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REVIEW ARTICLE

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Crop residues: applications of lignocellulosic biomass in the context of a biorefinery

Abstract Interest in lignocellulosic biomass conversion technologies has increased recently because of their potential to reduce the dependency on non-renewable feedstocks. Residues from a variety of crops are the major source of lignocellulose, which is being produced in increasingly large quantities worldwide. The commercial exploitation of crop residues as feedstocks for biorefineries which could be used to produce a variety of goods such as biofuels, biochemicals, bioplastics, and enzymes is an attractive approach not only for adding value to residues but also for providing renewable products required by the expanding bioeconomy market. Moreover, the implementation of biorefineries in different regions has the potential to add value to the specific crop residues produced in the region. In this review, several aspects of crop residue application in biorefineries are discussed, including the role of crop residues in the bioeconomy and circular economy concepts, the main technical aspects of crop residue conversion in biorefineries, the main crop residues generated in different regions of the world and their availability, the potential value-added bioproducts that can be extracted or produced from each crop residue, and the major advantages and challenges associated with crop residue utilization in biorefineries. Despite their potential, most biomass refining technologies are not sufficiently advanced or financially viable. Several technical obstacles, especially with regard to crop residue collection, handling, and pre-treatment, prevent the implementation of biorefineries on a commercial scale. Further research is needed to resolve these scale-up-related challenges. Increased governmental incentives and bioeconomic strategies are expected to boost the biorefinery market and the cost competitiveness of biorefinery products.

Keywords crop residue, biorefinery, bioproduct, biomass, circular bioeconomy, enzyme

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1 Introduction

Sustainable development is defined as “producing for the needs of today without compromising those of future generations” by the World Summit on Sustainable Development [1]. In this context, bioenergy is one of the several resources used to improve living standards and promote sustainable development using renewable sources for the generation of ‘clean energy’ and reduction of the dependence on fossil fuels [2]. The interest in lignocellulosic biomass conversion technologies has increased recently owing to their potential for energy and bioproduct generation without the use of non-renewable feedstocks; thus, these technologies can potentially contribute to air quality improvement and reduction of greenhouse gas (GHG) emissions [3].

Lignocellulosic biomass is mainly derived from plant materials, including crop residues, forest residues, wood crops, industrial wastes, municipal solid waste, and food waste. Additionally, grasses can be grown for biomass generation [2]. Lignocellulosic biomasses of different types are distributed worldwide but vary spatiotemporally in their availability. Each region produces a specific set of biomasses according to its agricultural and agro-industrial activity. These alternative feedstocks can be converted into a variety of bioproducts in biorefineries, including bioenergy (in the form of biofuels and bioelectricity), enzymes, chemicals, and materials (e.g., biosorbents and bioplastics) that are valuable to the market.

This review focuses on the importance of crop residues in the context of biorefineries and the circular bioeconomy concept. It summarizes the main crop residues generated in different regions of the world and their availability, the potential value-added bioproducts that can be extracted or produced from crop residues, and the major advantages and obstacles associated with crop residues utilization in biorefineries.

2 Crop residues in circular bioeconomy

The European Commission defines bioeconomy as “the production of renewable biological resources and the conversion of these resources and waste streams into value-added products, such as food, feed, bio-based products and bioenergy” [4]. The bioeconomy concept covers all the economic and industrial sectors and systems that use or process renewable biological resources (animals, plants, microorganisms, and derived biomass, including organic waste) as well as their functions and principles [4–6]. Importantly, a fundamental aspect of the bioeconomy is the mitigation of GHG emissions using renewable resources rather than fossil resources. For this reason, a shift from a fossil-based economy to a bio-based economy is seen as essential for achieving global climate targets set in the Paris Agreement [3]. Complimentary to the bioeconomy concept, a circular economy is based on the concept that the residues from one industrial process will be useful as feedstock for another, in such a way that the environmental impact will be almost zero and the residues, which were originally considered to be waste products, will have economic value [7], as demonstrated in Fig. 1.

In a circular economy, the “restoration” pathway replaces the “end-of-life” concept and residues are recycled, resulting in high-value-added products. By using residues as feedstock, the circular economy aims to add commercial value to otherwise discarded waste products and reduce environmental, economic, and social problems that arise from inappropriate residue disposal [8,9]. Combining both concepts, the circular bioeconomy is an economic system in which the basic building blocks for materials, chemicals, and energy are derived from renewable biological resources (including crop residues and byproducts from crop residue processing) and is described as an industrial system that is restorative or regenerative by design. In this context, biorefineries that use crop residues as feedstock to produce value-added products are key players in the circular economy [7,10].

3 Enzyme-based crop residue biorefineries

Crop residues have the potential to replace non-renewable resources owing to their high availability and structural composition (rich in polysaccharides and lignin). The increasing production of lignocellulosic biomass from crop residues as a result of the growing demand for agricultural products is currently raising environmental concerns. Consequently, interest in the utilization of crop residues as feedstock for biorefineries has increased, as it represents a biomass management tool that integrates recycling and remediation in an environmentally friendly manner [3], reduces the pollution generated by inappropriate disposal [11], and adds value via bioproduct generation.

Biorefineries based on lignocellulosic biomass, such as crop residues, have emerged as the most suitable substitutes for petroleum-based refineries. This new concept includes a wide range of new technologies capable of converting the structural components of biomass into bio-based products such as fuels, value-added co-products, and other applications [12,13]. There are several biorefin-

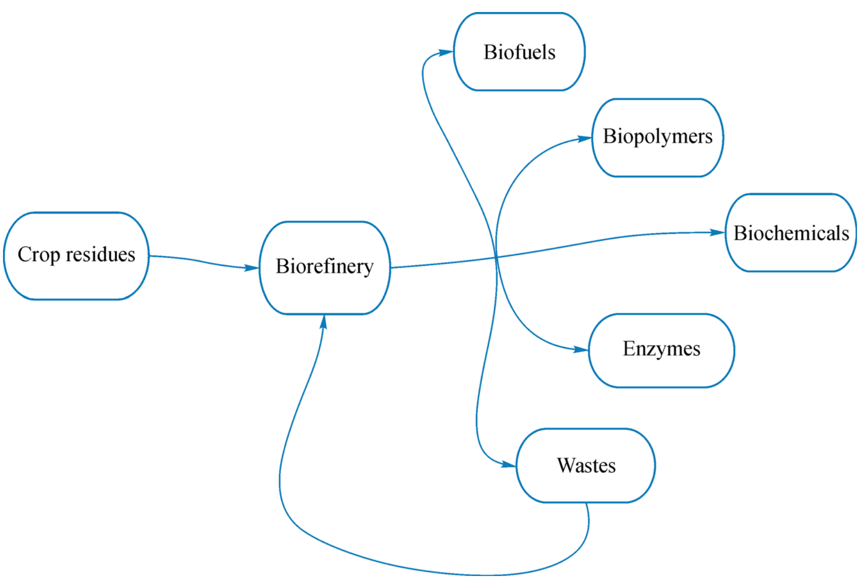

Fig. 1 Use of crop residues in the context of biorefineries and circular bioeconomy.

ery platforms (e.g., carbohydrates, syngas, lignin, and pyrolytic liquid) that can be employed as key intermediates between raw materials and final products [14].

Holocellulose (cellulose, hemicellulose, and pectin) and lignin are the main structural components of lignocellulosic raw materials. The complex three-dimensional constitution of these substrates involves physical and chemical interactions between holocellulose and lignin, ensuring structural stability and resistance of the plant cell wall [15,16]. The degradation of polymers from lignocellulose into their structural monomers, usually achieved via an enzymatic pathway, is essential for further synthesis of biofuels and building block chemicals in biorefineries [3].

A pool of enzymes (e.g., cellulases, hemicellulases, lytic polysaccharide monooxygenases, ligninases, and cellobiose dehydrogenases), in combination with other proteins (swollenins and expansins), is required to fully degrade the cell wall from crop residues [17]. In a natural system, this degradation is performed by microbial consortia that synthesize a broad range of hydrolytic and non-hydrolytic enzymes with different modes of action and broad and restricted specificities that act synergistically to disrupt and fully degrade plant biomass [18].

Based on this natural process, large-scale biomass degradation in biorefineries is achieved using enzymatic cocktails produced by selected microorganisms. Enzyme production is one of the most important steps for biomass refining to be economically viable, but the cost of production remains high. An understanding of enzymatic synergism is crucial to enhance the speed of enzymatic biomass conversion and reduce enzyme loads and hydrolysis time, important factors determining the cost of hydrolysis of lignocellulosic substrates [17]. It is necessary to select highly productive microorganism strains that demonstrate high expression of a wide range of carbohydrate-active enzymes (CAZymes) and lignin-degrading enzymes when cultured on different types of lignocellulosic substrates [17]. Filamentous fungi are generally employed as enzyme-producing organisms. *Trichoderma* [19,20], *Aspergillus* [21], and *Penicillium* species are frequently used for CAZyme production, whereas white-rot fungi are mostly used to produce lignin-degrading enzymes [22].

