This review presents data on the chemical composition of harvest residues and food industry by-products as widely abundant representatives of lignocellulosic waste biomass. Pretreatment methods, with special emphasis on biological methods, are presented as an important step in utilization of lignocellulosic waste biomass for the production of sustainable biofuels and high-value chemicals. Special attention was paid to the methods of lignin isolation and its possible utilization within lignocellulosic biorefinery. The objectives of circular bioeconomy and the main aspects of lignocellulosic biorefinery are highlighted. Finally, current data on industrial, pilot, and research and development plants used in Europe for the production of a variety of bio-based products from different feedstocks are presented.

Key words: biorefinery, circular bioeconomy, lignocellulosic biomass, sustainable development

Introduction

Lignocellulosic biomass (LB) comes from natural sources or processes that are constantly being replenished. Mostly, it is used for bioenergy, but in recent years considerable attention is given to LB as a source for the production of high-value chemicals. Thus, LB is considered as a renewable, abundant, and economical alternative to fossil resources.1

LB is found in large quantities almost everywhere in the world. It is estimated that 181.5 billion tonnes of LB are produced annually on Earth. Only 8.2 billion tonnes are currently used, of which 7 billion tonnes are mainly produced from dedicated agricultural, grass, and forest land.2 In contrast, non-renewable sources, such as oil, gas, and coal, can be found only in a certain number of countries in the world. Their exploitation causes pollution and climate change accompanied by gradual depletion. Although LB can be used for the production of sustainable biofuels, chemicals, and materials, the majority of the world’s energy sources and material products, especially chemicals, still come from fossil fuels, mainly oil and natural gas.3 Sustainable processes of LB utilization to produce bio-based products that achieve “zero concept” waste must be established.4 For that purpose, the concept of biorefineries has been proposed.3 The goal of the biorefinery is to transition to a more sustainable economic system that uses resources more efficiently, reduces overall waste generation, and allows the recycling of unavoidable waste as a source for the production of new products. However, finding efficient and, at the same time, sustainable technologies is a demanding task.

There are different biorefinery pathways from feedstock to product, depending on the composition and availability of the feedstock, the conversion technologies applied, and the production of the desired products. Several technological, logistical, and economical aspects should be solved before LB finds large application for sustainable biofuels and high-value chemicals production. A significant effort is dedicated to biological pretreatment methods by the use of white-rot fungi.5 Additionally, novel, eco-friendly, and natural deep eutectic solvents are explored for LB fractionation, lignin isolation, extraction of value-added products from lignin, and biotransformation.6–8

This review focuses on the general chemistry of LB and the chemical composition of typical representatives of the widely abundant lignocellulosic waste biomass, such as harvest residues and food industry by-products. The objective of this review is to increase understanding of the chemical complexity of LB waste resources, their availability, and challenges for potential lignocellulosic biorefinery applications. Recent research on the use of lignocellulosic waste biomass is discussed and divided into the following parts: LB pretreatment methods, lignin isolation methods, and the use of lignin in the production of various bio-products.
Lignocellulosic biomass chemistry

Lignocellulosic biomass is mainly comprised of lignin, cellulose, and hemicellulose, which are present in varying amounts and ratios, depending on the origin of the biomass. It also contains small amounts of pectin, protein, extractives, and inorganic compounds. The schematic representation of lignin, cellulose, and hemicellulose as the main components of LB is presented in Fig. 1.

Cellulose is the most abundant component of LB. It is a linear polymer of hundreds to over ten thousand glucose molecules linked by β-1,4 glycosidic bonds. The repeating unit of cellulose is cellobiose. Hydroxyl groups in cellulose are involved in several intra- and intermolecular hydrogen bonds, which result in various ordered crystalline arrangements. Unlike the crystalline region, the amorphous region of cellulose is easily degradable. Hemicellulose is a heteropolymer consisting of short, linear, and highly branched chains of different hexoses, pentoses, and sugar acids. Common hemicelluloses are galactans, xylans, mannans, and arabans. Hemicelluloses can be more easily enzymatically degraded compared to cellulose. However, certain oligomeric structures are recalcitrant due to the complex branching and acetylation patterns.

