



A review on the valorization of lignin from sugarcane by-products: From extraction to application

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ABSTRACT

The sugarcane industry generates several by-products including the harvest residue (straw) and the fibrous fraction following juice extraction (bagasse). The conversion of sugarcane industry by-products into value-added products is of paramount importance from a sustainable circular economy perspective. Also, the increase of second-generation bioethanol production has triggered the development of approaches to convert residues into functional bioproducts thus increasing the overall sustainability of the process. Lignin is the major biopolymer in nature, and one of the three main components of sugarcane bagasse (SCB) and straw (SCS) biomasses. Due to the potential of lignin as natural antioxidant, antimicrobial, and ultraviolet protector, lignin-based research and new product development have significantly increased. Therefore, this review aims at updating the progress on the valorization of SCS and SCB, and emphasizing their main potential bioactivities and applications, thus serving as a valuable reference material for the academy and industry. A brief introduction of the sugarcane and sugar industry in terms of by-products generation and current end-uses is presented. Recent research studies on SCB and SCS delignification techniques, lignin purification/separation and the main physical-chemical differences between SCS and SCB are covered. The most reported biological activities for sugarcane lignin and their potential applications in the cosmetic and materials fields are also detailed in this review.

1. Introduction

Sugarcane is a large perennial tropical grass belonging to the family *Gramineae* and the genus *Saccharum* [1]. Sugarcane is a major crop cultivated globally for sugar production [2]. Its distinguishing features are high biomass yield, sucrose content, and efficiency in accumulating solar energy. After the harvest of sugarcane, leaves and tops are left in the field while the sugarcane stalks are transported to sugar mills for the extraction of cane juice for sugar production [3]. Two major by-products from the sugarcane industry are the harvest residue (straw) and the fibrous fraction following juice extraction (bagasse). These post-harvest by-products have been suggested as an abundant and inexpensive source of lignocellulosic biomass [2]. Sugarcane bagasse (SCB) and sugarcane straw (SCS) are composed of cellulose, hemicellulose, and lignin, with lower amounts of extractives and ash [4]. SCB is almost completely used by the sugar industry as fuel for the boilers [5], while SCS is commonly

used as animal fodder or burnt in the field [6]. Lignocellulosic biomass has been recognized for its potential use to produce chemicals and materials, having the advantages of low cost and availability [7]. Lignin is the second most abundant biopolymer in nature [8]. The main functions attributed to lignin in the plant are elasticity and mechanical strength. It is a complex aromatic macromolecule formed by the dehydrogenative polymerization of three phenylpropanoid monomers coniferyl, synapyl, and *p*-coumaryl alcohols. In the specific case of sugarcane lignin, it is greatly acylated (*p*-coumaroylation) at their side chains, contains tricin flavonoid units, and has ferulate residues cross-coupled between arabinoxylan and lignin [4]. Studies have shown that SCB and SCS lignins are structurally different, the first one is syringyl-rich with predominance of alkyl-aryl ether substructures, whereas SCS is a guaiacyl-rich lignin with higher amounts of condensed structures. Additionally, the degree of acetylation is also different, being higher in SCB. These structural differences explain the need to apply

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harsher pre-treatment conditions to SCS.

The production of high-value lignin-derived products is still a challenge due to the complex structure of lignin, polydispersity, recalcitrance nature, dependence on the type of biomass, among others [9]. Additionally, lignin isolation, fractionation, modification, and characterization remain a challenge. Usually, the pre-treatment process drives the separation of the lignocellulosic biomass into the main components, being an efficient way of reducing the natural recalcitrance of the lignocellulose material mostly present in the cell wall [10]. A suitable pre-treatment method aims to efficiently extract lignin from the lignocellulosic and generate a lignin fraction of high purity and quality that can achieve the requirements for subsequent conversion steps. Once lignin is separated, its modification, fractionation, or depolymerization are demonstrated to be prominent ways to achieve the sustainable use of lignin. Lignin is part of the cellular wall and confers structural support, hydrophobicity, and resistance against microbial attack and oxidative stress, and among the components of lignocellulose, it is the most recalcitrant to chemical and biological degradation [11]. Hemicellulose is linked to cellulose and lignin by covalent bonds and fewer hydrogen bonds. Lignin acts as a glue and binds cellulose and hemicellulose which, in turn, makes the structure more moisture resistant and recalcitrant to chemical and biological degradation [3]. Research has been developed on sugarcane lignin extraction and isolation methods [11,12] and potential applications [13]. These waste streams - SCB and SCS - may constitute a lignocellulosic source in countries with high sugarcane production, as Brazil, India, and China [14]. Both SCB and SCS have high cellulose (30–40% (w/w)) content, which could be used to produce 2G ethanol via different chemical, physical or biological pre-treatments to convert them into fermentable sugars while separating and valorizing lignin as well. Another positive aspect of this raw material is that it does not require an increase in the harvesting area, because this residue has a high regeneration capacity and yield per unit area (80 t/ha). However, it has not been common practice to reuse the SCS to produce higher value-added products. Most of the straw is left in the fields to improve soil quality (water retention or erosion reduction) or it is used to generate heat and electricity. For example, 1 tonne of produced sugarcane, yields 280 kg of SCS, 50% of which remains in the fields and the other 50% are currently burned for energy generation. The effects of SCS removal on crop yield are site-specific and dependent on several factors including soil type, climate or weather patterns, quantity of SCS removal, and other crop management practices [15]. The SCS removal must be properly managed to avoid, for example, soil health degradation. Recommendations of optimum SCS removal from the fields must be designed in an integrated approach considering several factors, namely, local conditions, agricultural practices, characteristics of the SCS and intended end-use [16,17]. The adequate replacement of nutrients removed in SCS is determinant for the impact in the system sustainability [18]. Another relevant aspect is related to the expected increase in the use of mineral fertilizers, which may compromise the sustainability of sugarcane production and, consequently, reduce the environmental benefits of SCS for bioenergy production and other end-uses [19]. In this sense, one strategy could be the assessment of the nutrient composition of the SCS by-products from bioenergy production (e.g ash, boiler soot, and anaerobic biodegraded solid), and their application as replacers of the removed nutrients [19]. Given the distinctive physical, chemical, and morphological properties of SCS and SCB, it is important to analyze and characterize each individually to apply the most efficient pre-treatment and possible applications [14,20,21]. Based on the potential of lignin from sugarcane, relevant reviews have been published in the literature [11,12]. However, there is a lack of literature review in what concerns lignin from SCS or combining both SCB and SCS. Therefore, this review compiles the state-of-the-art on lignin extraction from both biomasses, its biological potential, and main applications.

2. Sugarcane industry

Recent concerns about climatic change and the exploration of alternatives to fossil fuels have focused global attention on sugarcane as a source of biomass [22]. The annual global production of sugarcane is about 328 Mt being Asia the main production region (44%) followed by South America (34%) [2]. The significance of the sugarcane industry is due not only to sugar production but also to its by-products. Sugar production from sugarcane generates several by-products applied for energy production. Although highly appealing for environmental and financial reasons, it remains economically unattractive [23]. Their low market value as compared to other biomasses is explained, at a certain extent, by the low density of SCB and SCS that, consequently, leads to high transport costs. Particularly for SCS, its collection from the fields may imply the need of pre-processing to remove contaminants, such as dirt and sand, resulting in high energy production costs. In the case of SCB, this by-product is generated inside of the processing factory, being easier to use for energy production. In this context, the conversion of by-products into value-added compounds and applications is crucial. The main solid by-products include plant tops, straw, bagasse, filter cake, and molasses, which can be grouped into two stages: those originated during the harvesting stage (tops and straw), and produced during the industrial processing (bagasse, filter cake, and molasses) (Fig. 1). The main components of the solid by-products include cellulose, hemicellulose, and lignin.