Either off-site enzyme production (in which one single enzyme-producing plant provides enzymes for multiple biorefinery plants) or on-site enzyme production (in which enzymes are produced in an operational unit annexed to a biorefinery plant) can be employed. On-site enzyme production in biorefineries may be a viable alternative to reduce costs and GHG emissions associated with enzyme production. In this approach, crude enzyme cocktails can be directly applied to crop residue hydrolysis with minimal enzyme processing and no transportation requirements [17]. In addition, the use of lignocellulosic biomass such as crop residues as a carbon source for on-site enzyme production (a process referred to as integrated enzyme production) enables the synthesis of enzyme consortia tailored to the topographic and bromatological characteristics of each particular lignocellulosic material [11,14,16–18,23]. In this case, depending on its structure and composition, each specific crop residue induces the production of a specific set of enzymes [23]. Integrated enzyme production adds further value to crop residues and broadens the portfolio of products produced in biorefineries, since enzymes are highly valuable biocatalysts (more valuable than biofuels) that have industrial applications other than crop residue biorefining, such as in the pulp and paper industry, textiles, detergents, animal feed, food, beverage, and nutraceuticals (e.g., probiotics, antioxidants, and vitamins) [24–28]. Figure 2 summarizes the different types of lignocellulose-degrading enzymes involved in biomass refining and other potential biotechnological applications. The use of crop residues for the production of enzymes is a promising market. The global market for enzymes has grown in recent years, reaching almost \$4.6 billion and \$4.9 billion in 2014 and 2015,

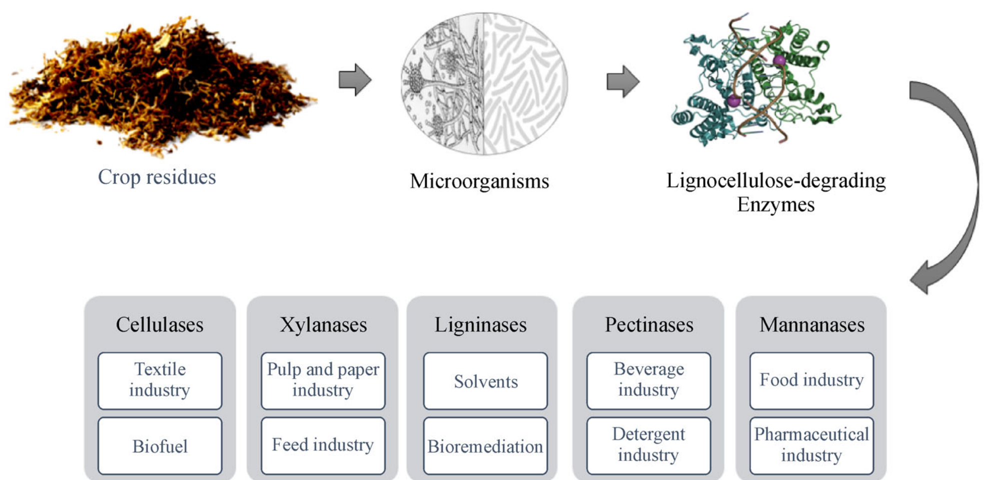

Fig. 2 Lignocellulose-degrading enzymes from microorganisms and their biotechnological applications.

respectively [29]. This market is expected to expand to around $6.3 billion by 2021, with a compound annual growth rate of 4.7% from 2016 to 2021 [29].

4 Global overview of crop residue generation

The term agricultural residue encompasses all plant biomass generated as a byproduct during harvesting or crop processing. Crop residues were defined by Searle and Marlins [30] as the parts of the aboveground plant that are not eaten nor have other primary uses. The residue ratio, or ratio of residues to the main crop product, is highly variable. These residues can be classified as primary, secondary, or tertiary [25,31]. Primary residues (e.g., rice straw, sugarcane top and straw, coffee husks, corn stalks and straw, wheat straw, empty palm fruit bunches and frond, and vine trimming shoots) are generated in the field at the time of harvest, while secondary residues (e.g., rice husks, sugarcane bagasse, corncobs, soybean hulls, distiller's dried grains, sand from sugarcane ash bagasse, wastewater, and black liquor) are co-produced during processing. Tertiary residues are the remains that arise from (partial) final consumption (e.g., food leftovers).

According to a study conducted by Tripathi et al. [32], cereal straw contributes to 66% of the world's residual plant biomass. Nevertheless, cereal primary residues (e.g., wheat straw, rice straw, and corn stover) cannot be entirely removed from the field and destined for bioenergy production and biorefining since these biomasses play a key role in maintaining the fertility, organic carbon levels, nitrogen levels, humidity, and the micro- and macrobiota of soils; stabilizing soil temperature; and preventing soil erosion [33–35]. Importantly, if biomass is removed, soil fertilizer must be added to compensate for biomass removal, but that does not compensate for other factors such as erosion, temperature, and humidity control [26,35]. Broad projections usually estimate that 60%–70% of crop residues must be left in the field for ecological purposes [27,30]. When individual crop residues are considered, the estimated average sustainable removal rate is 40% for wheat straw (ranging from 15% to 60%), 50% for corn stover (ranging from 25% to 80%), and around 60% for rice straw [28]; however, these are broad generalizations. The rates of sustainable biomass removal vary greatly according to not only crop type, but also a number of other site-specific factors such as soil characteristics, climate pattern, the slope of the terrain, and farming practices such as tillage and crop rotation [28,35]. Residue removal from the field is also restricted by the costs and technical limitations of biomass collection, baling, handling, and transportation [36]. The amount of collected crop residues that may be utilized for bioenergy production and biorefining is further limited by other competing uses of the biomass, such as feed for livestock, animal bedding, horticulture, substrate for mushroom production, and traditional burning for heat [28,30]. The effects of crop residue removal on soil fertility, crop yields, and GHG emissions have been studied, but further efforts are required to calculate the sustainable balance between biomass-to-soil and biomass-to-bioproduct conversions with respect to their environmental, economic, and social impacts [33].

Crop residues are not equally distributed worldwide; they have distinct regional characteristics, and their availability varies spatiotemporally. Table 1 summarizes the agricultural production and the associated residue generation of different crops globally and the main countries producing each crop during the 2016 and 2017 harvest. Figure 3 shows a map of the main agricultural residues produced in each continent. The major crop residues produced in each global region are discussed below.

4.1 Americas

A substantial area of land in the American continent is exploited for agriculture and, consequently, a considerable amount of crop residue is produced each year. Brazil and Argentina are the main producers and exporters of food in South America, with 43 and 37 million hectares available for agriculture, respectively. Brazil is the world's largest producer of sugarcane, coffee, and oranges and is a major producer of soybean, corn, cotton, and beans, while Argentina mainly produces corn, soybean, wheat, and grape [38]. Large-scale agricultural production results in the generation of large amounts of residues [38]. The US, in turn, is the world's largest producer of corn, soybeans, and sorghum and a major producer of wheat. Currently, however, approximately 90% of corn residues in the US are left in the fields after harvesting, and less than 1% of the residue is collected for industrial processing [38,44,45], indicating that these residues are still an untapped renewable resource and that the corn residue conversion industry is still in its infancy.

4.2 Asia

Asia is also a major producer of crop residue. After Brazil, India and China are the largest producers of sugarcane [46]. The Asian continent is the main producer of wheat (43%), and China and India account for more than half of the global cotton production. Moreover, about 90% of the world's rice is produced in Asia, especially in Bangladesh, China, and India. About 65% of the apples produced in the world also come from Asia, with China accounting for 50% of the global production. After processing, approximately 25% of an apple's weight becomes a residue [42].

Table 1 Correlation between the annual production of different crops and the generation of crop residues

Plantations	Leading producers	Global production /t	Total global wastes /t	Residues	Cellulose /%	Hemicellulose /%	Lignin /%	References
Cotton	China (25%), India (22%), USA (15%), Pakistan (8%), Brazil (5%)	6.54E + 07	9.81E + 07	Cotton sheets, cotton stalks	80	*	*	[37–39]
Rice	China (19%), India (18%), Indonesia (8%), Bangladesh (6%), Vietnam (4%)	7.41E + 08	1.10E + 07	Rice straw, rice hulls	25.1–38	27–37.1	8–15.2	[16,37,38,40]
Coffee	Brazil (33%), Vietnam (16%), Colombia (8%), Indonesia (7%), Ethiopia (5%)	9.22E + 06	3.67E + 06	Coffee husks, coffee pulp, wastewater	37.2	24.9	*	[37,38,41]
Sugarcane	Brazil (41%), India (18%), China (6%), Thailand (5%), Pakistan (3%)	1.89E + 09	4.73E + 08	Sugarcane bagasse, cane straw	43 –39	26 – 30	22–25	[16,37,38,40]
Barley	Russia (20%), Germany (11%), France (11%), Australia (11%), Ukraine (10%)	1.41E + 08	1.78E + 06	Barley straw	39.6	24.7	17.2	[16,37,38]
Beans	Myanmar (19%), India (14%), Brazil (10%), USA (5%), United Republic of Tanzania (4%)	2.68E + 07	3.66E + 05	Peel beans	*	*	*	[37,38]
Orange	Brazil (24%), China (12%), India (10%), USA (7%), Mexico (6%)	7.32E + 07	4.29E + 07	Orange peel, orange bagasse	*	*	*	[37,38]
Apple	China (50%), USA (5%), Poland (4%), Turkey (3%), India (3%)	8.93E + 07	5.85E + 07	Apple pomace	*	*	*	[37,38,42]
Corn	USA (36%), China (22%), Brazil (6%), Argentina (4%), Mexico (3%)	1.06E + 09	7.49E + 08	Corncobs, corn straw	37.3	25.5	13.8 – 16.7	[15,16,37,38,43]
Soybean	USA (35%), Brazil (28%), Argentina (17%), India (4%), China (3%)	3.35E + 08	2.98E + 08	Soybean hull	25	11.9	17.6	[16,37,38]
Sorghum	USA (19%), Nigeria (11%), Sudan (10%), Mexico (8%), Ethiopia (7%)	6.39E + 07	3.54E + 07	Sorghum straw	36	18	15.5	[16,37,38]
Wheat	China (17%), India (12%), Russia (10%), USA (8%), Canada (3%)	7.69E + 08	1.13E + 07	Wheat straw	35–37.3	24–28.7	17.8–25	[16,37,38,40]
Grape	China (19%), Italy (11%), USA (9%), France (8%), Spain (8%)	7.74E + 07	1.24E + 07	Grape pomace	*	*	*	[37,38]