Lignin is a complex, amorphous, and structurally diverse aromatic heteropolymer, with cross-linked racemic macromolecules, and is relatively hydrophobic. It fills the space between hemicellulose and covers the cellulose skeleton making lignocellulosic matrices. Predominant structural components of lignin are monolignols (phenylpropanoid aryl-C3 units): p-coumaryl alcohol (H, 4-hydroxyl phenyl), coniferyl alcohol (G, guaiacyl), and sinapyl alcohol (S, siringyl) linked by C–O and C–C bonds. These three units differ in the number of methoxy groups in their phenolic rings. Their ratio within the polymer varies among different plants, wood tissues, and cell wall layers. For example, grass contains all three subunits (H, G and S), hardwood contains G and S subunits, while softwood is mostly comprised of G subunits. Lignin can be classified as natural, which is described previously, and technical or industrial lignin. Industrial lignin has diverse macromolecular structures due to various chemical modifications, and contains impurities depending on the applied LB treatments.
Harvest residues and food industry by-products

Knowledge of the chemical composition of the LB is very important because the selection of pretreatment method depends on the type and composition of biomass. Generally, in modern bioenergy systems, LB supply chain can be divided into forest biomass (treetops, branches, and unmerchantable stems, wood processing residues such as wood chips, sawdust, and shavings), harvest residues, food or feed processing residues, energy crops (including food crops such as sugar cane, oil palm, corn), waste of biological origin (manure) and household, commercial or municipal organic waste. In this paper, the possibility of using harvest residues and food processing residues (food industry by-products) in biorefineries is considered. Therefore, the literature data on the lignin, cellulose, and hemicellulose content in different harvest residues and food industry by-products are reviewed and shown in Table 1 and Table 2, respectively. For those materials, the combined term “agro-food waste” is also often found in literature. As seen from the composition of polymers (Table 1 and Table 2), they differ for the same type of material. Plant variety, agronomic measures of cultivation, weather conditions, harvesting methods, and storage conditions are all factors that influence the chemical composition of harvest residues. In the case of food industry by-products, in addition to the aforementioned, industrial process conditions also contribute to the chemical composition of the resulting waste or by-products. A good example is the chemical composition of brewer’s spent grains, which is strongly influenced by the brewing process, which depends on the type of beer produced and the specific brewing processes, unique to each brewery.

Lignocellulosic biomass pretreatment methods and lignin isolation

The best way to utilize LB is a cascade process, since it considers the composition characteristics and the nature of cellulose, hemicellulose and lignin. To achieve cascade utilization, the pretreatment step is required. After pretreatment, the conventional separation methods (extraction, regeneration, centrifugation, filtration, distillation, drying) are used. Separation is followed by the process of producing high-value chemicals from the individual components. Cellulose is mainly hydrolyzed to glucose, which can be further converted to different chemicals of biofuels, while hemicellulose is mainly hydrolyzed to xylose and converted to xyitol. Regarding lignin, no efficient approach or protocol has yet been developed to ensure high conversion of lignin into desired products. Much research has been devoted to the separation of lignin and its use for a variety of useful products by chemical, thermochemical or biochemical routes.

Generally, LB pretreatment methods can be divided into physical, chemical, physicochemical, biological methods, performed alone or in various combinations. However, not all of those methods are eco-friendly or sustainable. Most of them have a negative influence on the environment due to a large amount of chemicals used in the process, and/or are energy-intensive. Physical methods are mechanical (grinding, milling, chopping), sonication, mechanical extrusion, freezing, ozonolysis, pyrolysis, and more recently, pulsed-electric field pretreatments. Physical pretreatment methods require high energy utilization, and are therefore expensive for large-scale implementation. Among chemical methods, acid and alkali pretreatment are
The most commonly used. Although they can achieve high solubilization of cellulose and hemicellulose, and removal of lignin, those methods cause a high environmental burden. The other chemical methods are oxidative and organosolv pretreatment, ozonolysis, the use of ionic liquids and novel natural deep eutectic solvents. Physicochemical pretreatment methods include ammonia fiber explosion, ultrasonication, autohydrolysis, liquid hot water, wet oxidation, and CO2 explosion pretreatment. Biological pretreatment methods are described in the next chapter.

Based on the applied method of lignin isolation, various types of industrial lignin can be produced. Organosolv and soda lignin are produced during the sulfur-free pulping process, while lignosulfonate and Kraft lignin are produced in the sulfur-containing pulping process. All of these processes are based on the application of chemicals and/or high temperatures, and therefore could not be considered sustainable or environmentally friendly.

