from *P. ostreatus* shown lignin degradation at 30°C and pH 4 yielding 2,6-dimethoxy-1,4-benzoquinone, benzoic acid, butyl phthalate, and bis(2-ethylhexyl) phthalate [71]. Laccase can be isolated from fungi and bacteria; it is able to oxidize phenolic compounds; however, it can cooperate with mediators (small molecules able to transfer an electron) to degrade nonphenolic compounds [72]. In spite fungal laccases are selected, not only bacterial laccases have higher thermostability and an extended pH range of use but also they represent a good alternative to lignin depolymerization [73]. The company MetGen Oy has designed the enzyme MetZyme® LIGNO™, a genetically laccase of bacteria origin that can perform its activity in extremely alkaline pH and at elevated temperatures [74]. The enzyme immobilization has also been attempted to improve product separation and catalyzation because the enzymes can be made reusable through techniques such as cross-linking of enzymes, immobilization onto nanomaterials, or entrapping on beads [75]. Laccases from *Fomes fomentarius* and *T. versicolor* were cross-linked showing higher catalytic efficiency, stabilities, and high reusability compared with the free laccase [76]. Other efforts have been made to design multienzyme biocatalysts to improve stability and efficiency of lignin degradation. Co-immobilization of laccase and horseradish peroxidase by cross-linking maintains their activity and improves enzyme stability [77].

3. New biomaterials

Cellulose is the most abundant polymer in the world. It is a linear polymer of β-D-glucose molecules linked by β(1 → 4) bonds. Due to this bond, each molecule has the ability to rotate 180° with regard to the previous one, forming long linear chains that are stabilized by the presence of hydrogen bonds and join chains to others. The cellulose micelle is made up approximately from 60 to 70 cellulose chains, and the union of 20 or 30 cellulose micelles achieves a semicrystalline packing and the formation of microfibrils. However, the morphology, size, and other characteristics depend on the cellulose origin, and according to the above, cellulose microfibrils (MFC)/nanofibrils (NFC), cellulose nanocrystals (CNCs), and bacterial nanocellulose (BNC) can be obtained [78].

3.1 Micro/nanofibrillated cellulose (MFC/NFC)

Microfibrillated cellulose (MFC) is obtained with the longitudinally disintegration of cellulose fibers by multiple mechanical shearing actions; in this way, a three-dimensional network of cellulose microfibrils (10–100 nm) is achieved, which has a higher surface area than conventional cellulose fibers. Due to its structure, MFC has the ability to form gels. Different mechanical treatment procedures have been reported to obtain MFC (high-pressure homogenization and grinding for example) and various pretreatments to facilitate the mechanical treatment (enzymatic, acid hydrolysis, mechanical cutting pretreatments, etc.) [79]. The mechanical properties of MFCs are higher compared to lignocellulosic fibers because they have a more homogeneous structure. The main application of MFCs is in the packaging industry due to its excellent mechanical and barrier properties, which are required in this sector [80]. Adel et al. [81] obtained micro/nanofibrillated cellulose from lignocellulosic residues (rice straw, sugarcane bagasse, cotton stalk) and botnia softwood Kraft pulp. First, the lignocellulosic residues were subjected to an alkaline pretreatment to eliminate the lignin, and later, the mechanical treatment was applied to them using a mill. According to their results, the crystallinity index of MFC increased and the length of the fibers that correspond to lignocellulosic residues decreased compared to the fibers of the pulp. And they concluded that the MFC obtained have optimal mechanical and optical properties; therefore, they can be used as reinforcement in the paper-making industry. Nanofibrillated cellulose (NFC) is obtained by delamination of wood pulp (wood, sugar beet, potato tuber, hemp, flax, etc.) by mechanical pressure before and/or after chemical enzymatic treatment with a diameter between 5 and 60 nm and its length in several micrometers. It exhibits amorphous and crystalline domains and high specific surface area. Nanofibrillated cellulose (NFC)/polyvinyl alcohol (PVA) nanocomposites are prepared by dispersion of nanofibers obtained from several biomass sources, normally at low contents (1–10%), into PVA aqueous solutions typically followed by solvent casting. Frone et al. [82] also used cellulose nanofibers obtained from microcrystalline cellulose by ultrasonic treatment as reinforcement (at lower 1–5 wt%) dispersed in PVA. In summary, these materials exhibit a high aspect ratio and specific surface area, excellent flexibility and strength, low thermal expansion, high optical transparency, and barrier properties. Consequently, they can be used to form strong transparent films and aerogels, as a rheology modifier and strength additive in the paper-making industry, like a constituent of food packaging and in different biomedical applications (drug delivery) [79].