Note: *No data available

4.3 Africa

In 2016, Africa produced 24 billion tons of agro-industrial residue [38]. The pattern of African consumption has risen (5%) above the world average (2.3%), and residues from the production of rice, wheat, sorghum, millet, and beans represent a significant amount of waste in the North and South African regions [47,48]. Corn is the main crop cultivated in the African continent, with South Africa, Nigeria, and Ethiopia producing substantial quantities of this crop and thus generating large amounts of residue related to corn [38].

4.4 Europe

Europe is one of the world's largest producers and suppliers of food and fiber, accounting for about 20% of global cereal, 32% of wheat, and more than 60% of oat production [16,38]. Corn cultivation has high water requirements during crop development. Despite the periods of constant droughts and heat waves, Europe is the third-largest producer of corn in the world, surpassed only by the Americas and Asia [49,50]. According to Olesen et al. [50], measures are currently being adopted in many European regions to adapt to climate changes and maintain the current crop yields, including the use of new cultivars and changes to the cultivation timing and tillage and fertilization practices with a focus on the conservation of soil and groundwater. Countries such as Ukraine, Russia, France, and Romania, which have the most significant resources for irrigation, lead the production and manufacture of feed and animal feed silage. However, 16% of the total production becomes residue [38].

4.5 Oceania

Oceania's agriculture is characterized by the production of low-intensity and large-scale crops due to vast tracts of arable land [51]. The primary cultures include wheat, oat, and sugarcane, all of which generate large amounts of residues. In many cases, oats serve as a rotation crop in some states of Australia due to its ability to break the pest life-cycle and renewal of pasture fields. Currently, with the encouragement of conservation agriculture and increased organic agriculture, Oceania is the largest organic producer in the world, with 17.3 million hectares planted (40% world production) [52]. With this practice, lesser plant residues accumulate since they are largely recycled back to the soil as an organic soil management strategy [53].

5 Applications of crop residues

The use of crop residues as feedstock for bioproducts is promising because of their abundance and low cost [54]. However, most technologies for the conversion of crop residues to biochemicals, biomaterials, and eco-friendly fuels are not yet fully developed to the industrial scale and are not cost competitive. Several technologies developed by academia and the private sector are available at different technology readiness levels (TRL) [14,55]. Some of these technologies are at TRL 1 and 2, requiring extensive research and time before they can be industrially applied. Others are at TRL 8, indicating that they are ready for implementation with an already existing technology or a technology platform. However, their commercial feasibility is uncertain. Tables 2–7 and Fig. 4 exhibit several

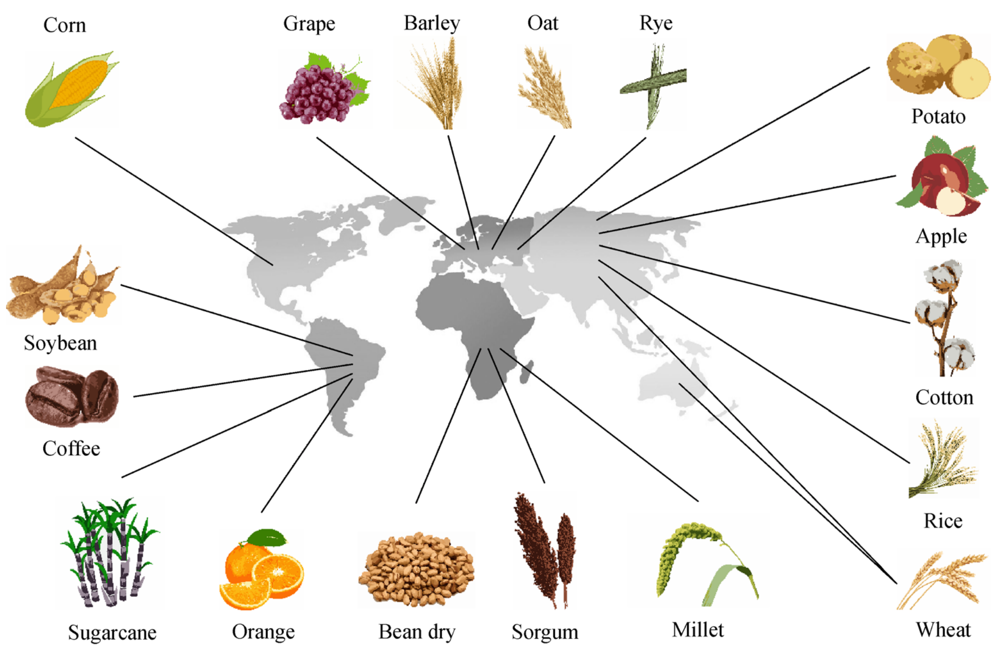

Fig. 3 An overview of the main agricultural crops produced in the world.

potential biotechnological applications of crop residue products, including in the production of biofuels, biomaterials, enzymes, and nutraceuticals. None of the examples mentioned in Tables 2–7 are currently being practiced commercially, except for bioethanol production from sugarcane, corn, and wheat residues. The production of bioethanol from crop residues at a commercial scale has been conducted intermittently since 2014 by different companies around the world, including the USA, Brazil, and European countries such as Italy, and new commercial-size facilities are planned or are under construction in different countries. Nevertheless, several technical problems, as discussed later in the text, and the narrow profit margins of lignocellulosic ethanol have forced several commercial operating units to curtail or cease production, either permanently or temporarily, and dedicate research and development efforts toward overcoming technical hurdles [3,56,57].

Bioenergy production has traditionally been the focus of biomass conversion research. Different assessments on the bioenergy potentials by 2050 have been performed, and different researchers have reported divergent results due to differences in the methodological approaches and assumptions applied [58]. Beringer et al. [59] pointed out that a combination of all biomass sources may provide between 130 and 270 EJ/a in 2050, equivalent to 15%–25% of the world' s future energy demand. In this case, energy crops would account for 20%–60% of the total potential depending on land availability and the proportion of irrigated area. On the other hand, a reassessment of global bioenergy potential in 2050 made by Searle and Malins [30] estimated that the maximum plausible limit for sustainable energy crop production would be 40–110 EJ/a.

Although bioenergy has traditionally been the focus of biomass conversion, other bioproducts of higher value, such as chemicals, plastics, and enzymes, could improve the overall competitiveness of biorefineries. The production of organic acids, biodegradable plastics, or enzymes from biomass residue feedstock will add to twice the commercial value compared with electricity, animal feed, and fuel production [60]. From chemical and biotechnological perspectives, almost all chemicals and building blocks for plastics can be made using renewable raw materials [61]. For example, the replacement of bisphenol A, a chemical compound used since the 1960s in the manufacture of synthetic polymers (e.g., polycarbonate plastics and epoxy resins) and widely distributed in products used daily (e.g., packaging and bottles), with aromatic building blocks from biological sources, such as phenols, is an innovative strategy for application in the polymers and plastic industries [61]. Moreover, the variety of natural polyphenols allows an array of different possibilities for fine-tuning to a specific application, which is not possible with monostructural chemicals such as bisphenol A [62]. According to de Jong et al. [63], the global production of bio-based chemicals and polymers is estimated to be around 50 million tons per year.