Kraft lignin represents 85% of the world’s industrial lignin. It is obtained in the chemical process of pulping wood and non-wood pulp with sodium sulfide (Na2S) and sodium hydroxide solution (NaOH) at a temperature of 160–180 °C and pH 9–13.5. Kraft lignin is soluble at pH > 10 and has a lower sulfur content (up to 3%) compared to lignosulfonate lignin (4–8%), which is obtained by pulping only a certain wood in the presence of bisulfite ions (HSO3-) at 120–150 °C and pH 2–12 for 1–5 h. Lignosulfonate lignin has high ash content and needs to be purified before further use for the production of energy or chemicals. It is soluble in acids, alkali, and polar solvents. Lignosulfonates can be used in the prevention of scaling in hot and cooling waters, and as solvent for micronutrients in liquid fertilizers. Soda lignin is formed in the process of soda pulping non-wood materials such as agricultural waste (straw, bagasse, grass, etc.) using 13–16% sodium hydroxide solution at a temperature of 150–200 °C and pH 9.5–13. This type of lignin does not contain sulfur, which makes it suitable for the production of adhesives according to environmentally friendly principles. Organosolv lignin is like sulfur-free lignin, and is obtained by pulping fibrous wood residues and food industry residues using organic solvents (mixture of water/ethanol or methanol, acetic acid, etc.) at a temperature of 150–200 °C, using 13–16% sodium hydroxide solution at a temperature of 150–200 °C and pH 9.5–13. This type of lignin does not contain sulfur, which makes it suitable for the production of adhesives according to environmentally friendly principles. Organosolv lignin differ from other industrial lignin because it contains fewer impurities, has a lower molecular weight, and is water insoluble.

## Biological pretreatment methods

Biological pretreatments can be performed by selected microorganism, microbial consortium or enzyme(s). A comprehensive review on valorization of harvest residues and food-processing industry by-products by solid-state fermentation using various microorganisms was recently published by Šečer et al. The majority of research has been dedicated to fungal-based solid-state pretreatment, particularly to the use of white-rot fungi from the class of Basidiomycetes. White-rot fungi improve the

### Table 2 – Chemical composition of different food industry by-products

| Industrial by-products         | Cellulose, %DM | Hemicellulose, %DM | Lignin, %DM |
|-------------------------------|----------------|--------------------|-------------|
| Apple pomace                  | 47.5           | 27.8               | 14.8–22.4   |
| Barley husk                   | 39.0           | 12.0               | 22.0        |
| Brewer’s spent grain          | 12.0–40.2      | 28.4–40.0          | 11.5–27.7   |
| Corn cob                      | 33.7           | 31.9               | 6.1         |
| Flax oil cake                 | 8.2            | 4.6                | 6.0         |
| Grape pomace                  | 9.2–14.5       | 4.0–10.3           | 11.6–41.3   |
| Hemp oil cake                 | 22.5           | 14.2               | 16.7        |
| Hull-less pumpkin oil cake    | 4.4            | 6.7                | 0.7         |
| Olive mill waste              | 24.8–33.8      | 13–16.3            | 13.3–15.8   |
| Rapeseed cake                 | 15.9           | 12.5               | 6.6         |
| Rice bran                     | 34.0           | 28.2               | 24.8        |
| Rye bran                      | 5.0–6.0        | ND                 | 3.5–4.4     |
| Sugar beet pulp               | 21.5           | 30.0               | 3.9         |
| Sugarcane bagasse             | 36.9–45.7      | 25.6–29.6          | 18.9–26.1   |
| Wheat bran                    | 9.0–12.0       | 38.9               | 3.0–5.0     |

ND – not determined
biodegradability of lignocellulose by increasing the pore size of the material through penetration of the mycelium, and breaking the bonds between polysaccharides and lignin, removing lignin, releasing cellulose, and reducing the degree of polymerization of cellulose.

However, this method has several drawbacks, such as long duration, loss of organic matter during the treatment, technical challenge for the scale-up, and possible contamination. Although white-rot fungi break down lignin, they are unable to utilize it as an energy source; therefore, it is assumed that they degrade lignin to access the cellulose.