3.2 Bacterial cellulose (BC)

Bacterial cellulose is produced by bacteria such as *Acetobacter xylinus* or *Gluconacetobacter xylinus* [78]. Its structure is similar to the original cellulose but

with an ultrafine three-dimensional network of nanofibers with an average diameter 100 times thinner than that of common plant fibers [79]. BC has high water retention due to the fact of being very hydrophilic and having high crystallinity, is relatively inexpensive to produce, and is widely used in biomedical applications (carriers for drug delivery, artificial skin and blood vessels, tissue engineering, etc.); hence, it promotes physical interaction with microorganisms and other active compounds because of its high porosity and surface area [83]. Azeredo et al. [84] explored the possibility of using BC as a raw material in the food and packaging industry applications, and they concluded that the use of this material is increasing and therefore its production cost is decreasing. However, research in this area continues to develop.

3.3 Cellulose nanocrystals (CNCs)

Cellulose nanocrystals are obtained by enzymatic hydrolysis and have the following characteristics: elongated, less flexible, cylindrical, and rod-like nanoparticles with 4–70 nm in width, 100–6000 nm in length, and 54–88% crystallinity index [85]. Gopi et al. [86] used hydrochloric acid to carry out the hydrolysis of cellulose and obtained an improvement in the thermal stability of the CNCs but with a significant agglomeration of the crystals. Park et al. [87] demonstrated a facile and green method of CNC extraction that uses only an high-pressure homogenization (HPH). The obtained CNCs presented rod-like shapes with a size distribution of 4–14 nm for width and 60–20 nm for length. Nanocrystalline cellulose (CNC) was dispersed in an alginate matrix for film application by Huq et al. [88]. They observed that with a small amount of CNC (approximately 5% wt), the mechanical and barrier properties of the films made were improved by comparing with an alginate film. According to the results obtained by infrared spectroscopy (FTIR), they concluded that there was a molecular interaction between the CNC and the alginate through hydrogen bonds. In summary, the morphology and size of cellulose nanocrystals vary according to the kind of lignocellulosic biomass, extraction method, and manufacturing conditions. Nanocellulosic materials can be characterized by employing a variety of techniques [89]: X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), helium pycnometer, differential scanning calorimetry (DSC), thermogravimetric analysis, transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), and atomic force (AFM) among others. On the other hand, cellulose nanocrystals not only consist of primary reactive sites (i.e., hydroxyl groups) but also they possess higher surface area to volume ratio, making CNC highly reactive and easy to be functionalized. The most common surface modifications of CNCs are sulfonation, TEMPO-mediated oxidation, esterification, etherification, silylation, urethanization, amidation, polymer grafting, etc. The applications having the greatest potential due to the high available amount of volume on cellulose nanomaterials are placed in the following industries: automotive (body components, interiors), construction (air and water filtration, insulation, and soundproofing), packaging (fiber/plastic replacement, filler, coating, film), paper (filler, coatings), personal care (cosmetics), textiles (clothing), aerogels, aerospace (structural, interiors), industrial (viscosity modifiers, water purification), paint, sensors (medical, environmental, and industrial), electronics, photonic structures, etc. [90].

4. Recovery of chemical compounds of industrial interest

Diverse processes can be used to release lignin as the main product for the revaluation of different biomasses with high-value applications. Each process uses respective chemical agents to extract and obtain different materials from lignocellulosic biomass and produces other materials with different compositions and

properties. There are distinct chemical processes of biomass hydrolysis, which use acids, bases, or enzymatic hydrolysis and others (other processes can be used, but their description would come out of the focus of this chapter) whose choice mainly depends on the material structure and characteristics desired for the products to be recovered. However, various sources of lignocellulosic materials need to be considered separately since they have different compositions of cellulose, hemicellulose, and lignin. Against all odds, the depolymerization process of the lignocellulosic biomass is a common goal for all different feedstocks for the production of all types of chemicals [91]. In particular, polyphenolic acids are a group of chemical compounds that are widely distributed in plant biomasses. Those compounds are important antioxidants that efficiently interact with biomolecules such as DNA, RNA, lipids, proteins, enzymes, and other cellular molecules to produce desired results. Due to the benefic effects, that can be useful for preventing the oxidation in foods, and therapeutic human disorders [92], all of them can be used with potential applications in the pharmacy, food, cosmetic, and nutraceutical industries.

