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Wood-lignin: supply, extraction processes and use as bio-based material

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Abstract

Wood is the main source of lignin in the world. This generic term "Lignin" describes a large group of aromatic biopolymers, i.e. the second most abundant class of biopolymers on Earth. It accounts for approximately 30 % of wood weight while conferring rigidity and antimicrobial properties to wood. Since lignin is combined with cellulose and hemicellulose in biomass, this will constitute a limiting factor in the bioconversion of wood into pulp or second-generation biofuels through the biochemical pathway. These processes generate a huge quantity of lignin as by-products, mainly used as fuels for energy savings. Recently, alternative routes towards lignin's valorization were emphasized (e.g. as bio-based resins, adhesives, or composites), but they strongly depend on lignin's chemical structure, also dependent on fractionation process. Therefore, this review aims to summarize the strong interplay between extraction processes, resource supply, and recent uses of lignin into bio-based materials.

Keywords: Lignin; wood; extraction process; polymer; bio-based material.

1. Introduction

A large variety of biopolymers are present in prokaryotic and eukaryotic living matter. They can be divided in 8 major families depending on their chemical structures. They are polyamino acids (or protein), nucleic acids such as DNA or RNA, polysaccharides as hemicelluloses, pectins or celluloses, cutin and polymalic acid, organic polyoxoesters including polyhydroxyalkanoic acids, polythioesters, polyphosphate (the single example of inorganic polyester biosynthesized), polyisoprenoids and polyphenol as humic acid and the well-known lignin. Lignin is a natural polymer chemically constituted of three phenylpropane units (empirical formula of $C_{31}H_{34}O_{11}$): coniferyl alcohol (G), sinapyl alcohol (S), and low amounts of p-coumaryl alcohol (H) [1]. It should be noted that the structure and concentration of lignin vary among botanical sources, plant tissue, age, and type or cell wall layers. For this reason, some authors are referring to the term "lignins" at plural to emphasize on the diversity of lignin forms. Lignin has highly branched chemical structure with different functional groups such as methoxy (CH_3O), carboxyl (COOH) and carbonyl (C=O). The most common linkages identified in these polymers are β-O-4, α-O-4, β-5, β–β, 5-5′, 4-O-5 and β-1′ [2]. Lignin constitutes the major source of phenolic compounds on Earth and the second most abundant macromolecule group after cellulose. These macromolecules' structural characterization is relatively complicated, and some interrogations remain. Lignin is found in some vascular plants' cell walls where it is linked to cellulose and hemicelluloses forming lignin-carbohydrate complexes (LCC). Regarding these assemblies, isolation of lignin from biomass is, therefore, a challenge. The proportion of lignin is about 15-40 % (w/w) in the wood [3] whereas it is often less than 15 % (w/w) in annual plants like herbs [4]. Annually, about 150 billion tons of lignin is synthesized by Earth plants making this biopolymer one of the most abundant bioresources which stores about 0.082 % of all the solar radiation intercepted by the Earth surface and about 95 billion tons of the carbon in the Earth crust [5].

Hence, wood-derived lignin has attracted great attention over the past decades due to its availability and versatile properties. Using the word “lignin”, 119360 references are available in the portal of chemistry SciFinder Scholar. Refining this result with the term “wood” gives a score of 27385 references including articles, reviews, patents, books and other. Finally, this data should be compared with the “material” concept leading to 7888 references selected, 5050 of them being published after 2000. **Figure 1** clearly illustrates the latest excitement of the industrial and scientific communities for this complex biopolymer often considered as a by-product from biorefinery of second generation or papermaking industry, poorly valorized such as with internal energy production by combustion.