To degrade the lignin, white-rot fungi produce ligninolytic enzymes (LEs). LEs are produced in small amounts and their optimal activities can be achieved through optimization of the media composition by supplementation with salts, low molecular weight phenolic compounds, and nutrition sources. However, the mechanism of LEs function is not completely known. Major LEs are laccase (Lacc), lignin peroxidase (LiP), manganese peroxidase (MnP), and versatile peroxidase (VP). The catalytic mechanism of Lacc in oxidation of phenolic and nonphenolic substrates is presented in Fig. 2a, while the catalytic mechanisms of LiP and MnP are presented in Figs. 2b and 2c, respectively.

Laccase (benzenediol: oxygen oxidoreductase, EC 1.10.3.2) can be considered as the key enzyme involved in lignin oxidation, modification or degradation. Laccases have high redox potential and are active towards a variety of substrates (phenolic and nonphenolic compounds), they can accept molecular oxygen, without the need for costly cofactors. Oxidation of phenolic substrates involves removal of one electron from the phenolic hydroxyl groups to form phenyl hydroxyl radicals. With nonphenolic substrates, the use of mediators is essential. The most efficient laccase mediators are 1-hydroxybenzotriazole (HBT), N-hydroxyphthalimide (HPI), violuric acid (VLA), N-hydroxyacetanilide (NHA), N-hydroxyacetanilide (HAA) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). There have been many reviews in the last few years on laccase application for analytical, industrial, and environmental purposes.

While laccases are involved in the degradation of lignin, cellulose and hemicellulose are degraded by cellulases and hemicellulases, respectively (Figs. 3a and 3b). The product of depolymerization of cellulose is glucose, whereas the degradation of hemicelluloses releases a mixture of different hexoses and pentoses. There are three types of cellulases (Fig. 3a), namely, endoglucanases (carboxymethyl cellulase...
cellulase), exoglucanases (cellbiohydrolase), and β-glucosidase. To completely hydrolyze cellulose to glucose, all three enzymes are required. Endoglucanases randomly dissociate amorphous parts of cellulose, whereas exoglucanases extract cellobiose from crystalline parts of cellulose. β-glucosidases transform cellobiose to glucose, which can be used, e.g., for bioplastics and biofuels production. However, the high cost and low efficiency of cellulases are the major issues in industrial-scale LB enzymatic degradation.

Large amounts of enzymes are required to produce concentrated glucose solutions due to substrate and product inhibition. Thermally stable cellulases and the immobilization of enzymes on solid supports have been investigated to improve the economics of cellulose degradation. Additionally, protein engineering and directed evolution are powerful technologies to improve enzyme properties such as increased activity, decreased product inhibition, increased thermal stability, improved performance in nonconventional media, and pH stability.

Hemicellulases include a group of enzymes involved in the hydrolysis of galactans, xylans, mannans, and arabinans. The major hemicellulases are endoxylanase (1,4-β-d xylan xylanohydrolase), which hydrolyzes β-d-xylano pyanosyl linkages of xylan to form xylo-oligosaccharides, and β-d xylosidase (xylobiase), which catalyzes hydrolysis of xylobiose or xylo-oligosaccharides from the nonreducing end, releasing d-xylose in the hydrolysates (Fig. 3b). Xylose is a low-calorie sweetener and versatile feedstock for xylitol production. Many cellulases and hemicellulases that act on insoluble substrates have catalytic domain connected by a flexible peptide linker to a carbohydrate-binding module, which anchors the enzyme to the solid substrate. Carbohydrate-binding modules assist biomass hydrolysis by effectively increasing the concentration of their enzymes near the substrate surface and, depending on amino acid sequence and resulting shape, provide specificity to a certain substrate or substrate region (such as reducing or nonreducing ends).
Lignocellulosic biorefinery in sustainable development and circular bioeconomy

The concept and objectives of the circular economy and the bioeconomy overlap, hence the combined term circular bioeconomy is introduced. The circular bioeconomy is based solely on the use of natural sources, and enables greater environmental sustainability compared to the use of fossil resources. It promotes human imitation of natural processes and activities, and seeks to make all processes circular by reusing the waste produced and using all outputs as inputs to other processes. Bioeconomies are highly dependent on the availability of resources and logistics. Therefore, the development of bioeconomies may depend on strong cooperation between regions that are rich in biosources and regions that have appropriate technology but insufficient resources. Effective biomass utilization through the strategic use of resources is essential for the production of valuable products, sustainable development, and the maximization of environmental and socioeconomic benefits.