According to the 2018 market data [64], the global production of bioplastics is expected to increase by

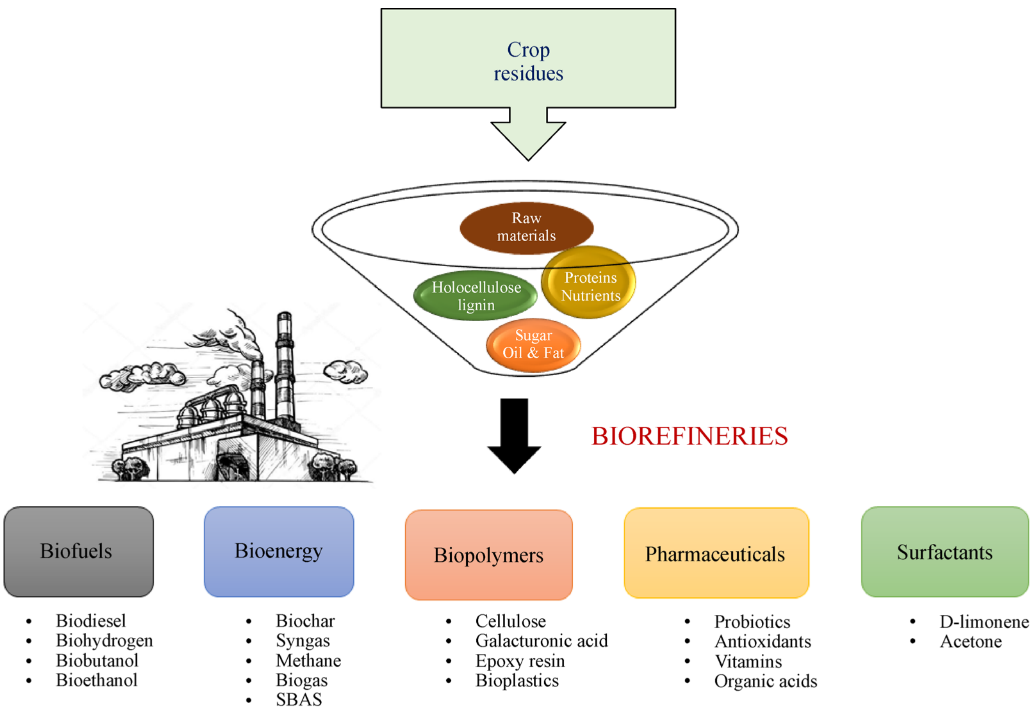

Fig. 4 An overview of crop residue applications in lignocellulose-based biorefineries.

Table 2 Biorefinery applications of coffee residues

Residue	Application	Conversion process	Reference
Coffee silverskin	Production of levulinic acid	Water-soluble phenolics were extracted from CS through hydrothermal pre-treatment in a microwave reactor. Pretreated CS was then subjected to diluted hydrochloric acid treatment in a microwave reactor with varying biomass loadings, acid concentrations and reaction temperature/ time to produce levulinic acid	[79]
Coffee silverskin	Production of α-amylase	SSF process using a fungal strain *Neurospora crassa* CFR 308	[80]
Coffee wastes	Production of biogas	Alkaline and acid pre-treatments of a mixture composed of coffee seed skin, seed refuse and coffee product refuse followed by the inoculum of cow and chicken manure and an anaerobic sludge taken from a domestic water treatment system	[89]
Coffee wastewater	Production of bioethanol	Batch fermentation using *Hanseniaspora uvarum* UFLA CAF76 as inoculum in ground coffee pulp mixed with coffee wastewater	[90]
Coffee husks	Production of endoglucanase	Steam-exploded coffee husks were used as substrate for cellulase production using *Rhizopus stolonifer* CFR 307 under SSF. Fermentation parameters (pH, moisture and fermentation time) were optimized through response surface methodology (RSM). Enzymes thus produced were applied in ethanol production from coffee husks and as additive in detergent formulation	[86]
Coffee husks	Production of gibberellic acid	SSF and SmF fermentation of alkali pretreated coffee husks and cassava bagasse (7:3, dry wt) employing *Gibberella fujokuroi* LPB-06	[91]
Coffee husks	Production of carotenoids	Alkaline-pretreated coffee husks were used as substrate for *Rhodotorula mucilaginosa* CCMA0156 as carotenoid-producing strain under SmF. Intracellular carotenoids were extracted with different organic solvents	[92]
Coffee husks	Production of xylanase and cellulase	Multispecies SSF process applying a specialized consortium of microorganisms (*Pseudoxanthomonas taiwanensis, Sphingobacterium composti, Cyberlindnera jardinii* and *Barnettozyma californica* among others)	[81]
Coffee pulp	Cultivation of mushrooms	Six strains of *Pleurotus* were grown in a mixture of coffee pulp and wheat straw	[93]
Coffee pulp	Production of pectinase	SSF process employing *Aspergillus niger* AW96 and SmF process employing *A. niger* AW99	[82]
Spent coffee ground	Production of biodiesel	Oil was extracted from SCG with hexane. Oil transesterification reaction was performed with ethanol or methanol via enzymatic catalysis with three commercial enzymes (Lipozymes RM 1M, TL 100L, and CALBL)	[73]

approximately 3.8% per year (from 2.05 million tons to approximately 2.44 million tons per year in the period 2017–2022). Approximately 62% of consumer product companies aim to switch their packaging to sustainable packing [61]. Despite the notable growth in bioplastics market, it is not prospering to its full potential possibly due to, at least in part, insufficient governmental incentives. Comparatively, the biofuel market in several countries such as Brazil, US, and members of the EU is largely driven by national support policies and legislation, including mandates for obligatory biofuel blending, differential taxation systems, subsidies, and official targets for the reduction of GHG emissions [65]. Other bio-based products, such as bioplastics, that may replace fossil-based analogs are not under government incentives to the same extent as biofuels and should receive greater attention from policymakers [66]. The employment of similar bioeconomy strategies in the bioplastics sector as well as to other bio-based chemicals and materials, is expected to accelerate growth rates by expanding consumer markets and by enabling competitive pricing [66].

In the upcoming sections, some of the major crop residues are described, together with their potential for bioproduct generation.

5.1 Coffee

Coffee is the world's 111th most-traded commodity in value and 119th in quantity, according to the International Trade Centre (ITC) [67,68]. Brazil is currently the largest producer, with 2.95 million tons produced in 2019 [69]. Depending on the type of post-harvest processing, different types of coffee residues can be generated, such as husks, skin, pulp, and wastewater [70–72]. More than 45% of the biomass from coffee production represents residues [27]. The global production of coffee residues in 2016 was estimated to be 9.2 million tons. Therefore, coffee residues represent a sizable opportunity to produce enzymes, biofuels, and other value-added products [38].

Several previous reports have discussed the possible applications of coffee residues (Table 2). The use of oil extracted from spent coffee grounds (SCG) for the production of biodiesel via enzymatic transesterification with ethanol is an example of a promising approach for the

Table 3 Biorefinery applications of soybean residues

Residue	Application	Conversion process	Reference
Soybean hulls	Production of protease, β- amylase, α-amylase	SSF process using a fungal strain *Penicillium* spp. LEMIA 38221 in different conditions (pH, temperature and substrate concentration)	[98]
Soybean hulls	Production of ethanol	Soybean residue was pretreated with dilute H_2SO_4 and subjected to separate hydrolysis and fermentation employing commercial cellulase cocktails (a mixture of C-Tec 2 and Viscozyme L) and *S. cerevisiae* (wild-type strain or the KCCM 1129 strain adapted to high galactose concentrations)	[94]
Soybean hulls and citric pulp	Production of gibberellic acid	SSF performed with *Fusarium moniliforme* LPB 03 optimized for physical and chemical conditions (pH, initial humidity and composition of nutritive solution)	[97]
Soybean oil deodorizer distillate	Production of biodiesel	CaO obtained from calcined duck eggshell was used as catalyst for the esterification of SODD with methanol	[19]
Soybean straw	Production of biogas	Solid-state anaerobic digestion (SS-AD) of soybean processing waste (consisting of soybeans, soybean straw and soybean oil extraction residues) and hay with the effluent from a mesophilic liquid anaerobic digester as inoculum	[102]
Okara	Production of β-glucosidase	Fresh and heat-treated okara were subjected to SSF process using *Saccharomyces cerevisiae* r.f. *bayanus*	[96]
Okara	Production of probiotic	A probiotic creamy sauce was produced with *Lactobacillus acidophilus* LA3-fermented okara flour plus soymilk and different types of gelling components	[104]
Okara	Production of citric acid	Solid-state mixed fermentation of okara with *Aspergillus terreus* (involved in okara saccharification) and *Aspergillus niger* (responsible for citric acid production)	[105]
Soybean meal	Production of lipase	SSF process applying DCCR design to evaluate spore concentration, cultivation and humidity parameters affecting the enzymatic production by *Penicillium* sp. S4	[99]
Soybean meal	Production of cellulase	Cellulase production by *Chaetomium globosum* BCC5776 was performed under SmF conditions in optimized medium containing 1% soybean meal, 1% empty palm fruit bunch and 2% Avicel®. Home-made enzyme system was supplemented with commercial β-glucosidase (Novozyme® 188) and hemicellulases (Accellerase® XY) for the efficient hydrolysis of alkaline-pretreated rice straw	[106]
Soybean residues	Production of bioethanol	Two residues, i.e. skim (protein-rich fraction) and insoluble fiber (carbohydrate-rich fraction), generated from soybean oil extraction were used as additives in dry-grind corn fermentation for ethanol production. The addition of skim and/or insoluble fiber enhanced ethanol production by decreasing the corn fermentation time, increased corn distillers oil recovery from this tillage and increased the protein content while reducing fiber and oil contents of distillers dried grains	[107]

valorization of coffee grounds [73]. The use of SCG as a versatile feedstock for the production of biodiesel (from SCG extracted oil), biohydrogen (from glycerin generated as a co-product from biodiesel production), and ethanol or fuel pellets (from the remaining solid waste generated after oil extraction from SCG) has also been proposed [74]. Utilization of coffee residues such as coffee husks and pulp to feed animals has long been reported [75] as well as the use of SCG as livestock feed for ruminants, pigs, chickens, and rabbits [76].