4.1 Chemicals derived from alkaline-based methods

Alkaline pretreatment is one of the most intensively studied technologies for biomass delignification [93], and the application of alkaline liquid with NaOH into the bagasse to obtain a black liquor that contains value-added chemicals has been investigated. This procedure is useful for the releasing of chemical compounds in different biomasses; particularly, this method has been commonly used for the processing of the switchgrass (*Panicum virgatum*), corn stover (*Zea mays*), and forestry biomasses. Due to their abundance and availability, the use of the process can produce a different number of high-value fine chemicals such as sugars, vanillin, isoeugenol, guaiacylpropanol, guaiacylethanol, ferulic, p-coumaric, and syringic acids [94, 95]. For example, different woody species of *Quercus* and *Robinia* were subjected to alkaline hydrolysis, and liquors were analyzed by GC-MS. The authors recovered and identified specific bioactive phenols for each woody species such as gallic acid, coniferyl alcohol, vanillic acid, syringaldehyde, and traces of epicatechin and catechin [96]. For the optimum alkali treatment concentration in sweet sorghum bagasse, different types of phenolic species were determined with the use of alkali treatments between concentrations of 3.0 and 6.0 M NaOH, resulting in high concentrations of phenol, 4-ethylphenol, and guaiacol [97].

4.2 Chemicals derived from acid-based methods

The acidic pretreatment is a contemporaneous method for the processing of different cereal straws. Nowadays, acidic and alkaline methods are used especially with other methods such as enzymatic hydrolysis for the production of fermentable sugar and polyphenols. Dilute sulfuric acid pretreatment was used on corn stover feedstock and storage for 3 months, resulting in nonobservable microbial infestation. The cellulose content was stable while the hemicellulose content exhibited a slight decrease in furfural and oligomers, and the concentration of chemical compounds such as *O*-glucose and *O*-xylose was also constant [98]. In recent years, the focus has been on the use of other types of biomasses of fruit, for example, apple pomace, citrus, bananas, and mango among others [99]. In that aspect, different solutions of sulfuric acids were used for the valorization of apple pomace and the production of fermentable sugars and organic acids; the hemicellulose of the biomass was hydrolyzed, and the obtained liquor contained different concentrations of sugars such as glucose, xylose, arabinose, rhamnose, and galacturonic acid [100]. Those are new examples of the use of the acidic digestion of new biomasses with new co-products with a high application mainly in food industries.

4.3 Chemicals derived from hot water methods

Hot water, also known as autohydrolysis, hydrolyzes hemicellulose to release acetyl chemical groups and diverse polyphenols and removes lignin, making cellulose fibers more accessible [101]. The hot water method is very extreme, due to the fact that this method uses water at high temperatures usually between 170 and 230°C [102]. The resulting liquor contains different concentrations of sugars and chemical constituents such as polyphenols. Polyphenol compounds are covalently attached to the cell wall constituents such as cellulose, hemicelluloses, lignin, pectin, and structural proteins [103]. For example, hydroxycinnamic and hydroxybenzoic acids form ether linkages with lignin through their hydroxyl groups in the aromatic ring and ester linkages with structural carbohydrates and proteins through their carboxylic group [104]. Therefore, the recovery of the polyphenols can be made by selective extraction with ethyl acetate, purified and cleaned with resins to obtain a high yield of polyphenols with a direct use in food industries [105]. Ares-Péon et al. characterized phenolic compounds from liquors of stems maize (*Zea mays*) and *Eucalyptus globulus* with the use of hot water. Those authors found high recoveries of different polyphenols such as vanillin, ferulic, coumaric, sinapinic, hydroxybenzoic acids, guaiacol, and others. In addition, strong antioxidant activities have been reported in oligosaccharides esterified with polyphenols compounds derived from cell wall of diverse biomasses subjected to hot water methods. For example, in heteroxylans, such as arabinoxylan or glucuronoxylan, the main and predominant component is the hemicellulosic chain polymer, found in hardwoods, brans, and other softwoods [106], which can link some esterified phenolic acids to the oligosaccharides chain. In that sense, Rivas et al. [107] analyzed, by autohydrolysis, samples of liquor from rice husks, *Eucalyptus globulus* wood, and *Pinus pinaster* and found high amounts of hemicellulose-derived saccharides with esterified polyphenols. The samples displayed higher antiradical activities against strong antioxidants such as DPPH, ABTS, and ferric-reducing power; in addition, the polyphenol samples exerted high antioxidant protection to β-carotene-linoleic emulsions. The authors concluded that those antioxidant activities were mainly due to the esterification of polyphenols such as ferulic, syringic, and vanillic acids found in these polymers. Autohydrolysis has been used to extract polysaccharides and polyphenolic compounds from different biomass sources such as coffee, *Eucalyptus* and hazelnut shells among others, with high antioxidant activities [108, 109].