This review focuses on SCB and SCS biomasses due to their potential as sources of lignin. As previously mentioned, SCS consists essentially of green leaves, dried leaves, stalks, and plant tops [23]. In terms of chemical composition it is composed of 19–32% lignin, 38–42% cellulose, 19–35% hemicellulose, and 5–7% ash [4,24,25]. One of the largest cellulosic agro-industrial by-products is bagasse [13]. SCB is a fibrous material generated after crushing and squeezing the sugarcane stalks to obtain the raw sugar juice [26]. Interestingly, literature is more extensive regarding the SCB chemical composition, exhibiting contents in lignin (17–25%), cellulose (30–40%) and hemicellulose (19–28%), and ash (5–20%) [4,27–35].

3. Lignin extraction

The extraction of lignin from lignocellulosic materials involves a pre-treatment to break the lignocellulosic bonds. The majority of the sugarcane delignification studies are dedicated to cellulose conversion [11, 36,37] and some studies are focused on the influence of lignin structure on cellulose or hemicellulose enzymatic hydrolysis [31,33,39,40]. Literature regarding SCB is more extensive than SCS probably due to the lignin structure since SCB contains higher syringyl content and lower condensation degree favouring the material pre-treatment [4]. On the contrary, SCS contains a higher content of condensed structures [4]. These factors - lignin structure, degree of polymerization, hemicellulose and cellulose content, syringyl to guaiacyl ratio, and others - confer the recalcitrant nature of lignocellulosic biomass to enzymatic and microbial degradation, thus posing a problem towards its industrial valorization to bioenergy, biomaterials, and high-value chemicals [21,41,42]. Some approaches have been tested to reduce the recalcitrance of lignin from SCS. An example is the study carried out by Batista et al. [42]; Authors used a factorial design for a hydrothermal process and the results were 195 °C and 10 min residence time as the optimum point to remove ~85.45% of hemicellulose and low cellulose solubilization (9.80%) [42]. Nevertheless, the authors concluded that the hydrothermal pre-treatment had an adverse effect on lignin recondensation in the solid matrix, particularly at higher temperatures.

Still, on SCS, the modification of cellulose obtained from this biomass into cellulose acetate and carboxymethylcellulose was studied [43]. Although the primary goal of this work was not lignin valorization, the applied methods were suitable for lignin extraction. Firstly, the authors employed an acid pre-treatment using 10% (v/v) H₂SO₄ and 1/10 (w/v)

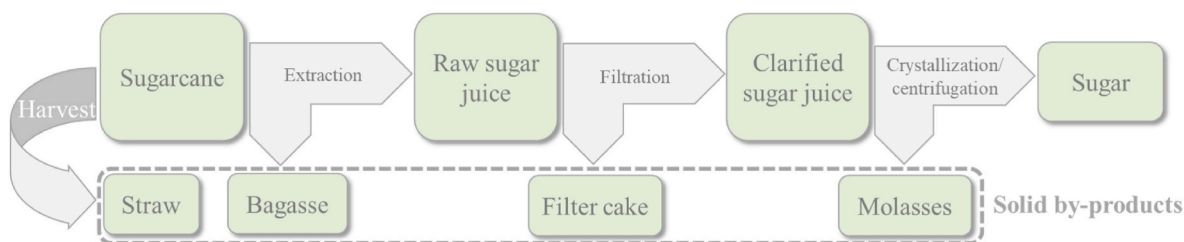


Fig. 1. Schematic representation of solid by-products generation in the sugar industry. Adapted from Ref. [38].

solid/liquid ratio of dry SCS loading at 100 °C for 1 h. With this step, the authors removed 52.22% of lignin from the initial biomass (into the liquor). After this, an alkaline pre-treatment was applied with a solution of 5% (w/v) NaOH and 1/10 (w/v) solid/liquid ratio of dry acid-pretreated material loading at 100 °C for 1 h. With the alkaline pre-treatment it was possible to solubilize the remaining 84.77% of lignin, leaving a solid with only ~6% of lignin.

Other studies have been carried out aiming at valorizing lignin from SCS as the one using a combination of microbial degradation followed by an organosolv pulping [44]. In this case, the SCS was first subjected to fungal treatment followed by delignification using refluxing under atmospheric pressure in an aqueous solution of acetic acid containing HCl as catalyst (fixed at 0.3% (w/w)). The authors performed a factorial design testing the acetic acid concentration (73 or 93%, w/w), the ratio between liquor and straw (16 or 30 w/w), and the straw type (with fungal pre-treated or untreated) at a temperature of 115 ± 5 °C. The results showed that this fungus (*Ceriporiopsis subvermispora*) is selective to lignin degradation, thus resulting in a decrease at the concentrations of chemicals used as well as the process conditions (temperature and time). Lignin from SCS was also obtained by sulfur dioxide-alcohol-water fractionation with 99% purity [24,45]. A more recent approach involved the imidazolium-based ionic liquid (IL) pre-treatment of SCS. It was concluded that IL pre-treatment of SCS followed by low-temperature pyrolysis can also be an efficient route for biorefinery production [25].

As mentioned before, the research on lignin extracted from SCB is more extensive as compared to SCS [4,12,46,47] and some reviews have been already published [11,12]. The most common processes used are alkaline [33,48–50], acid [29,51], and organosolv [51,52] pre-treatments. A schematic graphic of the most relevant processes for

lignin extraction is presented in Fig. 2. Other lignin extraction studies on SCB include IL [32,53,54], deep eutectic solvents (DES) [55], organosolv extraction in supercritical conditions [56] and, hydrotropic extraction [57]. Some of these studies and lignin chemical properties are summarized in Table 1, where most studies use dried milled and sieved biomass. The physicochemical characterization of lignin is often disregarded and, for this reason, a complete characterization of the SCB lignin obtained in these studies was not found. Lignin purities obtained were greater than 90% with minor sugar content (<3.5%) and inorganic contaminants. The extraction of lignin from SCB using different alkaline pre-treatments, namely sodium hydroxide, alkaline ethanol, and alkaline hydrogen peroxide was studied [33]. Lignin was extracted using 96% dioxane at 50 °C for 48 h. A control without alkaline pre-treatment was also tested. Lignin fractions with more than 90% of purity were obtained, being the purest one isolated with the AHP pre-treatment (~95%). Another investigation using response surface methodology combined with Box-Behnken design for alkaline pre-treatments of SCB was pursued [50]. In this work, three parameters were tested: NaOH concentration (3, 5 and 7% w/v), extraction temperature, (115, 125, 135 °C), and extraction time (30, 45 and 60 min). The process was optimized in terms of total phenolic content (TPC), trolox equivalent antioxidant capacity (TEAC), and sun protection factor (SPF) of the obtained lignin-rich fractions. TPC was measured using the Folin–Ciocalteu assay, which is a colorimetric method based on electron transfer reactions between the Folin–Ciocalteu reagent and phenolic compounds [58]. Gallic acid was used as a reference compound and results are expressed as gallic acid equivalents (GAE). TEAC assay is an electron transfer based method and uses 2,2'-azinobis (3-ethylbenzothiazoline-6-sulfonic acid) radical cation (ABTS^{•+}) to evaluate the antioxidant capacity by spectrophotometry. The unstable free cationic