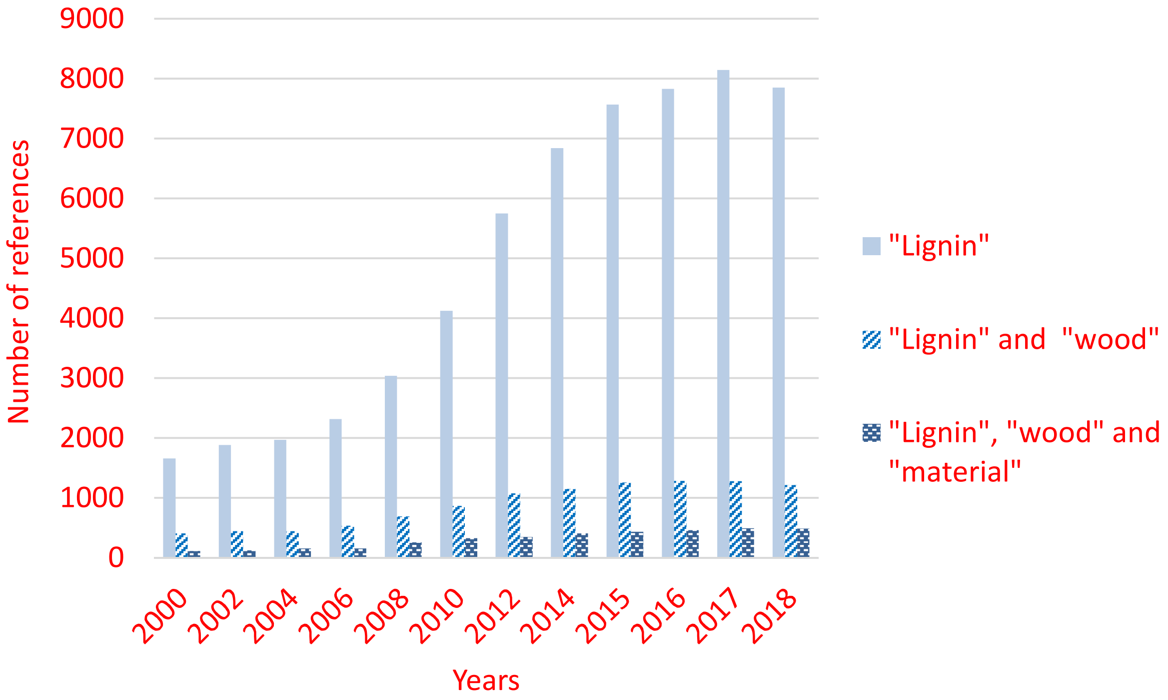

Figure 1. Number of references per year between 2000 and 2018 using the key words “lignin” and the combination “lignin” and “wood” or “lignin” and “wood” and “material”.

In 2014, the global lignin market was valued at 775 million US$ and is expected to be of 900 million US$ in 2020 [6]. The annual growth rate between 2018 and 2020 will probably reach 2.5 %. However, lignin is more and more considered as a significant candidate for oil-based products’ replacement in the manufacturing of carbon-based compounds such as chemicals and materials. Indeed, depletion of conventional fuel reserves has prompted the need for the exploration of renewable resources. In this context, the bio-based economy requires the sustainable utilization of bioresources to produce widely consumed products such as plastics, adhesives, chemicals or fuels [7,8]. Therefore, lignin valorization could be economically viable since its low cost and profuse availability as a by-product striking opportunities. The whole process of valorization cannot be fully productive without the development of both cost-effective and green methodologies [9]. Recent advances on traditional or innovative processes for lignin extraction are highlighted in this paper. Over the last decades, lignin was added to various polymers to form blends or composites.

2. Occurrence of native lignin, its structure and its biodegradation

2.1. Role of lignin in plants evolution

When plants invaded land, they had to adapt specifically their physiology to UV radiations, desiccation, and nutrients rarefaction [10]. Tracheophytes, that include all seed plants like the angiosperm and conifer phylums, were the most successful species in exploiting terrestrial environments [11,12]. This group was the first having a lignified tissue, called xylem, with the function of transporting water and nutrients from roots to leaves. Some characteristic xylem cells are the tracheides that permit water transportation [13]. Lignin precursor metabolism allowed the formation of cuticles to protect plants from drought [14]. Lignin was acting as a waterproofing agent that embedded cellulose microfibrils. Intramolecular hydrogen bonding between cellulose microfibrils was enhanced, resulting in a higher stiffness that prevented cells to collapse when subjected to negative pressures. Presence of lignin can only be proven in Mesozoic plant fossils that lived about 250 million years ago although scientists believe that lignin appeared 440 million years ago during Silurian times since xylem-like elements were found.

2.2. Lignin structure and its formation

In 1956, isolation of lignin was described for the first time [15]. This lignin was extracted with dioxane-water (96:4) from spruce wood for 6 weeks and called milled wood lignin. *p*-coumaryl, coniferyl, and sinapyl alcohols were found to be precursors to lignin and called monolignols. They are hydroxycinnamic alcohols containing an aromatic ring and a side-chain of three carbons designated as α, β, and γ. According to the numbering system of lignin, phenol carbon is numbered 4 and the side-chain attachment to the aromatic ring is numbered 1. As depicted in **Figure 2**, monolignols differ in the substitution degree on the aromatic ring on positions 3 and 5 [16]. Therefore, the structure of lignin can be decomposed between guaiacyl units (G) which have one aryl-OCH_3 groups and are derived from coniferyl alcohol, syringyl units (S) which have two aryl-OCH_3 groups and are derived from sinapyl alcohol, and *p*-hydroxyphenyl units (H) which have no OCH_3 groups and are derived from *p*-coumaryl alcohol. The first complete structure of lignin was proposed by Adler in 1977 who described lignin as a “highly branched biopolymer containing various methoxy, carboxylic, phenolic and aliphatic hydroxyl, and carbonyl functional groups” [17].