4.4 Chemicals derived from enzymatic-based methods

Different enzymes have been involved in the lignin break down in order to release value-added chemical compounds, with different uses in the food industries. It is important to note that alkaline and acidic methods can support the delignification of the biomasses residues to support the use of enzymatic digestion and obtain mainly sugars, polyphenols, and organic acids. Biomasses such as sugarcane, maize, agave, and sweet sorghum bagasse are widely used for the sugar and phenol extractions [110]. There are other nonconventional biomasses that can use this type of acidic or alkaline pretreatments for the degradation of hemicellulose and therefore obtain fermentable sugars and release antioxidant molecules. For example, biomasses such as corn cobs, orange, and pomegranate peels produced high yields of glucose and reduced sugars employing alkaline and enzymatic treatments [111]. Pomegranate biomass contains a high concentration of fermentable sugars that can be used in ethanol production and secondary polyphenols derived from the chemical hydrolysis. Pomegranate biomass contains a high concentration of fermentable sugars that can be used in ethanol production and secondary polyphenols derived from the chemical hydrolysis, due to this fact, pomegranate peels were subjected to acidic hydrolysis,

and after an enzymatic process with cellulase there were released different fermentable sugars, moreover, bioethanol in presence of ethanol-producing microorganisms was produced. High concentrations of different sugars were released, with acid hydrolysis, such as glucose, xylose, cellobiose, arabinose, and fructose, with a range of ethanol production between 4.2 and 14.3 g/L [112]. Similarly, Talekar et al. [113] incorporated hydrothermal processing in combination with acid and enzymatic hydrolysis in pomegranate peels to recover pectin, phenols, and bioethanol. They recovered pectin ranges of 19–21% and phenolic compounds between 10.6 and 11.8%.

5. Pellets elaboration

Pellets are a type of biomass fuel, that is made from different agroindustrial biomasses; as an example, pellets are a derivative of forest biomass such as wood, sawdust, fruit shells, and kernels as well as agricultural remains derived from straw, corn stove, rice husk, and additionally from plant species with energetic potential such as *Jatropha* and *Ricinus communis* [114], which serve as a source of energy; therefore, it is a good way to use and recycle agricultural surpluses. However, the pellet production is not only focused on using them in the energy industries as solid fuel and thus avoid the use of nonrenewable energy resources such as coal, natural gas, nuclear energy, and oil [115]. Nowadays, the high cost of fossil fuels has led to a high consumption of energy pellets, mainly, since some biomasses are capable of producing a similar calorific index than the oil. Hence, the use of biomass as a heating fuel had an increase in the last decade [116]. Besides, biomass is considered as a carbon-neutral fuel due to the fact that there are no additional carbon dioxide concentrations like fossil energies [117]. However, for the pellets to be used in restaurant kitchens and home kitchens, the biomass must be treated to avoid toxic pollutants for health. For example, it is known that after the consumption of biomass pellets, these produce ashes, which in their contents have high concentrations of chlorides, sulfides, carbonates, and silica among others that can be toxic to the health [118]. Different authors have pretreated the biomass with methodologies such as alkaline hydrolysis and heat treatment to obtain liquors rich in ashes, sugars, and other chemicals. In that sense, Retsina and Pylkkanen (2014) [119] used different treatments of the feedstock to produce an extract liquor that contained different chemicals such as soluble ash, hemicellulosic oligomers, acetic acid, dissolved lignin, and cellulose; the authors produced low-ash biomass ready to be transformed into energetic pellets. One of the most important parameters in the pellet production is its durability and is given by the pellet durability index (PDI). In order to achieve those parameters of PDI, strategies have been implemented to remove lignocellulose and sugars efficiently with the use of alkaline hydrolysis. Those molecules influence the final PDI of the pellet and its energetic capacity. For example, Tang et al. (2018), evaluated the release of lignin, soluble sugars, and whole particle size on the PDI of the untreated and treated Poplar (*Populus* spp.) wood sawdust, with a combination of alkaline and acid pretreatments and steam. The authors presented that PDI increased with those treatments, more specifically, with acidic pretreatment.