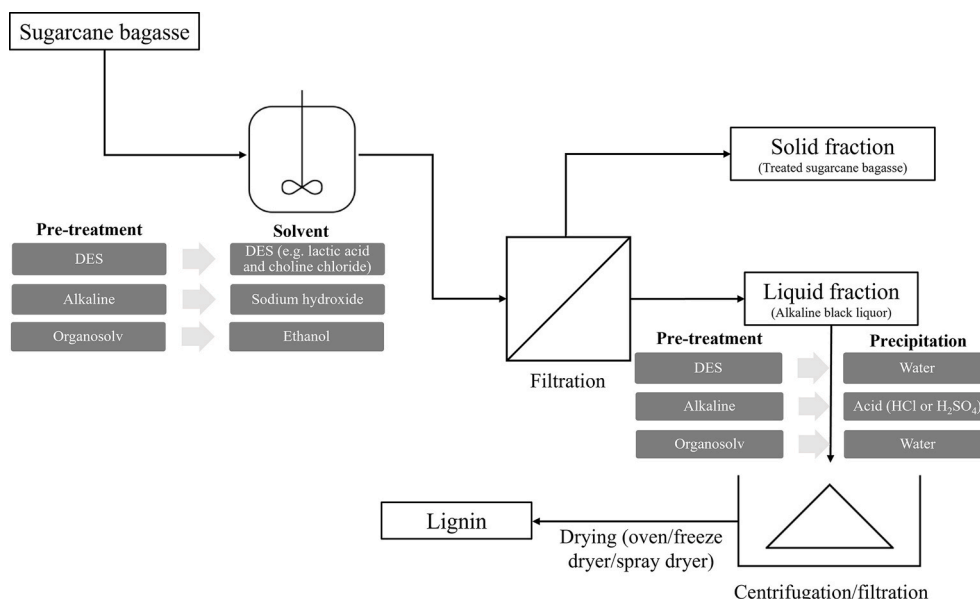


Fig. 2. Graphical schematic of lignin extraction methods from sugarcane bagasse. DES - Deep Eutectic solvent.

Table 1
Recent studies for lignin extraction from sugarcane bagasse and respective precipitation methodologies and physical-chemical characterization.

Pre-treatment	Extraction conditions	Precipitation	Washing	Drying	Appearance	Lignin (%)	Sugars (%)	Ash (%)	Mw (Da) Mn (Da) PD	OH groups (mmol g ⁻¹ of lignin)	Ref.
Acetosolv process	Concentrated acetic acid aqueous solution (95%) with HCl 0.1% (w/w) as the catalyst. t: 15 min (a) or 40 min (b) T: 187 °C	Pre-concentration in rotary evaporator followed by precipitation with water at 60 °C	N.a.	Oven drying (60 °C for 24 h)	N.a.	(a) N.a. (b) 88	N.a.	N.a.	(a) 2480 248 10 (b) 2438 312 7.8	N.a.	[29]
Alkaline (industrial pulping process OPAL S.A., Colombia)	Sodium hydroxide	Concentrated sulphuric acid (36 N) until pH 2	Water until pH 6	Oven drying (60 °C for 24 h)	Dark brown powder	92.1		2.6	18926 2255 8.39	N.a.	[48]
Organosolv acid hydrolysis	Ethanol (50–80% v/v)/water (20–50% v/v) mixture; catalyst: sulphuric acid (0.01N–0.05 N); P: 20–30 bar; T: 80–180 °C	N.a.	Water 70 °C for 30 min	Oven drying (40 °C until constant weight)	N.a.	N.a.	N.a.	N.a.	N.a. N.a. N.a.	Aliphatic: 0.75; S–OH: 0.58; G–OH: 0.47; H–OH: 0.53; 5-condensed: 0.27; total phenolic: 1.85; carboxylic acids: 0.17	[52]
Ionic liquid assisted extraction	IL [EMIM]oAc t: 120 min T: 140 °C, S/L ratio 1:20 600 rpm After extraction, the medium was supplemented with 1:1 (v/v) acetone/deionized water and filtered to remove solids.	The filtrate was heated to evaporate acetone to precipitate lignin	N.a.	Oven drying	N.a.	N.a.	N.a.	N.a.	1769 1098 1.61	N.a.	[32]
Dilute acid	1.09% aqueous sulphuric acid mixture S/L ratio 1:2.8 t: 30 min T: 121 °C	Extracted solid is i) soxhlet extracted with toluene/ethanol (2:1 v/v), ii) washed, iii) ball milled, iv) Cellulase digestion, v) Dioxane extraction 96%, S/L ratio 1:20, T: 50 °C; t: 48 h, vi) solvent evaporation	No washing	Freeze drying	N.a.	97.29 ± 0.62	0.22 + 0.69	0.98 ± 0.12	5591 2142 2.61	0.52 ± 0.02	[51]
Alkaline	2% (w/v) Sodium hydroxide L/S ratio 1:20 t: 2 h T: 80 °C		N.a.	Freeze drying	N.a.	96.17 ± 0.40	0.35 + 0.19	0.71 ± 0.06	6636 3268 2.03	0.43 ± 0.02	
Organosolv	60% (v/v) Ethanol L/S ratio 1:10 t: 45 min T: 160 °C		N.a.	Freeze drying	N.a.	95.05 ± 0.40	0.59 + 0.72	0.92 ± 0.06	6441 4181 1.51	0.60 ± 0.02	
Hot liquid water (Hydrothermal)	Hot liquid water pre-treatment L/S ratio 1:20 t: 30 min T: 180 °C		N.a.	Freeze drying	N.a.	95.70 ± 0.46	0.78 + 1.11	0.42 ± 0.04	6557 3540 1.85	0.26 ± 0.02	
Cellulolytic enzyme treatment	96% (v/v) dioxane extraction S/L 20 t: 48 h T: 50 °C (prior Soxhlet extraction with toluene/ethanol (2:1 v/v) followed by cellulase digestion)	Solvent evaporation	N.a.	Freeze drying	N.a.	93.73 ± 0.63	1.96 + 1.61	1.27 ± 0.21	8114 6030 1.35	0.50 ± 0.01	
Alkaline	2% (w/v) sodium hydroxide T: 80 °C in a pressure bottle: 2 h, S/L 1/20	Extracted solid is i) soxhlet extracted with toluene/ethanol, ii) dried iii) ball milled, iv) Cellulase digestion, v) Dioxane extraction 96%, S/L ratio 1:20, T: 50 °C; t: 48 h, vi)	N.a.	Freeze drying	N.a.	92.46 ± 0.43	0.95 + 1.36	1.70 ± 0.35	4875 3577 1.36	0.40 ± 0.05	[33]

(continued on next page)

Table 1 (continued)