Biorefineries are industrial processes that aim to produce multiple value-added industrial products, fuels, and chemicals from various feedstocks. Biorefineries are generally developed in response to the instability of the petrochemical industry, and out of concern for sustainable energy development and climate change. Biorefinery operations can be made more competitive by using lignocellulosic feedstocks and integrating multiple revenue streams, which is then referred to as lignocellulosic biorefineries. In lignocellulosic biorefineries no single microorganism can catalyze all process steps. By combining specific strains and targeting multiple products, full biomass valorization could be achieved. It is important to emphasize that lignocellulosic biomass as a feedstock in lignocellulosic biorefineries can only be considered after intensive evaluation of production costs, availability, and market value. Although various lignocellulosic energy crops are often used in biorefineries, much effort is dedicated to the use of lignocellulosic waste biomass. In order to develop a sustainable biorefinery, it is important to take an integrated approach to biofuel production and the production of high-value-added chemicals, which is explained further herein, where high value-added chemicals refer to those produced from lignin.

Biofuels from lignocellulosic biomass

Considering the feedstock and technologies used for biofuel production, both liquid (bioethanol, biobutanol, biodiesel) and gas biofuels (biogas, hydrogen, syngas) are classified into four generations. The 1st generation biofuels come from biomass which is also a food source, which is the main drawback. The 2nd generation biofuels come from non-food biomass, the 3rd generation fuels use algae, and the 4th generation biofuels are the result of developments in plant biology and biotechnology (metabolic engineering) in carbon capture and storage technology.

Lignocellulosic waste biomass is a non-food biomass and is used as a feedstock for 2nd generation biofuel production. There are still some technical and economic hurdles to overcome before 2nd generation biofuels becomes more positioned at an industrial scale. The first challenge is related to the availability, storage, and transport of lignocellulosic waste biomass to the biofuel plant, in case it is not available near the plant. The second problem is technological, due to lignocellulose recalcitrant structure resistant to degradation. Most of the efficient pretreatment methods are not environmentally friendly, while those that are, suffer from some disadvantages as described previously. To solve the first challenge, harvesting, transporting, storing, and delivering large volumes of high-quality lignin LB throughout the whole year to a biofuel plant requires careful logistical analysis before plant investment and construction. Transportation of a massive volume of feedstock in an energy-saving manner to the biorefineries is a challenge. To solve the second problem, technological, integration of the process of biofuel production together with the production of other products (e.g., feed or high-value chemicals) should be considered to be located at one place in lignocellulosic biorefineries.

High-value lignin-based products

Due to the high content of carbon (up to 80%), hydrogen (up to 6%), and high C/O ratio, lignin is a potential source of highly-valued aromatic compounds (phenols, vanillin, polymer building blocks), synthetic gas (syngas), and hydrogen. It can be used as an additive/binder in the production of cement and biofuels. Furthermore, lignin can be used in the development of packaging materials (e.g., food packaging), in the production of polymer, and bioplastics. It can also be used for therapeutic purposes due to its antioxidant, antimicrobial, and anticancer effects. The conversion of lignin into value-added products involves three steps: isolation, depolymerization and final upgrading of the obtained platform chemicals. However, the isolation of lignin from lignocellulose is not easy due to its complex structure, poor solubility, and unclear reactivity. Therefore, the industrial use of lignin for the production of value-added products is still limited, and almost...
all industrial lignin is combusted to produce heat and electricity, whereas only 1–2 % of lignin is chemically transformed for industrial application.\textsuperscript{107}

Industrial lignin is mostly produced by extraction from lignocellulosic biomass or industrial by-products using mechanical, chemical, or enzymatic methods.\textsuperscript{80,108} In paper production and wood processing, after the separation of cellulose and hemicellulose, considerable amounts (10–50 %) of black (spent) fluid remain as a by-product, from which industrial lignin can be extracted. There are different types of black liquor (Kraft spent liquor, soda spent liquor, neutral sulfite semi-chemical spent liquor, etc.) depending on the raw material, the pulping process, and the cooking method used in the paper production. The properties of black liquor have influence on the further production process of desired products.