Coffee silverskin (CS) can be used as a raw material to obtain antioxidants and vitamin E [77] via aqueous or ethanolic extraction or for the production of various compounds, including biobutanol through acetone–butanol–ethanol fermentation [78], levulinic acid [79] via acid-catalyzed hydrothermal conversion or via solid-state fermentation (SSF) of CS via enzyme (e.g., α-amylase [80], xylanases, cellulases [81] and pectinases [82]) produced by filamentous fungi such as *Neurospora crassa*, *Aspergillus niger* or microbial communities of lignocellulose-degrading bacteria, filamentous fungi, and yeasts. The high carbohydrate (30%) and lignin (30%) contents make CS a suitable substrate for application in biorefineries [83]. The high nitrogen content in CS and SGC makes these residues important sources of organic agricultural fertilizers or soil conditioners in small proportions (below 10%) without harming the environment [84]. Cellulose nanocrystals (CNC) are also a valuable material with a wide range of applications that can be obtained from CS through alkali treatment followed by sulfuric acid hydrolysis. CS-derived CNCs have been applied as reinforcing agents to obtain polylactic acid (PLA)/CNC bio-nanocomposites, which can improve the physical properties of PLA-based plastics. PLA-based plastics have been used in the industrial packaging of food and medical supplies, and the enhanced properties conferred by CNC addition can expand the applicability of this material [83]. Being a source of soluble dietary fibers and phenolic compounds, CS is also a potential functional food ingredient with antioxidant and prebiotic activity [85].

Several authors have also reported the use of different coffee samples to produce a range of different enzymes.

Table 4 Biorefinery applications of sugarcane residues

Residue	Application	Conversion process	Reference
Sugarcane bagasse and citrus residues	Production of glycosyl hydrolases	RSM methodology to select the best enzyme inducing biomass (sugarcane bagasse, soybean bran, wheat bran, apple bagasse or citrus bagasse) using *Annulohypoxylon stygium* in SmF process	[127]
Sugarcane bagasse	Production of xylanases	Pretreated SCB was used as substrate for *Aspergillus terreus* in SmF	[128]
Sugarcane bagasse	Production of xylanase	SmF process employing pretreated SCB and *Emericella nidulans*	[13]
Sugarcane bagasse	Production of endoglucanase	Enzymatically liquefied sugarcane bagasse was used as substrate for endoglucanase production by *Aspergillus niger* A12. The produced enzymes were then applied to liquefy sugarcane bagasse for later use as substrate for enzyme production in a closed-loop strategy	[12]
Sugarcane bagasse	Production of cellulase, β-glucosidase and xylanase	Mathematical model describes enzyme production by *Trichoderma harzianum* P4P11 through variation of substrate concentration, cell growth and induction of different enzyme classes (cellulases, β-glucosidases and xylanases) using steam-exploded and alkali-pretreated SCB	[116]
Sugarcane bagasse	Production of biobutanol	Biorefinery model was created based on Aspen Plus® simulations to produce sugar, ethanol and butanol (25:50:25 configuration) employing strains of *Saccharomyces cerevisiae*, *Clostridium saccharoperbutylacetonicum* or mutant strain *Clostridium beijerinckii* BA101	[126]
Sugarcane bagasse	Production of levulinic acid	Biorefinery model that fractionates SCB and wheat straw using liquid hot water pre-treatment and enzymatic hydrolysis with commercial cocktail Cellic® CTec2	[119]
Sugarcane straw	Production of bioethanol	Application of the semi-mechanistic model using SS hydrothermal pretreated with and without alkali delignification with 4% NaOH and enzymatic hydrolysis employing Cellic® CTec2	[129]
Sugarcane straw	Production of lignin	Lignin with high degree of purity (> 98%) and low sulfur content (< 2%) was extracted from sugarcane straw through SO_2-ethanol-water fractionation at different temperatures (135°C–160°C)	[123]
Sugarcane straw	Production of xylitol	The hemicellulosic hydrolysate obtained through dilute acid pre-treatment of sugarcane straw with 1% H_2SO_4 was fermented with *Candida guillermondii* FT20037 using three nutritional supplementation conditions	[64]

Table 5 Biorefinery applications of corn residues

Residue	Application	Conversion process	Reference
Corn stover	Production of methane	Chicken manure supplemented with corn stover or maize silage was used as substrate for methane production via anaerobic digestion	[141]
Corncobs	Production of prebiotic xylooligosaccharides	Milled corncobs were alkaline pretreated with various concentrations (2%, 4%, 8% and 12%) of NaOH or KOH following incubation with *Enterococcus faecium* TCD3, *E. fecalis* CCD10, *Lactobacillus maltromicus* MTCC108 and *Lactobacillus viridiscens* NCIM2167	[142]
Corncobs	Production of biosorbent	Biosorbents were prepared by treating corncobs with H_3PO_4, H_2SO_4, HNO_3, NaOH, or Na_2CO_3	[134]
Corncobs	Production of biogas	Corncobs were subjected to alkaline extrusion pre-treatment (0.4% NaOH) and hydrolyzed with commercial endoglucanase (Novozymes Ultraflo® L) or crude enzyme extract from *Aspergillus terreus* CECT 2808 grown on corncobs under SSF condition. A mesophilic anaerobic sludge was used as inoculum for biogas production through anaerobic digestion of hydrolyzed corncobs	[143]
Corncobs	Production of microcrystalline cellulose	Steam explosion pre-treatment of cotton gin wastes and corncobs followed by 20% NaOH extraction, 25% H_2O_2 bleaching and microcrystalline cellulose conversion with HCl, H_2SO_4 and Spezyme CP® cellulase enzyme preparation	[138]
Corncobs	Production of cellulase	SSF process employing *Trichoderma reesei* ZU-02	[144]

For example, coffee husks were used as a substrate for endoglucanase production by *Rhizopus stolonifer*, and the enzymes were then applied in ethanol production by simultaneous saccharification and fermentation of coffee husks and as a detergent additive for improved washing [86]. Dias et al. [87] tested the production of β-glucosidases by *Bacillus subtilis* in coffee pulp in submerged fermentation, obtaining a maximum yield of 22.59 IU/L in 24 h at 36.6°C with a pH of 3.64. Furthermore, a mixture of coffee pulp waste and pineapple waste was used for the production of cellulases by *Acinetobacter* sp. TSK-MASC under solid-state fermentation, yielding up to 888 U/mL under optimized conditions [88].

Table 6 Biorefinery applications of wheat residues

Residue	Application	Conversion process	Reference
Wheat straw	Production of bioethanol	H_2SO_4-catalyzed steam explosion pre-treatment of wheat straw followed by SSF process employing Novozymes A/S cellulase/β-glucosidase cocktail and *Kluyveromyces marxianus* CECT 10875	[147]
Wheat straw	Production of biogas	Pre-treatment of wheat straw with *N*-methylmorphine, *N*-oxide, ethanol (Organosolv) or NaOH followed by anaerobic digestion using a digestate from local manure and dairy residue anaerobic digestion plant as inoculum	[148]
Wheat straw	Biosorption of cadmium and copper	Wheat straw was pretreated with 10% HNO_3 and neutralized with 1N NaOH before being used as an efficient biosorbent of Cd^{2+} and Cu^{2+}	[150]
Wheat straw	Production of bacterial cellulose	Wheat straw was pretreated with ionic liquid [(AMIM)Cl] under optimized conditions, saccharified with commercial cellulase and the straw hydrolysate was employed as the carbon source for the production of bacterial cellulose by *Gluconacetobacter xylinus* ATCC 23770	[151]
Wheat straw	Production of levulinic acid	The production of levulinic acid from acid hydrolysis of wheat straw was optimized with RSM methodology (effects of temperature, sulfuric acid concentration, reaction time of production and liquid: solid ratio were analyzed to increase yield)	[152]
Wheat straw	Mushroom cultivation	Rice and wheat straw without supplementation were used as a substrate for growing *Pleurotus sajor-caju* where relative humidity, temperature and ventilation were strictly controlled	[153]
Wheat straw	Production of bioethanol	Native non-adapted *Saccharomyces cerevisiae* are often used in a combination of physicochemical pre-treatments of wheat straw	[146]