Pre-treatment	Extraction conditions	Precipitation	Washing	Drying	Appearance	Lignin (%)	Sugars (%)	Ash (%)	Mw (Da) Mn (Da) PD	OH groups (mmol g ⁻¹ of lignin)	Ref.
Alkaline organosolv	1% (w/v) NaOH + 60% (v/v) ethanol S/L: 1:20 t: 2 h T: 80 °C	solvent evaporation up to 1/20; vii) precipitation with ethanol	N.a.	Freeze drying	N.a.	93.64 ± 0.54	0.81 + 1.19	1.48 ± 0.06	6272 4858 1.29	0.27 ± 0.03	
Alkaline hydrogen peroxide	1% (w/v) NaOH 42% (v/v) H ₂ O ₂ S/L: 1:20 t: 2 h T: 80 °C	Extracted solid is i) soxhlet extracted with toluene/ethanol, ii) dried iii) ball milled, iv) Cellulase digestion, v) Dioxane extraction 96%, S/L ratio 1:20, T: 50 °C; t: 48 h, vi) solvent evaporation up to 1/20; vii) precipitation with ethanol	N.a.	Freeze drying	N.a.	95.01 ± 0.95	N.a.	1.57 ± 0.13	5321 2676 1.99	0.15 ± 0.03	[33]
Cellulolytic enzyme treatment	96% (v/v) dioxane extraction S/L 20 t: 48 h T: 50 °C (prior Soxhlet extraction with toluene/ethanol followed by cellulase digestion)	Solvent evaporation up to 1/20; and lignin precipitation with ethanol	N.a.	Freeze drying	N.a.	90.84 ± 0.82	2.04 + 2.71	2.07 ± 0.20	7418 6423 1.15	0.58 ± 0.04	

N.a. – Not available. Mw - Weight average molecular weight; Mn - Number average molecular weight; PD – Polydispersity; OH – Hydroxyl group; S/L – solid-liquid ratio t – extraction time T – extraction temperature, P – extraction pressure; H–OH – p-hydroxyphenyl units; G-OH – guaiacyl units; S–OH – Syringyl unit; IL [EMIM]oAc - Ionic liquid 1-ethyl-3-methylimidazolium acetate.

radical ABTS^{•+} can receive one electron by the molecule, involving a discoloration of the ABTS^{•+} dark blue solution. Trolox was used as a radical scavenger reference for the comparison of the radical scavenging activities of phenolic compounds and the results were expressed in Trolox equivalents. SPF is a well-recognized indicator of the efficacy of a sunscreen product. Generally, two types of *in vitro* SPF methods are performed by spectrophotometry. Methods which involve the measurement of absorption or the transmission of UV radiation (UVB, 290–320 nm and UVA, 320–400 nm) through sunscreen product films in quartz plates, and methods in which the absorption characteristics of the sunscreen's agents are determined based on spectrophotometric analysis of dilute solutions [59]. The SPF values are determined according to a mathematical equation developed by Mansur et al. [60]. The optimum condition was 7% (w/w) NaOH, 135 °C, and an extraction time of 47.92 min, where lignin was extracted with an efficiency of 78.93%. Using acidic conditions, Hassanpour et al. [61,62] used a two-step process to produce fermentable sugars. The first step consisted in using a dilute acid (H₂SO₄) pre-treatment at 130 °C or 170 °C, followed by an acidic crude glycerol pre-treatment at temperatures of 130 °C, 150 °C, and 170 °C. Two lignin fractions were obtained: soluble lignin (in diluted acid liquor) was recovered using ethanol and dilution with water, and the pre-treated solids were washed, enzymatically hydrolyzed and freeze-dried to yield the insoluble lignin. Between 67 and 85% of lignin present in the initial SCB (untreated) was recovered from the liquid and solid fractions. The authors also confirmed that the pre-treatment conditions affected the distribution of lignin in both solid and liquid fractions and the number of β-O-4 linkages.

Some studies are focused on the optimization of the extraction conditions depending on the target applications [29,50,56,63]. For instance, regarding the production of phenolic resin, Pinheiro et al. [29] applied the design of experiments to analyze the effect of acetosolv extraction time and temperature on outputs such as extraction yield (the mass of lignin extracted by the acetosolv process per lignin mass in crude fiber) and specific lignin production (the mass of lignin extracted per substrate) using aqueous acetic acid at a concentration of 95% (w/w) and catalyst HCl 0.1% (w/w). Based on the maximization of the extraction yield, the optimum extraction conditions were 40 min at 187 °C. On the other hand, for maximizing specific lignin production 15 min was the selected extraction time, displaying purity of 88%. The lignins at the optimal condition displayed H/G/S ratios of 1.0/0.43–0.50/0.13–0.28.

Ionic liquids (ILs) have been posed as sustainable and alternative solvents for the extraction of lignin, with yields of around 70%. One drawback of ILs is their high price, which can be probably overcome by recycling them [35,53,54]. Another group of “green” solvents that can even be a replacement for ILs are the DES. DES are obtained by mixing two or more reagents forming a eutectic mixture. Some studies of DES applied to SCB have already been published [55,64]. Pre-treatment with formic acid:choline chloride (ChCl) successfully extracted lignin from SCB [64]. Seven different DES solvents including ChCl:oxalic acid, ChCl:glycerol, ChCl:lactic acid, ChCl:urea, ChCl:imidazole, ChCl:sorbitol and ChCl:succinic anhydride were investigated for their efficacy in this biomass fractionation, and for improving cellulose and xylan digestibility. A novel combinatorial pre-treatment approach based on ultrasonic irradiation and DES (ChCl:glycerol) was demonstrated as an effective approach for the deconstruction of SCB to improve sugar yield [55].

Delignification of SCB with hydrotropic aqueous solutions was applied by Ansari and co-workers [57]. Hydrotropic extraction is commonly used in literature to extract bioactive compounds from plant materials. It has the advantage of allowing an easy recovery and recycling of the solvent without using hazardous chemicals. The authors have accomplished 85% delignification degree by applying alkylbenzene sulfonate solution of 30% (w/v) at 115 °C for 240 min and a solid-liquid ratio of 1:19. Lignin was recovered by toluene or water dilution extractions, being the latter the more efficient method. The

obtained lignin was of irregular shape, an average molecular weight of 3791 Da with a polydispersity index (ratio of weight average by number average molecular weight) of approximately 1 and thermal stable up to 360 °C.

4. Lignin purification and modification

After extracting lignin from the biomass, it is necessary to perform a separation and isolation step that strongly depends on the pre-treatment solvent used. Currently, the biggest supplier of lignin is the paper and pulp industry (in the form of black liquors), which utilizes an alkaline process (kraft process). Lignin obtained from this process is usually isolated by acid precipitation [65]. Lignin derived from steam-exploded SCB followed by alkaline extraction was precipitated in series at different pH values from 12 to 2 using H₂SO₄ at room temperature [66]. This allowed to overcome lignin's inherent heterogeneity, which is a drawback for some value-added applications. For each pH value (10, 8, 6, 4, and 2), the solution was centrifuged and only the supernatant was used for the subsequent precipitation at a different pH (e.g. the supernatant with pH 8 would be used to generate the supernatant with pH 6). The authors observed that the fractions at pH value < 4 resulted in lignin with low-polydispersity and low molecular weight. From the small-angle X-ray scattering (SAXS) data, fractions obtained at pH > 4 had more nanoparticles and larger aggregates of lignin, whereas fractions obtained at pH 4 and pH 2 consisted of small nanometer-sized and low molecular weight polyphenols clusters. Furthermore, the fraction obtained at pH 2 exhibited the highest total phenolic content and radical scavenging capacity. Nevertheless, this process has the disadvantage of requiring more acid for precipitation and several separation stages.

Other strategies reported in the literature include flocculation, ethanol or water addition, or even adsorption [67]. Organic solvent fractionation is also a technique that has been studied [68,69]. Membrane technology is a strategy applied to increase lignin purity without the use of different pH values, solvents, and several separation steps. The main advantages include low energy and chemical consumption and the capability of separating components by molecular weight. This technique has been used in pulp and paper mills, particularly for the treatment of bleach plant effluent and fractionation of spent sulphite liquor [70]. Ultrafiltration membrane process was applied for kraft black liquor fractionation in a continuous plant in Finland [71]. In order to achieve lignin with higher purity and yield, and narrower molecular weight distribution, other membrane processes have been applied to different liquors, at laboratory and pilot scales [72–75].