6. Market of eco-friendly and high added-value products derived from lignocellulosic wastes

In recent years, a great number of studies have focused on the use of lignocellulosic waste due to the high volume generated by the agroindustrial sector and

the need to manufacture new eco-friendly materials. Through a specialized search in the innovation platform "Lens" and using the keywords "cellulose," "hemicellulose," "lignin," "nanocellulose," and "novel" between 2006 and 2020, an increase is shown in the production of research papers regarding cellulose, lignin, and nanocellulose. On the other hand, **Table 1** shows the estimated market size of some of the major high value-added products from lignocellulosic waste before the

Lignocellulosic waste	Estimated market size before COVID-19	Applications	Negative impact	Opportunities	References
Cellulose	$48.37 billion USD by 2025	Textile, paper, fiber-reinforced, and starch foams	Stranded supply chains, breach of contracts, supply chain shortage, and temporary closure of department stores	Increased the digital market, strengthening of the local supply chain, new buying and selling cycle, personal hygiene and protections equipment, made of corrugated paper, demand for toilet paper and sanitizing wipes, and medical materials packaging	[120–123]
Hemicellulose	$1.3 billion USD by 2007	Ethanol and fermentation products	Fuel ethanol consumption decreased	Opportunities in disinfection of medical materials and equipment	[124, 125]
Lignin	Lignin market size worth $1.12 billion USD by 2027	Adhesives and binders	Temporary business closure, automotive supply chain, and automotive adhesives	Packaging adhesives and adhesives for medical applications	[126, 127]
Nanocellulose	$0.78 billion USD by 2025	Biomedical, personal care, oil gas, paint, coatings, food, paper processing, and composites	Disruption in production and supply chains	Development antimicrobial surfaces and packaging	[128, 129]
Biocomposites	$46.30 billion USD by 2025	Transport, construction, and electronics	Temporary closure of assembly plants	Medical applications	[92]

Table 1.
Estimated market of products from lignocellulosic waste.

COVID-19 pandemic as well as the negative impacts and area of opportunity caused by COVID-19. Based on the report by Global Market Insight [130], the market size for nanocellulose was close to 146.7 million USD in 2019 and is expected to grow to 418.2 million USD in 2026 because the global nanocellulose market indicates an increase in demand for certain applications by 2026, like paper processing, food and beverage packaging, paint and coatings, among others. It is important to mention that the term "nanocellulose" used in this report includes micro/nanofibrillated cellulose, cellulose nanocrystals, and bacterial nanocellulose. Among the main nanocellulose manufacturing companies [128], we can mention: Fiberlan technologies (UK), Borregard (Norway), Nippon Paper Industries (Japan), Celluforce (Canada), etc. Due to the COVID-19 pandemic, demand also increased in the pulp and paper industry, mainly in personal hygiene paper products, food packaging products, corrugates packaging materials, and medical specialty papers [120]. Based on the above, we can conclude that the materials obtained from lignocellulosic residues have a wide field of application and have been successfully positioning themselves in the market before and after COVID-19.

7. Conclusions

The use of lignocellulosic waste is an alternative to generate environmentally friendly products with high added value. There is a variety of methods to modify the surface of cellulose fibers both to obtain biofuels and to improve their compatibility with a polymeric matrix and in this way, develop biocomposites with high mechanical performance to be used mainly in the automotive and packaging sectors. Likewise, from the chemical treatment waste, the black liquor is generated, and it can be reused for the generation of high added-value compounds. On the other hand, lignocellulosic residues have had a high growth potential in the market in a wide variety of applications; however, the COVID-19 pandemic has increased the use of some of these products mainly in medical applications and in the packaging industry.

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Conflicts of interest

The authors of this chapter do not have potential conflicts of interest.

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