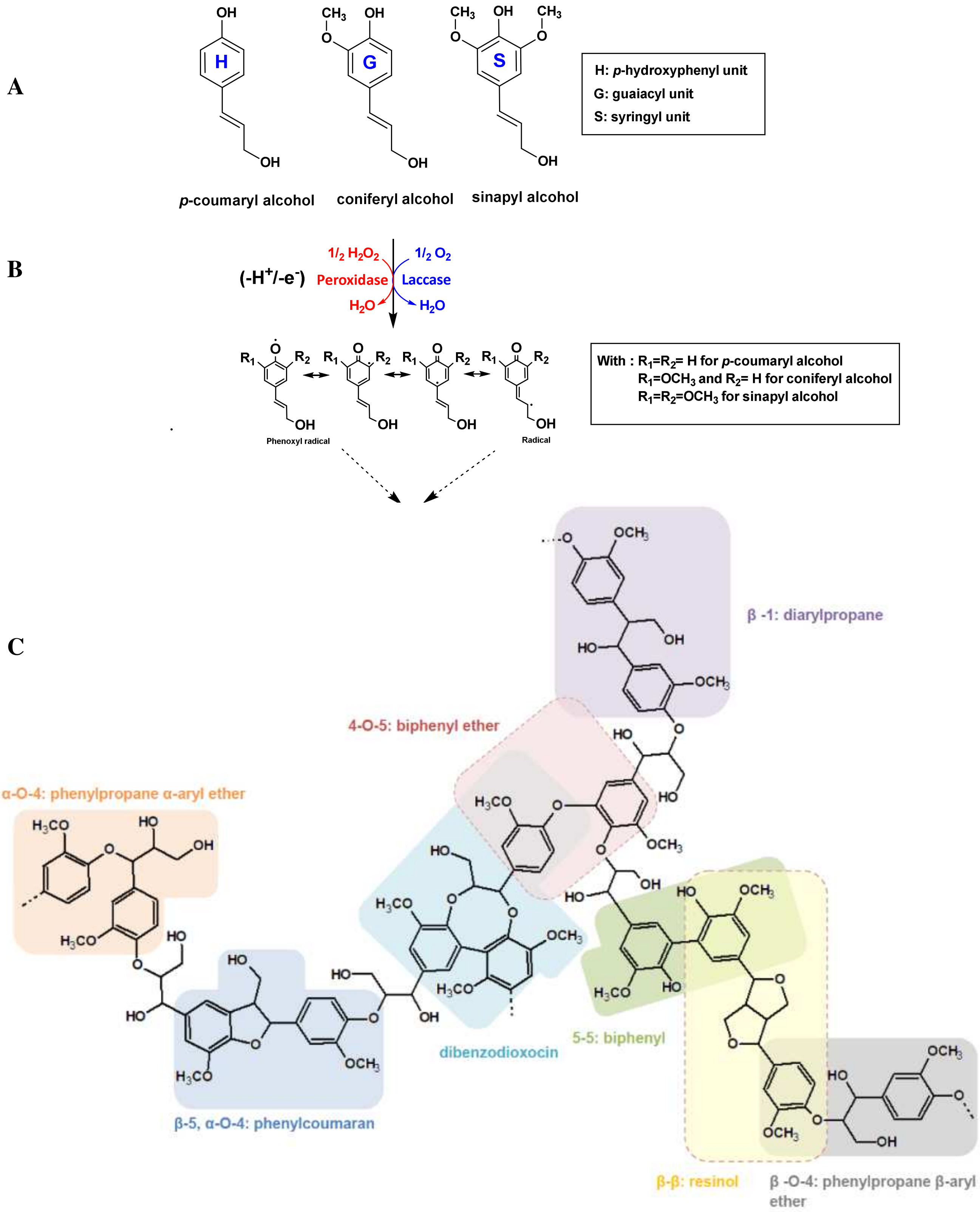

Figure 2. General way toward the synthesis of lignin-hemicellulose complex in lignocelluloses wood matrix. (A) chemical structures of monolignols (lignin monomers), (B) enzymatic synthesis of monolignols radicals, (C) lignin structure with main units.