To improve the chemical properties of lignin obtained after the pre-treatment, modifications can be performed in different ways: depolymerization/fragmentation and modification of functional groups (e.g. hydroxyl groups) [76]. Lignin depolymerization and modification can be achieved via thermochemical processes such as hydrolysis, hydrolysis (or hydrocracking), pyrolysis, solvolysis, and oxidation. Depolymerization is mostly characterized by using harsh conditions (high temperatures and pressures) in conjunction with catalysts [77]. It is worth mentioning some studies regarding depolymerization of lignin extracted from SCB since, to the best of our knowledge, no study was published in terms of SCS. One catalyst, a monomeric anthraquinone acid (AQCOOH), in the presence of glucose and sodium hydroxide (in water) to depolymerize lignin from SCB was used [78]. The authors reported an increase from 0.75 to 1.30 mmol g⁻¹ of carboxylic acid functional groups (before and after reaction). A more innovative approach was reported in the literature, where the depolymerization of lignin was carried out using cooperative ILs pairs (for example, 1-butyl-3-methylimidazolium chloride/1-(4-sulfobutyl)-3-methylimidazolium) [76]. Optimization of the conditions (extraction temperature and time) was conducted, being 250 °C for 30 min the optimum point; a lignin conversion of 66.7% and a yield of a phenolic monomer of 14.5% (w/w) were achieved. A “greener” approach was adopted where the incorporation of hydrogen gas was avoided [79]. To perform an

oxidation–hydrogenation catalytic process, methanol or ethanol were used as solvents with Pd/C acting as a catalyst in the presence of atmospheric pressure oxygen. Under the optimum reaction conditions, methanol as solvent, the temperature of 250 °C, and reaction time of 8 h, they obtained 55% ester selectivity and a ferulic acid and *p*-coumaric acid-derived aromatic esters yield of 31.7% (w/w).

Chemical modifications of functional groups present in lignin, such as hydroxyl, methoxy, carbonyl, and carboxyl groups were proposed. These modifications - nitration, amination, alkylation/dealkylation, carboxylation, and halogenation - usually promote the reactivity of hydroxyl groups or change the nature of chemically active sites, to increase their chemical reactivity or its solubility, for example. These modifications have been studied to a lesser extent than reactions involving hydroxyl groups [80]. In terms of the functionalization of phenolic and hydroxyl groups, the most common modifications involve esterification, etherification, and subsequent reaction with isocyanates and silylation [81]. Lignin from SCB was modified by oxidation, hydroxymethylation, and sulfonation into a water-soluble lignosulfonate. Results demonstrated that the aromatic units of water-soluble lignosulfonate were maintained and effectively sulfonated, improving the dispersing efficiency [49]. Sulfometylation was performed for producing water-soluble lignin by providing an anionic charge density to the molecules without significant molecular alteration. The study demonstrated that modified lignin extracted from SCB accomplished emulsifier properties for the production of oil-in-water nanoemulsions that have both high physical and oxidative stability [82]. Chemical modifications by acetylation, epoxidation, and hydroxymethylation reactions of lignin from SCB were applied. The authors found that epoxy lignin was the most effective for antibacterial activity, and confirmed the importance of methoxy groups for antioxidant activity [83].

5. Lignin characterization

Lignin extraction and purification methods generally cause structural changes on the lignin macromolecular matrix and, thus, a proper characterization is necessary to define the most suitable applications. Being a complex aromatic biopolymer bonded to carbohydrates, lignin characterization is challenging and should combine several techniques [84]. The evaluation of physical-chemical lignin properties can be accomplished by applying wet chemistry, spectroscopic and chromatographic methodologies, along with thermal and mechanical analyses [84,85]. All these methodologies are well detailed in the literature [85, 86]. Briefly, the wet chemistry techniques relate to conventional methods applied to lignin chemistry and include elemental analysis, functional groups quantification (O-methyl, total and phenolic hydroxyls, and carbonyl and carboxyl groups), and degradation methods for inter-unit linkages assessment (e.g. nitrobenzene oxidation or thioacidolysis). Structural characterization can be accomplished by spectroscopy methods such as ¹H, ¹³C, and ³¹P Nuclear Magnetic Resonance (NMR) spectroscopy, two-dimensional (2D) NMR by heteronuclear single-quantum coherence, Fourier-Transform Infrared Spectroscopy analysis, Raman spectroscopy, and surface analysis by X-ray Photoelectron Spectroscopy. The chromatographic techniques include the assessment of the molecular weight and polydispersity via gel permeation chromatography. The thermal properties of lignin can be evaluated by thermal gravimetric analysis and differential scanning calorimetry and mechanical properties by dynamic mechanical properties [9,87].

6. Biological properties

This section is dedicated to a relevant topic encompassing the lignin biological properties such as antioxidant, antimicrobial, and prebiotic, with a focus on the lignin from sugarcane by-products.

6.1. Antimicrobial activity

The antimicrobial activity of lignin is related to plant sources and attributed to the phenolic components, particularly the side-chain structure and its functional groups [88]. Lignin has been recognized to exhibit antimicrobial activity originated from two of their three basic monomers: coniferyl alcohol and sinapyl alcohol [89]. Most of the phenolic compounds that are considered antimicrobial agents contain hydroxyl groups. These functional groups are currently considered involved in the antimicrobial action, by disrupting the bacteria cell membrane structure, eventually causing the leakage of cell components [90]. Also, the number and position of substituents in the benzene ring of phenolic acids influence the antibacterial potential of these acids against different microorganisms [91]. In general, the presence of a double bond in the α and β positions of the side chain and a methyl group in the γ position of the phenolic fragment shows the highest efficacy against microbes [88]. More, variations in antibacterial activities among bacteria may reflect differences in cell surface structures between Gram-negative and Gram-positive species [91]. Although several studies have been published examining the antimicrobial activity of lignin, to the best of our knowledge, this topic is still underexplored. However, some studies regarding the antimicrobial activity of lignin from different sources are available in the literature [92–95]. For example, in a study carried out by Kaur et al., methoxy and epoxy groups were found to be responsible for antibacterial activity in lignin from SCB chemically modified (epoxidation and hydroxymethylation) [83]. Other relevant studies have been reported for lignin from SCB and summarized in Table 2.

The experimental methodology adopted also influences the assessment of antimicrobial activity. Methodologies commonly employed are the broth dilution method and filter paper disc. Sunthornvarabhas et al. used resazurin solution for Minimal Inhibitory Concentration (MIC) assessment based on a color change, a pink color indicates microorganism growth, while a brown color means growth inhibition [96]. Broth dilution method was used to identify MIC and minimum bactericidal concentration (MBC) of the lignin extracts, with the tested concentration of lignin solution ranging from 16 to 131,072 $\mu\text{g mL}^{-1}$. The tested extracts were added to sterile Mueller Hinton broth into microtiter plates before the diluted bacterial suspension (final inoculum of 10^5 bacteria mL^{-1}). The positive control was a mixture of nutrient broth and lignin extracts, and the negative control was a mixture of nutrient broth and *Staphylococcus epidermidis*. The MIC was identified by observing the lowest concentration of the extracts that caused a change in color of resazurin solution after 24 h of incubation at 37 °C. The minimum bactericidal concentration (MBC) was determined by subculture of the well showing no apparent growth (brown color) in a sterile agar plate. The least concentration showing no visible growth on agar subculture was taken as MBC value. However, the typical lignin brown color is considered a limiting factor for antimicrobial activity by broth dilution method, due to the color interference on the interpretation of results.