Table 7 Biorefinery applications of rice residues

Residue	Application	Conversion process	Reference
Rice straw	Production of cellulase	SmF process employing milled straw treated with 1.25% or 5% NH_4OH using *Trichoderma reesei* ATCC-66589 and *Humicola insolens* ATCC-26908 as enzyme producers	[158]
Rice straw	Production of biochar	Straw and rice husks of two different varieties (*Koshihikari* and IR50404) were exposed to high pyrolysis temperatures (300°C–800°C)	[166]
Rice straw	Production of biobutanol	The enzymatic hydrolysate of non-pretreated rice straw was used as carbon source for ABE fermentation with *Clostridium saccharoperbutylacetonicum* N1-4 for biobutanol production. High initial cell concentration under non-sterile conditions achieved the similar butanol yields obtained under sterile conditions	[168]
Rice straw	Production of bioelectricity	Impregnation of rice straw with $FeCl_3$ solution (10% w/v) followed by heat pre-treatment and enzymatic hydrolysis with enzyme pool from *Aspergillus niger* and *Trichoderma reesei*. The fuel cell reactor was loaded with the diluted hydrolysate in an anode compartment including dissolved air as the final electron acceptor	[169]
Rice residues (straw and husk)	Production of nanosilica	Rice residues were burned until ash generation and treated with sodium hydroxide. Sodium silicate was precipitated with HCl or H_2SO_4, washed, dried and burned at 575°C to obtain nanosilica powder	[167]
Rice straw	Production of lignin-degrading enzymes	*Myrothecium roridum* LG7 was employed for the biological pre-treatment (delignification) of a mixture of rice straw and herbaceous weed *Parthenium* sp. under SSF condition. Partially delignified biomass was more susceptible to saccharification with commercial cellulase enzymes (Accellerase® 1500) than untreated biomass	[162]
Rice husk	Production of lignin, cellulose nanocrystals and silica	Sequential acid leaching (HCl) and alkaline extraction (NaOH) were used to recover high purity lignin from rice husks. The remaining cellulose-rich solids were bleached with chlorine free treatment to yield cellulose nanocrystals. Silica was also recovered from the aqueous supernatant of lignin extraction	[170]

5.2 Soybean

Several studies have reported the biotechnological use of soy residues (Table 3). Soybean pulp, also known as okara and biji, is generated during the production of soymilk, tofu, or fried bean curd. Approximately 1.1 kg of fresh soybean pulp containing 76%–80% moisture was obtained by processing 1.0 kg of dry beans to produce soymilk or tofu [94]. Okara composition also makes it an appropriate material for the production of foodstuffs for human or pet consumption due to its antioxidant and anti-inflammatory activities. Solid-state fermentation of okara with *Saccharomyces cerevisiae* further improves its nutritional value by increasing its protein content, total phenolics, and antioxidant activity [95,96]. Furthermore, other soybean residues have been investigated as raw materials for the generation of various bioproducts, usually by solid-state fermentation with filamentous fungi. Phytohormones such as gibberellic acid, have been produced via SSF of soy husks with *Fusarium moniliforme* [97]. SSF of residues from the soybean harvest (including small and broken grains, pods, stems, and leaves) with *Penicillium* spp. have also been applied for the production of protease, β-amylases, α-amylase, and CMCase [98]. Soybean meal has been used for lipase production by *Penicillium* spp. through SSF [99].

An engineered strain of *Trichoderma reesei* was grown in several agricultural residues, and soybean hulls were found to have suitable characteristics (low viscosity, nontoxicity, and high nutrient availability) to produce large quantities of cellulases. These enzymes were then used in the hydrolysis of sugarcane bagasse (SCB), which releases high amounts of glucose [100]. Soybean hulls have also been used for the production of xylanases from *Aspergillus foetidus* [101].

Zhu et al. [102] studied the potential use of processed soybean residues (straw and bran) supplemented with digested hay for anaerobic fermentation to generate biogas (methane). It was observed that the co-digestion of the substrates increased biogas yield by 148% compared to that from single fermentation.

Soybean oil deodorizer distillate (SODD) is a byproduct of soybean oil refineries and rich in free fatty acids and triglycerides, making it a cheap carbon source for biodiesel production and a potential substitute for neutral refined soybean oil and degummed trans-esterified soybean oil (typically used in the food industry). Trans-esterification of SODD has been performed with the addition of calcinated duck eggshells (source of cheap calcium carbonate, which is transformed into CaO at high temperatures) to produce 94.6% biodiesel [19]. Granjo et al. [103] integrated the production of biodiesel into a model soybean refinery and managed to reduce the cost of biodiesel per ton of processed soybeans by 16.6%, obtaining higher commercial values in cataloged byproducts (SODD and lecithin) that were not previously part of the production chain.

5.3 Sugarcane

Sugarcane processing generates an average of 12.5% and 14% of straw and bagasse and (dry basis), respectively, and both residues present immense potential for use as feedstock in biorefineries in sugarcane producing regions (Table 4) [108,109].

Sugarcane bagasse (SCB) is the main residue in sugarcane processing and it is obtained after the grinding process for extracting the juice [46]. SCB has long been used to produce hemicellulolytic and cellulolytic enzymes. Xylanases have been successfully produced by *Aspergillus terreus* [110], *Emericella nidulans* [13], and *Penicillium echinulatum* [111], among many other fungi, using SCB as a carbon source. Cellulases and cellulolytic cocktails have also been produced using SCB as a substrate and high-yielding strains such as *Aspergillus tubingensis* [112], *Talaromyces verruculosus* [113], *Aspergillus niger* (pectinase and cellulases) [12,114,115], *Trichoderma harzianum* [116], and *Galactomyces* sp [117].

SCB usually requires a pre-treatment step prior to conversion or refining into valuable products. A combination of pretreated SCB and cane leaf matter has been investigated as a raw material for animal feeds and biofuel production in biorefineries. Steam explosion (StEx) and ammonium fiber expansion (AFEX™) increased the enzymatic digestibility of sugarcane crop residues, resulting in an estimated yield of 3881 L and 5214 L of cellulosic ethanol per hectare of sugarcane-cultivating land, respectively, under industrially relevant conditions [118]. SCB can also be used as a source of hexoses for the synthesis of levulinic acid, a platform chemical with a wide range of applications. A combination of liquid hot water pre-treatment of pelletized SCB (200°C, 30 min, 1% biomass), enzymatic hydrolysis of pre-treatment-derived cellulignin with cellulases (50°C, pH 5 for 45 min), and acid-catalyzed thermal conversion of SCB-derived glucose to levulinic acid (206°C, 30 min, and 0.63 mol/L methane sulfonic acid) resulted in a yield of 67.7% of the maximum predicted levulinic acid yield. Solvent and sulfur-free lignin with high molecular weight, an interesting co-product with multiple applications, was also obtained [119].

Sand from sugarcane ash bagasse (SBAS) is a residue generated after SCB burning for energy production in sugarcane mills. Owing to its high silica content (approximately 60%) and since it can be generated in large quantities (4 million tons in Brazil in 2017), it has been used to partially replace natural sand in the production of plaster for civil construction [120]. It has been verified that 30% of natural sand can be substituted with SBAS in plaster without altering the mechanical qualities of consistency and porosity, in addition to increasing durability.

Sugarcane straw (SS) consists of dry leaves and green tops left behind on fields to naturally decompose to improve soil quality or collected for bioenergy production (cellulosic ethanol or bioelectricity) representing one-third of the total primary energy obtained from sugarcane [121]. One ton of SS can produce 270 L of cellulosic ethanol (2G (Generation, processing stage in which ethanol was produced (1G- sugarcane juice and 2G sugarcane residues-bagasse and straw)), while 1 ton of sugarcane produces only 80 L of ethanol (1G) [122]. SS and SCB have similar compositions, with glucan, hemicellulose, lignin, and ash contents of 33.77%, 27.38%, 21.28%, and 6.23% (SS) and 37.74%, 27.23%, 20.57%, and 6.53% (SCB), respectively [108].

As for SCB, SS is also usually pretreated prior to conversion. SS has been studied for 2G ethanol production using organosolv pre-treatment [122,123]. The potential of

SS as a substrate for xylitol production has also been demonstrated by using dilute sulfuric acid pre-treatment and fermentation of the hemicellulose hydrolysate with *Candida guilliermondii* FTI 20037 [124]. SS is a potential raw material for the synthesis of cellulose acetate (CA) and carboxymethylcellulose (CMC). Candido and Gonçalves [125] proposed a four-step method for CA and CMC production from SS involving sequential acid (H_2SO_4 10% v/v) and alkaline (NaOH 5% w/v) treatments, a chelating process with EDTA, and a final bleaching step with H_2O_2 (5% v/v). CA with a high degree of substitution (2.72) was efficiently obtained, whereas a high-quality CMC product was not possible with the same process.

A biorefinery model in which sugars from sugarcane juice are diversified for the production of *n*-butanol (by acetone–butanol–ethanol fermentation with *Clostridium* cells), in addition to ethanol, sugar, and energy traditionally produced, was proposed by Mariano et al. [126] seeking alternatives to the fuel and chemical markets since butanol has the characteristics of higher blends such as automotive and aviation fuels as well as potential for application in the production of a wide range of chemicals and polymers.