Softwood lignin is mainly composed of G units whereas hardwood structure is governed by a S/G ratio. Nevertheless, in S2 layer of hardwood vessels, G-type lignin is predominant. This latter has a condensed structure that provides strength to the cell walls, subsequently withstanding higher compressive forces from the transportation fluids. Lignin polymer is formed in the wood-cells cytoplasm via a complex enzymatic pathway [18,19]. Biosynthesis of monolignols is initiated via the shikimate pathway, with the deamination of phenylalanine molecule as a starting point. More than 10 enzymes are involved in the formation of the monolignols [20,21]. They are firstly synthesized in the cytosol, then transported to the cell walls, and finally oxidized by laccase, peroxidase or other phenol oxidases enzymes leading to phenoxy radicals [22-24]. The phenoxy radicals are resonance-stabilized thus leading to several forms of radicals that further react to form lignin *via* a polymerization process called lignification. This polymerization begins at the cell corner of the middle lamella and the S1 layer of the secondary cell wall before spreading across the secondary wall towards the lumen [25,26]. Lignification cannot be simply impacted by monolignol biosynthesis. The timing between lignin polymerization and lignin deposition in the cell walls, after exportation, is poorly known but determinant for the final lignin structure. The discovery of monolignol transferase (PMT) opened the debate on how many dimers, trimers or oligomers are exported by plant cells for lignification [27,28]. The first product of the lignification process is a dimer of two oxidized monolignols, involving the C-β of one monomer and either the C5 (in G- and H-units) or the C-β of a second monomer [23, 29]. Polymer chain grows with the end-wise addition of a new monolignol radical. Crosslinking points are created by C5-C5 coupling, phenolic hydroxyl-C5 coupling, or the formation of dibenzodioxocin structures [30]. The coupling of the oxidized monolignols gives rise to several covalent bonds' formation, either ether or carbon-carbon bonds namely ether β-O-4, diphenyl ether 4-O-5, 5-5, phenylcoumaran β-5, pinoresinol β-β, dibenzodioxin, and diphenyl methane β-1 most common linkages [31].

C-β appears to be the most reactive position giving rise to abundant β-O-4, β-5, and β-β bonds. It has been determined that approximately 50 % of lignin bonds are β-O-4 ether type. β-O-4 is also the weakest bond destroyed during the pulping process. Sinapyl alcohol radicals cannot couple in C5 position and are restricted to covalent bonds in the 4-O-, the β -, and the C1 positions. Thus, hardwood lignin contains more β-O-4'-, β -β' bonds and fewer bonds on the C5 than softwood lignin, whereas the β-1´ bonds are approximately the same. Therefore, hardwood-lignin is believed to be more linear and less branched than softwood one. These differences explain why it is easier to make Kraft pulp from hardwoods than from softwoods. Another consequence of the presence of sinapyl alcohols in hardwood lignin is a higher content of methoxy groups. The radical coupling process involved in lignin formation is designated as dehydrogenative polymerization and is considered as a fully random process. Some authors showed with molecular dynamic simulations that a certain degree of order existed in lignin structure since β-O-4 guaiacyl bonds were parallel to the hemicelluloses and cellulose microfibrils [32,33].

2.3. Lignin-carbohydrates complex (LCC)

Existence of covalent bonds between lignin and carbohydrates was demonstrated in several studies [34-38]. The intricate assembly lignin-hemicelluloses-cellulose is known as LCC. As shown in **Figure 3**, lignin is covalently bonded mainly to xylan and glucomannan hemicelluloses [38]. Pectin could also form an ester linkage with lignin, but no evidence of such linkage exists. It has been proposed that in middle lamella region, lignin is surrounded by pectin and that a globular pectin–lignin complex is formed [37,39]. Pectin thus seems to have a role in controlling/regulating the shape of lignin in the middle lamella.