6.2. Antioxidant activity

The antioxidant activity of lignin is mainly attributed to the scavenging action of their phenolic structures on oxygen-containing reactive free radicals. There are several antioxidant methods to assess antioxidant activity. Among them, the method using 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical is one of the most applied. The reactivity of DPPH \cdot is far lower than that of oxygen-containing free radicals (OH \cdot , RO \cdot , ROO \cdot and O $_2^{\cdot-}$), and unlike them, the interaction rate is not diffusion-controlled [97]. The investigations into scavenging effects of lignin-related compounds on the DPPH radical have revealed the main role of the non-etherified phenolic hydroxyl groups, ortho-methoxy groups, and aliphatic hydroxyl groups in the side chain [97]. For the antioxidant activity of the lignin, free phenolic hydroxyl groups and ortho-methoxy substitution in aromatic rings are essential. The

Table 2
Antimicrobial activity reported for lignin from sugarcane bagasse: Minimal Inhibitory (MIC) and Minimal Bactericidal (MBC) concentrations.

Pre-treatment	Method	Tested concentrations	Microorganisms	Results		References
				MIC	MBC	
Alkaline (NaOH 1%)	Broth dilution method	16 to 131072 $\mu\text{g mL}^{-1}$	<i>Staphylococcus epidermidis</i> (DMST 15505)	4096 $\mu\text{g mL}^{-1}$	8192 $\mu\text{g mL}^{-1}$	[96]
Alkaline (NaOH 1, 5 and 10%)	Filter paper disc method	100–3000 $\mu\text{g}/\text{disc}$	<i>Bacillus aryabhatai</i> (KF 853102)	Lignin 200 $\mu\text{g}/\text{disc}$; Acetylated lignin 300 $\mu\text{g}/\text{disc}$; Epoxy lignin 100 $\mu\text{g}/\text{disc}$; Hydroxymethyl lignin 200 $\mu\text{g}/\text{disc}$.	N.a.	[83]
			<i>Klebsiella sp.</i> (KF 424316)	Lignin 300 $\mu\text{g}/\text{disc}$; Acetylated lignin 400 $\mu\text{g}/\text{disc}$; Epoxy lignin 200 $\mu\text{g}/\text{disc}$; Hydroxymethyl lignin 300 $\mu\text{g}/\text{disc}$.	N.a.	
Alkaline (NaOH 1 and 4%)	Broth dilution method	16 to 32768 $\mu\text{g mL}^{-1}$	<i>Staphylococcus epidermidis</i> (DMST 15505)	NaOH 1% 4096 $\mu\text{g mL}^{-1}$; NaOH 4% 8192 $\mu\text{g mL}^{-1}$; Commercial lignin 8192 $\mu\text{g mL}^{-1}$	8192 $\mu\text{g mL}^{-1}$; 8192 $\mu\text{g mL}^{-1}$; 16384 $\mu\text{g mL}^{-1}$	[158]
			<i>Staphylococcus aureus</i> (DMST 8840)	NaOH 1% 8192 $\mu\text{g mL}^{-1}$; NaOH 4% 8192 $\mu\text{g mL}^{-1}$; Commercial lignin 8192 $\mu\text{g mL}^{-1}$	16384 $\mu\text{g mL}^{-1}$; 32768 $\mu\text{g mL}^{-1}$; 32768 $\mu\text{g mL}^{-1}$	
			<i>Pseudomonas aeruginosa</i> (TISTR 781)	NaOH 1% 8192 $\mu\text{g mL}^{-1}$; NaOH 4% 8192 $\mu\text{g mL}^{-1}$; Commercial lignin 8192 $\mu\text{g mL}^{-1}$	32768 $\mu\text{g mL}^{-1}$; 32768 $\mu\text{g mL}^{-1}$; 32768 $\mu\text{g mL}^{-1}$	
			<i>Escherichia coli</i> (TISTR 780)	NaOH 1% 8192 $\mu\text{g mL}^{-1}$; NaOH 4% 8192 $\mu\text{g mL}^{-1}$; Commercial lignin 8192 $\mu\text{g mL}^{-1}$	16384 $\mu\text{g mL}^{-1}$; 32768 $\mu\text{g mL}^{-1}$; 32768 $\mu\text{g mL}^{-1}$	

N.a. - Not available

Table 3
Lignin antioxidant activity and chemical properties using sugarcane bagasse as raw material.

Pre-treatment	Carboxyl groups (mmol g^{-1})	Phenolic hydroxyl groups (mmol g^{-1})	Mw (Da)	Mn (Da)	Mw/Mn (PD – polydispersity)	Antioxidant method	Antioxidant results	Reference
Ethanol	2.39	2.29	2100	960	2.19	Hydrogen peroxide scavenging assay	IC50 = 545.1 mg L^{-1}	[108]
Alkaline (NaOH 10%, 140 °C)	3.43	4.36	4300	1500	2.86	Hydrogen peroxide scavenging assay	IC50 = 161.5 mg L^{-1}	
Alkaline (NaOH 10%, 98 °C)	N.a.	N.a.	N.a.	N.a.	N.a.	DPPH	Lignin EC50 = 0.38 mg mL^{-1} ; oxidized lignin EC50 = 4.00 mg mL^{-1}	[109]
Alkaline (NaOH 1%, fraction obtained at pH 2)	N.a.	3.54 ± 0.09	409	339	1.21	ORAC Hydrogen peroxide scavenging assay Peroxynitrite scavenging assay	10.2 ± 0.7 $\text{mmol Trolox equivalent g}^{-1}$ IC30 = 14.9 $\mu\text{g mL}^{-1}$ IC50 = 2.3 $\mu\text{g mL}^{-1}$	[66]
Alkaline (NaOH 1, 5 and 10%)	N.a.	Lignin - 1.04; hydroxymethyl lignin - 1.10	N.a.	N.a.	N.a.	DPPH	Lignin EC50 = 0.38 mg mL^{-1} ; acetylated lignin EC50 = 6.60 mg mL^{-1} ; epoxy lignin EC50 = 6.22 mg mL^{-1} ; hydroxymethyl lignin EC50 = 0.37 mg mL^{-1}	[83]
Alkaline (170 °C with 1.5% sodium hydroxide (NaOH) (w/v))	N.a.	N.a.	4291	764	5.62	DPPH	IC30 = 11.99 $\mu\text{g mL}^{-1}$	[111]
Organosolv (200 °C for 2 h with a 1:1 ethanol/water solution (w/w))	N.a.	N.a.	1330	626	2.12	DPPH	IC30 = 11.41 $\mu\text{g mL}^{-1}$	

N.a. - Not available; IC50 - Half-maximal inhibitory concentration; EC50 - Half-maximal effective concentration.

antioxidant activity of lignin is negatively affected by the carbonyl group in the side chain, high molecular weight, polydispersity, and heterogeneity [98].