A schematic overview of lignin isolation together with the potential products is presented in Fig. 4.\textsuperscript{13,107,109–111}

Although industrial lignin can be used directly in the production of certain chemicals (e.g., polyols), lignin must be modified or fragmented (by depolymerization or modification of functional or hydroxyl groups) for better use in the production of high-value products, as this increases the reactivity of lignin and creates new active sites. The most common methods for modifying lignin are oxidation, pyrolysis, hydrogenation, hydrolysis, gasification, and microbial transformation (Fig. 5).\textsuperscript{13,81,82,103,108,112}

One of the most important products of lignin modification are aromatic compounds, such as benzene, toluene, xylene, and phenolic compounds, which are precursors of various highly-valued lignin-based products, such as resins, polyesters, nylon fibers, and polyesters, among others.\textsuperscript{113}

The best known aromatic compound obtained with lignin modification by oxidation or microbial transformation, is vanillin. Vanillin is a precursor for the synthesis of various polymers.\textsuperscript{113,114} Microbial conversion offers a novel, inexpensive route to the production of high-value products, but the valorization of lignin in this way can be hindered by the tendency of the degraded lignin fractions to undergo repolymerization and condensation reactions.\textsuperscript{106}

Kraft lignin and lignosulfonate lignin have the highest commercial application. Kraft lignin products are shown in Fig. 4. They include lignosulfonates, technical carbons, bioplastics and coatings, binders and adhesives, and low-molecular weight compounds such as vanillin, quinines, aldehydes, etc.\textsuperscript{107,109} The important high-value products made from Kraft lignin are carbon fibers. They are characterized by high strength, low mass, high thermal and chemical stability, and corrosion resistance. Therefore, they are suitable for the manufacture of sports equipment and composite materials. They find their application in the automobile and aircraft industries. The advantage of lignin in the production of carbon fibers over nonrenewable materials such as polyacrylonitrile (PAN) and pitch, is its non-toxicity, lower melting point, and faster stabili-
zation. For the production of lignin-derived carbon fibers, it is necessary to extrude the isolated lignin into fibers, stabilize the fibers by oxidation, and finally pyrolyze them.\textsuperscript{113,115,116}

Among the possibilities for lignin utilization is the application of lignin in the production of plastics and new composites. Lignin-based plastics can be obtained by chemically modifying lignin by changing its properties such as viscosity and elasticity or by mixing lignin with certain polymers, e.g., with poly(ethylene oxide) or with acrylonitrile butadiene, which is used as a thermoplastic resin in the automotive industry, in the manufacture of toys, etc. The main limitation in the preparation of plastics using lignin is the immiscibility of lignin with most polymers, as the interactions between them are weak compared to the interactions between lignin molecules due to the large number of polar functional groups of lignin. However, by adding various coupling agents (e.g. polyalkylene oxide, polyvinyl alcohol, ethylene vinyl-acetate copolymer, etc.), it is possible to improve the dispersion and mixing of lignin with a particular polymer.

Kraft lignin can be used as a dispersant (e.g., in the manufacture of pesticides, cement, ceramics) and coagulant (e.g., in the removal of dyes from solvents in the textile industry), but with prior modification to lignosulfonates to increase its solubility in aqueous medium and increase charge density.\textsuperscript{117} Some of the modification processes are carboxymethylation,\textsuperscript{118} sulfomethylation,\textsuperscript{119} phenolation followed by sulfonation with sulfuric acid and sodium sulfite.\textsuperscript{120} Since lignin contains phenolic units in its structure, it can be used as a substitute in the commercial synthesis of phenol-formaldehyde-based adhesives. Moreover, pine Kraft lignin has been shown to contribute to better water absorption and mechanical properties such as strength, elasticity, etc. in the synthesis of lignin-phenol-formaldehyde compared to phenol-formaldehyde resin.\textsuperscript{121}

Lignosulfonate lignin is most commonly used as a dispersant and binder in the manufacture of cement and concrete mixes to reduce the water content and increase the rate of hardening. In general, the term dispersant is often used for surfactants, plasticizers or emulsifiers, depending on the field of application.\textsuperscript{113}