5.4 Corn

Corn is traditionally used as human food and animal feed, and its residues are mainly composed of starch, protein, fiber, and oil (Table 5). In 2018, corn has also been used to produce ethanol [107]. In the US, 38.4% and 37.6% of the total corn produced in 2015 were used for ethanol production and animal feed, respectively [130].

The unfermented residues from 1G corn ethanol production are referred to as distiller's dried grains with solubles (DDGS). The high levels of protein, fiber, and oil make DDGS a valuable residue from corn ethanol production. Usually, every 25 kg of corn grain produces approximately 10.5 L of ethanol, 7.5 kg of DDGS, and 0.3 kg of corn distillers oil (CDO) [109,131]. DDGS has long been applied to produce soluble sugars for further ethanol fermentation [107,132]. DDGS is also a promising raw material for the production of D-lactic acid. As proposed by Zaini et al. [133], D-lactic acid can be produced via separate hydrolysis and fermentation or simultaneous saccharification and fermentation of alkaline-pretreated DDGS using an Accelerate® 1500 cellulase mixture and *Lactobacillus coryniformis* subsp. *torquens*. Lactic acid is considered as one of the most useful chemicals and has attracted considerable global attention owing to its widespread applications in the food, chemical, cosmetic, textile, and pharmaceutical industries. It has also emerged in the bioplastics industry, where lactic acid serves as the building block for polylactic acid synthesis [133].

Corn cobs are high bulky waste (38% dry weight after grinding) with a high cellulose content (58%) and different functional chemical groups such as alcohols, aldehydes, ketones, acids, hydroxides, ethers, and phenolic compounds in their composition. Corn cobs have a high adsorption capacity, and therefore, their use as biosorbents for the bioremediation of contaminated wastewater has been proposed. It has been demonstrated that corn cobs, when milled and chemically modified with sodium carbonate, show a high porosity and surface area, a high adsorption capacity, and serve as an efficient low-cost biosorbent of carbofuran, a highly hazardous pesticide [134]. Other corn residues, such as maize silk, maize husk, and maize tassel, can be employed as biosorbents for the adsorption of methylene blue [135], iron [136] and cadmium [137].

Microcrystalline cellulose (MCC) is increasingly being used in the food and pharmaceutical industries in excipients, binders, and anti-adherents. Its production can be carried out through the pre-treatment of cellulose-rich lignocellulosic materials, such as corn cobs. Agblevor et al. obtained high MCC production when they performed a specific order of physical and chemical pre-treatments, including grinding of the residue, steam explosion to remove lignin and hemicellulose compounds, washing cellulosic fibers with 20% sodium hydroxide, and bleaching and neutralization with sulfuric acid. The degree of polymerization achieved was 549.8 compared to 427.4 for Avicel control [138].

Corn-oil-based feedstocks can be converted into biodiesel through a transesterification process. Lipase from *Thermomyces lanuginosa* was used in the transesterification of corn oil with ethanol. It was possible to obtain a reaction yield of 98.95 wt% with a fatty acid ethyl ester content of 69.2 wt%, with linoleate (C18:2) and oleate (C18:1) being the most significant esters (relative percentages, 42.97 wt% and 22.54 wt%, respectively) [139,140].

5.5 Wheat

Wheat straw is a byproduct of the wheat grain harvest, consisting of approximately 57% internodes, 10% knots, 18% leaves, 9% straw, and 6% rachis. Wheat straw is a source of cell wall polymers such as cellulose, hemicelluloses (mainly xylans), and lignin. Considering the residue/harvest ratio for each kg of wheat grain processed, approximately 1.3 kg of straw is generated, and approximately 850 million ton wheat residues are produced annually [145,146].

Wheat straw can be used as a raw feedstock for a wide variety of applications (Table 6). Biorefinery models based on wheat straw aiming to produce bioethanol [147], butanol [85,146], biohydrogen, and methane [148,149]. In the biorefinery model proposed by Kaparaju et al. [149], wheat straw was hydrothermally pretreated, generating a hemicellulose-rich hydrolysate and a cellulose-rich solid. Liquefaction and fermentation were carried out on the solid fraction for the generation of bioethanol (0.41 g-ethanol/g-glucose), while dark fermentation of the hemicellulose hydrolysate generated biohydrogen (178 mL/g sugars). The wastes from both processes were combined and inoculated with digested manure to produce biogas (methane) through anaerobic fermentation (0.32–0.38 m^3/kg volatile solids).

The chemical, electronic, and automotive industries generate large amounts of wastewater containing heavy metals, which must be treated before being discharged. Such treatments face methodological challenges such as precipitation and landfilling of solid sludge as well as financial constraints due to the high cost of operation and chemical equipment used during processing. Wheat straw is a potential economical source of biosorbent for removing metals such as cadmium and copper in wastewater, since it can be used directly without elaborate preparation [150].

Bacterial cellulose (BC) is a natural polymer of microorganisms that is free of hemicelluloses and lignins with high crystallinity and high degree of polymerization, in addition to high resistance to elastic traction. Wheat straw is a potential raw material for BC production. Chen et al. [151] used an ionic liquid, [AMIM]Cl, for the pre-treatment of wheat straw in order to increase the rate of enzymatic hydrolysis and the yield of fermentable sugars, which were then used as substrates for BC biosynthesis by *Gluconacetobacter xylinus*. After pre-treatment optimization (110°C, 90 min, 3% biomass), the sugar yield from pretreated straw was 71.2%, which corresponds to 3.6 times more than that from untreated straw (19.6%). The yield of BC produced from pretreated wheat straw hydrolysates was higher than that from glucose-based media.

5.6 Citrus fruit

The industrial processing of citrus fruit for juice production generates a large amount of residue. Annually, approximately 121 million tons of citrus fruit residues are produced, which represents about 50% of the fruit weight (peels, pulps, and seeds). These residues are a good source of sugar, oil, polyphenols, enzymes, minerals, and vitamins, and have considerable potential for the production of multiple high-valuable bioproducts [130].

A potential application of citrus residues includes the production of ethanol, biogas, pectin, and D-limonene in an integrated biorefining approach proposed by Pourbafrani et al. [154]. In this process, citrus waste is hydrolyzed with dilute acid under high temperature and pressure, yielding a hydrolysate containing limonene, pectin, and monosaccharides derived from the partial hydrolysis of cellulose and hemicellulose. Limonene, a potent inhibitor of ethanol and biogas fermentation, is efficiently evaporated from the hydrolysate through explosive pressure reduction (yield of 8.9 L limonene/t citrus waste). Pectin is recovered from the hydrolysate through ethanol precipitation and dried (yield of 38.8 kg/t), while the cellulose and hemicellulose-derived monosaccharides are fermented with *S. cerevisiae* to produce ethanol (39.6 L/t). The remaining material from the distillation of ethanol and remaining solids are combined and used to produce biogas via anaerobic digestion (45 m^3/t) [89]. In another approach, lemon peels can be steam exploded to extract D-limonene-containing essential oils (recovered in the condensate from steam explosion treatment), and the solid fraction is subsequently hydrolyzed with pectinases, cellulases, and β-glucosidases, which are fermented to generate bioethanol (60 L/1000 kg of lemon peels). Galacturonic acid (not fermented by *S. cerevisiae*) is generated as a co-product and has applications in the food, chemical, and pharmaceutical industries [155].

5.7 Rice

Paddy rice is the final product of the harvest, and threshing paddy rice grains produce, on an average, 25% husks, 10% bran and germ. Rice straw, on the other hand, is the byproduct of the vegetative part of the rice plant. Approximately 0.7–1.4 kg of rice straw is obtained from each kilogram of paddy rice processed depending on varieties, cutting-height of the stubbles, and moisture content during harvest [130,156,157]. The high cellulose content (40%–60% cellulose), wide availability in major producing areas and low acquisition cost of rice straw make this residue a promising feedstock for cellulase [106,158] and bioethanol production (Table 7). The theoretical ethanol production from rice straw could potentially reach up to 205 billion liters per year in Asia [159,160]. However, for economically viable management and development of ethanol production from rice residues, pre-treatments are needed to overcome biomass recalcitrance and release its constituents for later use.

Biological delignification of rice residues has been applied in different studies as an alternative to chemical pre-treatment, since it prevents the production of chemical inhibitors. Saritha et al. used an actinomycete isolate (*Streptomyces griseorubens*) under SSF of rice husk for 10 days to depolymerize 25% of the lignin, allowing subsequent saccharification efficiency of 97.8% while using an Accelerase® 1500 hydrolytic cocktail [16]. A micromycete fungi *Myrothecium roridum* grown on rice straw for 7 days caused structural changes in the lignin skeleton and altered cellulose crystallinity during the colonization period, significantly increasing the amount of reducing sugars released (455.81–509.65 mg/gds, gds (gram of dried solids)) and lignin removal (5.8–6.98 mg/gds) compared with those obtained when using raw biomass [162].