The antioxidant activity of lignin from different sources has been extensively studied and relationships with structural properties have been established [58,99–107]. The structural characteristics of lignin depend on several factors including the botanical origin, and environmental growth and extraction conditions. A summary of the antioxidant activity of lignin from SCB is presented in Table 3. A study with lignin from SCB extracted with different chemical procedures using ethanol and alkaline solutions was performed to evaluate their potential as antioxidants. Antioxidant activity of alkaline lignin was stronger than ethanol lignin due to its higher quantities of phenolic hydroxyl and methoxy groups that influenced more than its molecular mass and polydispersity [108]. Kaur and Uppal (2015) extracted lignin using an alkaline pre-treatment and tested the antioxidant activity of lignin and oxidized lignin. Lignin was found to have higher antioxidant activity than the oxidized one [109] as a result of its higher number of phenolic groups. The radical scavenging ability of phenolic compounds depends not only on the ability to form a phenoxyl radical but also on its stability. Phenolic structures with substituents that can stabilize the phenoxyl radicals have higher antioxidant activity. Since the methoxy groups at the ortho position stabilize phenoxyl radicals by resonance as well as hindering them from propagation, the antioxidant activity is enhanced. This antioxidant activity improvement was accomplished by the authors Kaur et al. [91], where ferulic acid was isolated and derivatized into amides. On the contrary, in oxidized lignin, conjugated carbonyl group of carboxylic acid had a negative effect on the antioxidant activity [109].

The DPPH radical scavenging potential of unmodified and modified lignins (by acetylation, epoxidation, and hydroxymethylation reactions) was reported in the literature [83]. Unmodified lignin was more active than the acetylated and epoxy lignin, probably due to the higher content of phenolic hydroxyl groups. In the case of the modified lignins, the hydroxyl groups were replaced by acetyl and epoxy groups in the respective derivatives of lignin, thus negatively affecting their capacity to scavenge the DPPH radical [83]. Hydroxymethyl lignin showed comparable antioxidant activity to unmodified lignin, as the phenolic hydroxyl groups remained intact in its structure [83]. Recent research studied the antioxidant potential of lignin and lignin nanoparticles obtained from SCB with two different processes, alkaline and organosolv. An investigation on the antioxidant activity of an aqueous solution of Ligmed-A by studying its protective effect on the hemolysis induced by 2, 2'-azobis(2-amidinopropane) dihydrochloride (AAPH) was performed. Ligmed-A is commercially available as an antidiarrheal drug for weaning pigs and is composed of about 90% sugarcane lignin and showed IC₅₀ of 106.63 $\mu\text{g mL}^{-1}$ [110]. Regarding to the lignin nanoparticles, the preparation method influenced their scavenging potential, since those obtained by solvent shifting methodology were more active as compared to the ones obtained by direct dialysis [111].

6.3. Prebiotic activity

Prebiotic is defined as an indigestible food ingredient that beneficially affects the host by selectively stimulating the growth and/or activity of one or a limited number of bacteria in the colon, and the host health [112]. Prebiotics are proposed to modify the intestinal microbiota thus stimulating the bacterial activities beneficial to the host and suppressing the bacterial activities adverse to host health [113]. Animal responses to purified lignin apparently depend on the dosage, animal species, and type and source of the lignin [114]. To the best of our knowledge, no studies have been developed using lignin from SCB and SCS. However, the potential of lignins as prebiotics have been reported for lignins from other plant sources. An example is a study carried out by Bezerra et al. focused on the influence of kraft lignin extracted from *Eucalyptus urograndis* wood - used as an additive in high-concentrate

diets - on the performance, ruminal health, meat traits, and oxidative stress control in lambs. However, no protective effect was observed on the rumen wall mucosa nor a positive effect on performance; instead, the kraft lignin showed antioxidant activity by thiobarbituric acid reactive substances assay with the increase of peroxidases activity [115]. A different study showed that the addition of low levels of lignin (1.25%) to broiler chicken diets improved gut integrity as measured by changes in villi height, goblet cell number, and populations of the beneficial bacteria, *Lactobacillus* and *Bifidobacteria* [116]. These findings suggest that purified lignin (Alcell®, coproduct of paper manufacture) may exert health benefits in monogastric animals and could potentially be considered as a natural feed additive. Based on the scarce published studies, more research is required before establishing the conclusive benefits of purified lignin on animal performance and health.

6.4. Cytotoxicity

The assessment of cytotoxicity is detrimental for potential applications of lignins, particularly, those in the food, pharmaceutical, and cosmetic industries. Some studies have assessed the cytotoxic effects of lignin from different sources, namely, hazelnut and walnut shells [117], eucalyptus [118], wheat straw [119], and wood of *Acacia nilotica* [120] with promising results of its non-cytotoxic behaviour. There are few studies involving the assessment of lignin cytotoxicity from SCB. In this context, Ugartondo et al. (2008) evaluated the cytotoxicity effects of lignins from different sources. The cell membrane integrity of human keratinocyte HaCaT and murine fibroblast 3T3 cells were studied to predict their skin irritation potential. Lignins seem to be more cytotoxic in the keratinocyte cell line, especially after 24 h. Lignins studied revealed cytotoxic effects, but only at very high concentrations. HaCaT cells were more sensitive than 3T3 cells, especially after 48 and 72 h [121]. The study established a correlation between cytotoxic effects and antioxidant activity. The stronger antioxidants were the most cytotoxic. Nevertheless, the effective antioxidant concentrations are smaller than the cytotoxic ones, suggesting that lignins exert antioxidant activity at non-cytotoxic concentrations [121]. Cytotoxic effects of lignin from SCB, rice straw, and sweet sorghum were tested on lung cancer cell line A549. IC₅₀ value, a concentration of a sample that is required for 50% inhibition *in vitro*, ranged from 12 to 18 $\mu\text{g mL}^{-1}$ indicating the potential of the three lignin samples as a natural anti-cancer agent. The results demonstrated that SCB lignin was the most promising due to its non-toxicity and good physicochemical compatibility as well as biodegradable properties [122]. Recently, the production of an antiviral substance from SCB by artificial structural alteration of the native lignin was reported. The conversion of this biomass into an antiviral substance by acidic glycerolysis strongly inhibited encephalomyocarditis virus replication with no detectable cytotoxicity [123]. Although some attempts have been made to address this issue, more studies are required concerning the cytotoxicity of lignin from SCB in different types of cell lines, as well as a correlation of chemical structure and functionality.

7. Applications

In terms of applications, lignin has the potential for high-value products in different fields such as cosmetics, materials, and textiles. Nevertheless, the use of lignin at an industrial scale represents several challenges, namely its unique chemical reactivity, the presence of various organic and inorganic impurities, and a non-uniform structure [124]. The following sections present the state-of-the-art for lignin applications, focusing on sugarcane-derived lignin.

7.1. Cosmetics

The exploration of safe and sustainable natural alternatives to synthetic ingredients for cosmetic products is a growing concern, due to the associated environmental impact and human health risk [117]. The