The dispersibility of lignosulfonates depends on the balance between molecular weight and species, and the number of functional groups. Various modifications of lignosulfonate lignin alter the properties of lignin. For example, oxidation or nitration of lignosulfonate increases the plasticizing ability in concrete. Reducing the sulfur content in lignosulfonate lignin increases hydrophobicity, and thus improves dispersibility. The same effect is achieved by increasing the molecular weight of lignosulfonates (10,000 – 50,000 g mol\textsuperscript{-1}) and oxidation reactions leading to increased availability of lignin functional groups and increased dispersibility. Lignosulfonate lignin is used as an additive in animal feed production, where it can have a binding
| ORIGIN OF LIGNIN | ISOLATION METHOD | MODIFICATION/FRAGMENTATION METHOD | BIOPRODUCT [PRODUCTIVITY / YIELD] |
|-----------------|-----------------|----------------------------------|----------------------------------|
| Barley straw    | Ultrasound extraction | Carbonisation (drying at 500 °C in N₂ atmosphere) and activation (CO₂ flow at 650-850 °C) | Lignin based composite (biosorbent)¹⁰³ |
| Cocoa pod husk  | Extraction by formic acid, choline chloride and a deep eutectic solvent | Oxidation: 170-190 °C, 2N NaOH, nitrobenzene | Activated carbon [18 – 47.2 %]¹³¹ |
| Coffee chaff    | Extraction: mixture of benzene and ethanol (2:1 v/v) | Pyrolysis (200-400 °C) | Lignin as plasticizer in cement paste¹³² |
| Corn stover     | Acid-alkali (H₂SO₄/NaOH) pre-treatment, 120 °C/30 min | Spinning, pre-oxidation in the air (200-300 °C) carbonization (300-1600 °C) in N₂ atmosphere | Vanillin, vanillic acid, syringaldehyde, syringic acid, p-hydroxybenzaldehyde [0.9-15.0 mol%]¹³³ |
| Lignocellulosic raw materials | Pre-treatment: organic modification | Carbonisation (drying at 500 °C in N₂ atmosphere) and activation (800-950 °C in a steam flow) | Phenols [10 %]¹¹⁴ |
| Olive stones    | Extraction: NaOH at 90 °C/6M H₂SO₄ at 75 °C | Pyrolysis (350-650 °C) | Carbon fibers (40-50 %)¹³⁵ |
| Peanut shell    | Acid-alkali (H₂SO₄/NaOH) pre-treatment, 120 °C/30 min | Pyrolysis (350-650 °C) | Activated carbon [12.2-25.3 %]¹³⁶ |
| Rice husk       | Biological pre-treatment with Serpula lacrymans; Extraction by water, ethanol and ethyl acetate | Pyrolysis (200-400 °C) | Kraft lignin as dye adsorbent¹³⁷ |
| Rice straw      | | | Bio-char [up to 42 %]¹³⁸, Bio-oil [up to 58 %]¹³⁸ |
| Sugar beet pulp | Extraction by formic acid, choline chloride and a deep eutectic solvent | Oxidation: CuSO₄, O₂, 4.3 bar, 156 °C | Bio-char [up to 42 %]¹³⁸, Bio-oil [up to 58 %]¹³⁸ |
| Sugarcane bagasse | Extraction with NaOH | Acetylation [pyridine : acetic anhydride/72 h], epoxidation (epichlorohydrin/3-6 h at 70 °C) and hydroxymethylation reactions (37 % formaldehyde at 50 °C/3-6 h) | Vanillin [2.596 µg g⁻¹]¹³⁹ |
| Wheat straw     | Organosolv process | Oxidation: 170 °C; 1M NaOM, NaAlO₂, nitrobenzene - air | Vanillin, vanillic acid [1.44 %]¹⁴⁰ |
|                 | Aquasolv process (hot water at 215 °C/50 bar/30 min) | Enzymatic hydrolysis (CTec2®, 50 °C, 72 h) | Lignin as plasticizer in cement paste¹³² |
|                 |                          | Pyrolysis (350-650 °C) | Sugarcane bagasse lignin (antioxidant)¹⁴¹ |
|                 |                          |                          | Monophenolic compounds, vanillin, syringaldehyde [5.7-18.1 %]¹⁴² |
|                 |                          |                          | Aquasolv lignin [85 %]¹⁴³ |
|                 |                          |                          | Bio-char [up to 42 %]¹³⁸, Bio-oil [up to 58 %]¹³⁸ |
|                 |                          |                          | Guaiacol and 4-vinylguaiacol (antioxidants)¹⁴⁴ |