A biorefinery model using rice straw to produce a broad range of bioproducts was reported by Moniz et al. [163]. Rice straw was first autohydrolysed, resulting in a hemicellulose-rich liquid that could be purified to obtain oligosaccharides. The remaining solid was treated with ethanol to obtain rich liquid lignin and a solid cellulose fraction. The ethanol-treated solids had 10% higher enzymatic digestibility than the autohydrolysed solids, owing to the removal of lignin [163]. In a similar study, rice straw hydrolyzed at 210°C under non-isothermal conditions produced liquor rich in oligosaccharides (40.1 g of oligosaccharides/100 g of initial xylan), which were purified by molecular weight using gel filtration chromatography. Different fractions containing oligosaccharides (XOS, GlcOS, and AcOS), small polysaccharides, di- and monosaccharides (xylose, arabinose, and glucose) as well as separate fractions of products and byproducts resulting from the decomposition of sugars (acetic acid, furan derivatives, and phenols) were obtained. This approach has enabled efficient purification and recovery of interesting categories of XOS that may have potential applications in the pharmaceutical, food, and food industries [164].

Although several biotechnological proposals have been presented for the use of rice husks and straw, burning is still the most common method of disposal of these residues. The open burning of rice residues, in addition to causing environmental problems, also means a waste of the biotechnological potential of the residues. Recently, the production of biochar from rice residues has presented an option for sustainable reuse in many countries. The potential of rice residues for biochar production is, among other things, due to their capacity to reach temperatures up to 1000°C [165]. Do et al. [166] examined the effect of rice variety and pyrolysis temperature on the properties of biochars produced from rice straw and rice husk at temperatures of 300°C–800°C. Biochars produced at high pyrolysis temperatures (> 500°C) presented greater surface area and higher silica content than did biochars produced at a lower temperature.

Organic silica dioxide is another bioproduct that can potentially be obtained from rice residues. Currently, the search for organic silica dioxide production from various sources has attracted considerable attention worldwide. It has been demonstrated that nanosilica can be obtained from rice straw and rice husk in two stages. First, ash from burnt rice residues was treated with a 25% sodium hydroxide solution and filtered to obtain dissolved sodium silicate. Then, the silica gel was precipitated from a solution of hydrochloric acid or sulfuric acid. The precipitate was washed, dried, and burned at 575°C to obtain the nanosilica powder. The silica content of the nanosilicate from rice husk and rice straw powders was 54.8% and 60.2%, respectively [167].

6 A few considerations on the implementation of crop residue biorefineries

One of the main obstacles limiting the development of a cost-effective crop residue biorefinery is the process of collecting the crop residue from the field and handling it through the refining process. Crop residues have low bulk density; therefore, densification (baling) of biomass is required before it can be transported to the biorefinery plant in order to optimize the transportation process. Secure storage of crop residues is also a challenge since fires have been reported in biorefinery plants of both pilot and commercial scales [171,172]. An alternative is to pretreat crop residues in a facility close to the field and densify the pretreated biomass in pellets before shipping it to the biorefinery plant, further minimizing the costs of transportation and the risks of storage of low bulk density biomass [171]. Pre-treatment itself, a fundamental step to ensure efficient enzymatic degradation, is an additional technical hurdle in pilot- and commercial-scale biorefineries. Scaling up biomass pre-treatment can be highly challenging, depending on the technology employed. Dilute acid pre-treatment, one of the leading pretreatment technologies developed for biorefineries, is particularly difficult to control throughout the process on a large scale, especially with regard to temperature and pH parameters. Dilute acid pre-treatment is currently not capable of controlling these parameters, leading to unacceptable damage of the equipment and the formation of compounds that inhibit enzyme activity and fermentation [159,171]. Further engineering work is required to achieve optimal pre-treatment efficiency on a large scale. Biomass impurities are also a problem in crop residue biorefineries. Since crop residues are usually allowed to touch the ground where they are left to dry, highly abrasive field debris such as soil, sand, and rocks are carried along with biomass in the biorefinery plant. The presence of mineral materials is tolerated to different extents depending on the equipment employed to handle biomass, and in some cases, they must be efficiently separated from biomass to avoid causing damage to the processing equipment. One possible solution to this issue would be to harvest biomass, without it touching the ground, which is technically possible but at the expense of slowing the harvest process. A middle ground between fast harvest and high-quality crop residue biomass would have to be achieved for both sides to be financially successful [171]. Another alternative would be to collect only the upper part of the plant, which contains less dirt, leaving the lower portions to maintain soil health [173].

In summary, current technologies are still not robust enough to be scaled up to a commercial size and provide stable industrial operations. The refining of structurally complex and recalcitrant lignocellulosic biomass requires twice the number of operational units and more expensive equipment (some not yet optimized from biomass handling at large scales) than food-based biorefineries. Large investments are required to scale up and successfully implement lignocellulosic biorefineries that can operate continuously [171].

A productive conversion process depends on the slow and progressive conversion of traditional fossil-based chains into innovative chains based on biomass. An increase in the use of residual biomass requires the establishment of new technological platforms through which the process of conversion, energy recovery, and the production of biological products are all integrated within an efficient and ecologically conscious biorefining system [174].

A major issue associated with the production of first-generation biofuels is the fuel versus food debate. First-generation biofuels require biomass from food-based crops, such as bioethanol from corn grains or sugarcane juice, resulting in a competition between food and fuel. A study investigating the production of corn-derived first-generation ethanol in the US showed that as the demand for ethanol increases, part of the agricultural land used for the production of food crops, such as soybean and wheat, is utilized for the production of corn for fuels (in a process called direct land use change, dLUC), resulting in an increase in food prices [20]. As an indirect consequence of the expansion of first-generation biofuel croplands, the suppression of native vegetation, for example, forests (locally or in other countries), for food production, may increase faster than it would have without first-generation biofuel expansion (in a process called indirect land use change, iLUC) [21]. An interesting example of a strategy for mitigating dLUC associated with first-generation biofuels is the Brazilian Soy Moratorium, which was able to slow down Amazon deforestation directly associated with soybean crop expansion (soybean oil is the main feedstock for first-generation biodiesel production in Brazil) by prohibiting soybean traders from purchasing soy grown on Amazon lands deforested after 2006. The Soy Moratorium, however, does not provide mechanisms to mitigate indirect Amazon deforestation (iLUC) for other purposes, such as cattle farming. Further zero-deforestation agreements and policies in the cattle sector and efforts to increase productivity in existing pasture lands are required to alleviate the iLUC in the Amazon associated with soybean production (and biodiesel produced therefrom) [175].

Both dLUC and iLUC can significantly compromise the GHG savings obtained by replacing fossil fuels with first-generation biofuels. A payback period that may last several years is required to compensate for the new GHG emissions associated with land use change provoked by first-generation biofuel croplands [21]. The extent of iLUC, in particular, is subject to much debate since it involves many variables and is not easily measured [176–179]. Both land use changes must be accounted for in the life-cycle GHG savings assessments related to first-generation biofuels and in decision-making for biofuel promotion.

Crop residue biorefineries display important advantages compared to food-based biorefineries in terms of GHG emissions and land use changes. In contrast to first-generation biofuels, the use of crop residues (instead of edible biomass) as feedstock for the production of second-generation biofuels avoids direct competition with food production and has implications on food prices. Second-generation biofuels also minimize land use change, promoting higher GHG emission savings compared to first-generation biofuels [177]. The higher GHG savings obtained from crop residues give second-generation fuels the status of 'advanced biofuels', i.e., having life-cycle GHG emissions reduced to at least 50% in comparison to fossil-derived fuel analogs (such as gasoline) [180].

7 Conclusions and perspectives

Since the global requirement for food is expected to double within the next 50 years, and the global demand for transportation fuel is expected to increase even more rapidly, there is a great need for renewable energy resources that do not cause significant environmental harm and do not compete with food supply. Currently, enormous quantities of crop residues are generated worldwide and their production is expected to grow even further with the increased demand for food. In this scenario, crop residues show great potential for use as non-food, renewable feedstocks for the production of value-added bioproducts such as biofuels, biochemicals, and biomaterials that can replace their fossil-derived analogs. The use of crop residues (instead of edible biomass) as feedstock in biorefineries addresses the food versus fuel controversy, land use change, and GHG emissions associated with food-based bioproducts. In addition, by providing renewable bioproducts and adding commercial value to otherwise discarded wastes and alleviating problems associated with environmental pollution, crop residue-based biorefineries have the potential to leverage global bioeconomy and circular economy. Unlike fossil resources which are unevenly distributed among nations, crop residues are generated worldwide. This allows for each region to valorize their own particular set of crop residues via biorefining, contributing to local economic development. In addition, it is possible that each region will produce a specific set of biorefinery bioproducts that will vary according to demand and with the type of crop residues available in each region.

Despite their huge potential, most technologies proposed for the conversion of crop residues into bioproducts are not yet technologically mature and cost competitive. Second-generation ethanol production, one of the most advanced biomass refining technologies available, still faces several technical challenges for implementation on a commercial scale, such as collecting crop residues from the field and handling during processing, biomass pretreatment, and enzymatic conversion. Further research is needed to overcome these scale-up-related obstacles. Increased governmental incentives and private initiatives on bioeconomy strategies, which are currently largely limited to biofuels, are also expected to boost the biorefinery market and the cost competitiveness of biorefinery products other than biofuels, such as bioplastics.

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