cosmetic potential of lignin arises from its unique and complex structure. Diverse functional groups in the lignin molecule, such as phenolic and aliphatic hydroxyls, carbonyls, and carboxyls have a beneficial effect on skin properties such as photo-protective, anti-aging, and skin-whitening properties [108,125]. Some studies explored the potential of lignin as an ingredient for cosmetic formulations. Natural sun blockers have been recently attracted considerable attention. Lignin has been explored as a natural sunscreen by *in vitro* Sun Protection Factor (SPF) methods as an attempt to replace typical harmful commercial chemical and physical ultraviolet (UV) protectors [126]. Also, the synergistic effect of lignin in sunscreen formulations has also been reported [127]. The studies available on this topic are for lignins from different biomass sources [125,128]. Concerning the application of lignin from sugarcane, only SCB has been explored and just few studies have been reported in the literature. Recently, the cosmetic potential of lignin extracts from alkaline-treated SCB was investigated [50]. The alkaline hydrolysis conditions for the extraction of lignin from SCB were optimized aiming at obtaining the most promising functional properties – phenolic content, antioxidant activity, and SPF – for cosmetic applications. Thus, the reported optimal conditions were NaOH solution at a concentration of 7% (w/v), the temperature of 135 °C, and residence time of 47.92 min. The optimal conditions yielded 69.41 ± 0.32 mg gallic acid equivalent/g extract for total phenolic content, 262.30 ± 2.98 mg Trolox equivalent/g extract for antioxidant activity, and 8.65 ± 0.21 for SPF. Based on the results, authors proposed SCB lignin extract as a promising bioactive multi-functional ingredient that can offer anti-aging, sun protection, and skin-lightening properties for sun care formulations [50]. Lignin demonstrated good potential as a natural UV protection ingredient in broad-spectrum (UVA and UVB) sunscreens. Another relevant information is that the UV blocking properties are increased with lower molecular weight fractions and with lignin in the form of micro- and nanoparticles as compared to non-modified lignin [129]. Nevertheless, one of the main constraints regarding lignin application in cosmetic products is its typical dark brown color. To overcome this limitation, Zhang et al. [130] suggested the use of solvent fractionation and acetylation to produce light-colored lignin from eucalyptus. The procedure consisted of kraft lignin fractionation by methanol/water to remove the condensed structures and then acetylation by acetic anhydride to block the free hydroxyls. After the two-step treatment, the color of lignin was highly lightened by 313.5% owing to the separation of dark-colored condensed structures and the blocking of free hydroxyls [130]. In this study, the light-colored lignin was blended with an SPF15 lotion, and the SPF of the blend was boosted from 15.3 to 75.2 in the presence of 8% lignin [130].

Despite the research on lignin as a cosmetic ingredient points out a tremendous potential, it is still in an embryonic phase as compared with other areas of application. For this reason, it is crucial to circumvent issues mainly related to color, along with complex structure, polydispersity in molecular weight, and some impurities [129].

7.2. Materials

Lignin from different sources has been explored for different materials, including nanoparticles, films and coatings, and textiles. This section summarizes the potential of lignin from sugarcane in the materials field.

7.2.1. Nanoparticles

In recent years, lignin nanoparticles have increased attention in a wide range of applications due to their unique properties. Lignins from different sources and isolations methods have been explored for the production of nanoparticles [131–133]. Some of the sources explored include elephant grass [134], Japanese cedar [135], poplar, berry, and fig [136], bamboo [137], and wood [138]. The studies reveal the enormous potential of lignins in this field for industrial applications. Recently, some applications with micro or nanosized lignin from SCB

have been reported, namely as a bioinsecticide [139], graphene microcrystal [140], nanostructured films [56], and biosorbent [141]. Bertolo et al. (2019) focused on the comparison between two environmentally friendly ways of obtaining colloidal lignin nanoparticles (solvent shifting and direct dialysis), considering minimal processing steps, and employing lignins derived from two SCB pre-treatments (alkaline and organosolv). Results showed that the preparation method had more influence over the properties of the nanoparticles than the physical and chemical properties of the raw materials [111]. However, investigation on the effect of the lignin source and lignin nanoparticles production methods in nanoparticles properties (morphology, physical stability and performance) is required [111]. The main drawback associated with lignin nanoparticles preparation is related to the use of hazardous solvents (e.g. acetone and dimethyl sulfoxide); consequently, it is desirable to develop eco-friendly methods for lignin nanoparticles synthesis maintaining optimum properties for specific applications [88]. Another important issue that needs to be addressed is the low yield of nanoparticles obtained by different methods, in order to integrate it into an economically viable biorefinery process chain [142]. Additionally, safety demonstration of various lignin grades remain of utmost importance for future applications in food, nanomedicine, and healthcare materials [143].

7.2.2. Films and coatings

The hydrophobic nature of lignin is an interesting property to explore for food packaging purposes, which includes films and coatings. Some studies are available for lignin from different sources reporting promising results for lignin application in films and coatings [144–149]. Besides hydrophobicity, the ability to absorb UV light, antioxidant and antimicrobial properties are unique features for the development of films and coating materials [150,151]. Lignin from SCB was already studied as a potential ingredient for chitosan films. The incorporation of lignin into chitosan films resulted in the decrease of water content and solubility of the composite films [152]. Lignin dispersed well and showed strong tensile strength and ductility in the films [152]. This study suggested that the incorporation of lignin into chitosan films may be applied for the development of an active food packaging material. SCB lignin at five different amounts (1, 3, 5, 10, and 15% (w/w)) was also blended with a composite film between polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP) by solvent casting. Both PVA and PVP were miscible with lignin due to intermolecular hydrogen bonding between OH groups of the PVA or PVP and lignin. According to the obtained migration results, the PVA films blending with lignin up to 3% (w/w) and the PVP films blending with lignin up to 5% (w/w) could be considered suitable for application in the fatty food packaging field [153]. Another study reported the effect of alkaline lignin from SCB, in the presence and absence of ethanol, on the fresh fruit shelf life. The test of coating formulas on limes demonstrated that coating solutions of 0.8% (w/w) xanthan gum and 1.5% (w/w) extracted lignin from 40% (w/w) NaOH had the potential to maintain weight loss and color change [154]. Higher antifungal activity was observed for limes coated with extracted lignin than limes coated with commercial lignin. These results could be explained by the presence of hemicellulose in extracted lignin molecules, which could act as a thick barrier against gas exchange between inner and outer environments. Studies of lignin from SCB towards the development of films and coatings are scarce, nevertheless the existing studies associated with the studies available for lignin from different sources are promising indicators for the development of research in this field.

7.2.3. Textile

Textiles are integrated in a group of materials, which have been widely used in clothes, domestic, medical, and technical applications. They are characterised by a unique combination of properties including strength, flexibility, elasticity, softness, durability, heat insulation, low weight, water absorbency/repellence, dyeability and resistance to

chemicals [155]. Lignin was reported as a fire retardant and dying on textiles [156]. Lignin has also been referred as a candidate to as a UV blocker and antibacterial properties for linen fabrics in the form of nanolignin [157]. Lignin from SCB was coated on fabric to be used as potential additional fabric in a sanitary mask [96]. Results obtained suggested the potential of lignin in filtration and antimicrobial textile applications. Although lignin has interesting properties to be explored for the textile industry, this field requires more research to validate the potential and safety of lignin application.

8. Conclusions

The valorization of bagasse and straw by-products from the sugarcane industry into value-added compounds is an emerging trend from a circular economy perspective. Lignin is one of the components with tremendous potential for application in different fields. Nevertheless, several factors need to be analyzed for the development of efficient, safe and economically viable products. Starting in the source of lignin, SCB and SCS, the costs associated with transport are considerable, as they have low density [23]. SCS is an overlooked raw material as it is either left in the fields or used to generate energy even though it has high cellulose and lignin contents. Therefore, most studies on lignin extraction and biological potential reported in the literature are for SCB. Lignin properties are related to biomass source and extraction process, and, for this reason, the source and pre-treatment selection is crucial for its valorization. SCB and SCS possess distinct chemical properties, and these are determined by the employed pre-treatment. In terms of biological potential, antimicrobial and antioxidant activities appear as the most promising ones. In addition, the capacity of lignin to protect from UV radiation can be a significant step forward in the use of lignin as a cosmetic ingredient. In terms of applications, despite the interesting results arising from the literature, the practical application of lignin is relatively complex. The validation of lignin-based products requires compliance with safety regulations and economic viability.

Data availability

No data was used for the research described in the article.

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