Fig. 6 – Some valuable products obtained from lignin isolated from agro-food waste
function, e.g., in the production of animal feed pellets, or it can be used as an encapsulating agent for fat-soluble vitamins, carotenoids, etc. 122,124 Organosolv and soda lignin, due to the absence of sulfur, have properties more similar to natural lignin than Kraft and lignosulfonate lignin, and have potential in the development of high-value products according to the environmentally friendly concept. Organosolv lignin is used as an additive for paints, coatings, and as a filler in the formulation of printing inks, while improving the viscosity properties of the products. 125 Although it can be used in the manufacture of most products like Kraft lignin, it is not suitable for binders and adhesives due to its low molecular weight. 97 Soda lignin is used in the production of phenolic resins, animal feed, dispersants, and polymer synthesis. 126

Phenolic resin, used as a wood adhesive, is commercially prepared on the basis of phenol-formaldehyde. Because of the carcinogenicity of formaldehyde, alternative compounds are being investigated for its replacement, such as aldehyde glyoxal, which is nontoxic and readily biodegradable. Since the structure of lignin is similar to that of phenol-formaldehyde, lignin can partially replace the phenolic part of the resin structure. Comparison of soda lignin and Kraft lignin in the preparation of lignin-phenol-glyoxal resin showed that the use of soda lignin results in a resin that has similar properties to a commercial phenol-formaldehyde resin compared to the resin where Kraft lignin was used. This is due to the better cross-linking of soda lignin with glyoxal due to the higher number of phenolic – OH groups and higher molecular weight compared to Kraft lignin, resulting in higher resin strength and viscosity. 127,128 Sameni et al. 129 demonstrated that the addition of soda lignin to high-density polyethylene, used in the packaging and automotive industries, significantly increases the tensile and flexural strength of the polymer due to the low molecular weight, low hydroxyl content, low polar component, and low sulfur content of the soda lignin.

Many compounds from lignin isolated from agro-food waste can be produced, as presented in Fig. 6. However, phenolic compounds are among the most important. 134 They can be used for the production of bioplastics, epoxy- and polyurethane resins, aromatic compound vanillin 133,139,140,142 and its precursor guaiacol. 144 Phenolic acids can be used as food additives to improve the nutritional, organoleptic, and biological properties of food products, as well as in the pharmaceutical sector. Carbon fibers 135 from lignin have great industrial potential (they have yet to be commercially applicable) due to their strength and wide applicability (e.g., in the automotive industry). 80 Activated charcoal 131,136 has good properties as an adsorbent and finds application in deodorization and purification of process streams. 80 Lignin-based bio-composites show good properties in heavy metal adsorption. 130

Distribution of the bio-based industry in EU

There is an extensive database of EU facilities at pilot and industrial scale, or laboratory level that produce different categories of bio-based products, available on Data portal of agro-economics Modeling – DataM: DataBio-based industry and biorefineries. 145 Bio-based products are categorized as chemicals, liquid biofuels, composites, and fibers, biomethane, pulp and paper, sugar, starch, and timber. Fig. 7 presents bio-based products from lignocellulosic biomass produced at industrial, pilot-scale and laboratory level in European Union. It is clearly visible that most of the feedstocks used for the commercial production of bio-based products originates from the forestry with pulp and paper, and timber as main products. It is interesting to observe that only one industrial scale facility uses forestry feedstock for biomethane production. The majority of commercial liquid biofuels and bio-based chemicals originates from the agricultural feedstock. Ninety-six pilot-scale facilities operate in the field of liquid fuels production using forestry or grasses and short rotation feedstocks.

Conclusion and future prospective

Lignocellulosic waste biomass is a valuable, renewable feedstock that can be used in lignocellulosic biorefineries for the production of bio-based products to reach sustainable development goals following the principles of circular bioeconomy. The production of multiple products from lignocellulosic biomass requires integration of various processes.

Considering the heterogeneous chemical composition of lignocellulose, the industry faces many challenges, such as the availability of a single type of biomass throughout the year. High processing cost, huge capital investment including transportation and storage cost for lignocellulosic biomass, efficient and sustainable lignocellulosic pretreatment and fractionation techniques focusing on lignin isolation, fractionation and modification are some of the main barriers for profitable biorefineries based on lignocellulosic waste as feedstock.

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