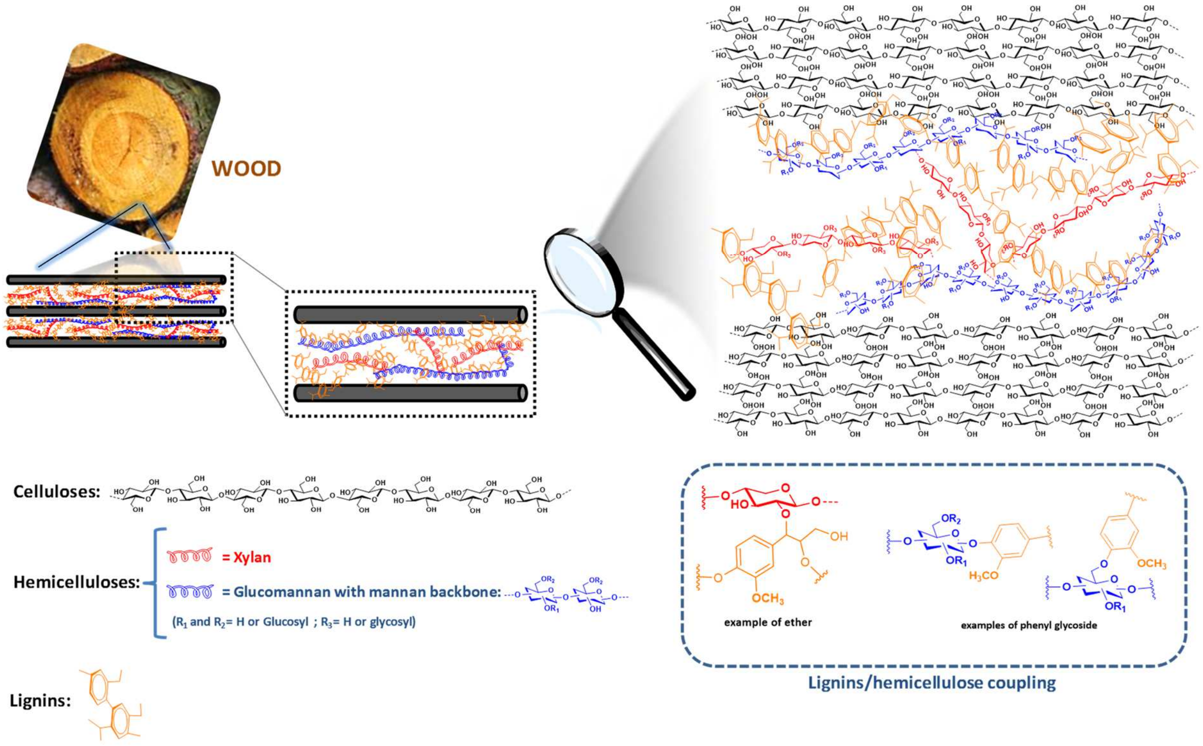

Figure 3. Schematic representation of lignocellulosic matrix from wood.

Hydrogen bonding occurs with cellulose making the LCC structure even more complex. To isolate lignin from wood, the cleavage of lignin-carbohydrates covalent bonds is required. Lawoko et al. (2004) found that about 90 % of the lignin in a spruce Kraft pulp was covalently linked to carbohydrates, the glucomannan–lignin complex being predominant [40]. An organization has been proposed by Salmen and Olsson (1998) where one lignin type is surrounded by xylan and another lignin type is surrounded by glucomannan [41]. Benzyl ester, benzyl ether, and glycosidic bonds are the three types of lignin-carbohydrates covalent linkages. In alkali media, the ester type is hydrolyzed readily, whereas the benzyl ether of an etherified unit is fairly stable even under alkaline pulping conditions. Covalent bonds between xylans and lignin contribute to the flexibility of fibrils [42].

2.4. Biodegradation of native lignin

Lignin biodegradation is part of carbon natural recycling on Earth and serves as a source of inspiration in biotechnology sector with applications in the pulp and paper industry and in the production of biofuels. Only a few fungi from the phylae *Basidiomycota*, *Ascomycota*, and

Deuteromycetes can degrade wood. They are generally grouped into white-rot, brown-rot, and soft-rot fungi according to the color of rooted wood. Among wood-rotting fungi only the white-rot fungi can degrade lignin (e.g. *Daldinia*, *Hypoxylon* and *Xylaria*) [43]. Ligninolytic oxidoreductases secreted by wood-rotting fungi are the only enzymes known to oxidize the phenylpropane units of lignin in nature; namely laccases, lignin-, Mn-, or versatile peroxidases [44]. In the case of lignin- and Mn- peroxidases, H_2O_2 molecule participates in oxidation/reduction mechanism. Wood cell walls components are usually removed simultaneously. However, some white-rot species attack selectively on the lignin and cannot degrade crystalline cellulose. For instance, it was demonstrated that *C. subvermispora* did not produce cellobiohydrolases [45]. Consequently, white-rot fungi lead to a white degraded product of cellulose. High lignified vessel elements with high contents of guaiacyl units are more resistant to white-rot fungi attack probably because they present hindering effects [43]. Brown-rot fungi (e.g *Gloeophyllum trabeum*) primarily degrade cellulose and hemicelluloses via Fenton reactions but they also have the ability of slightly modifying lignin. It was noticed that lignin content as well as the amount of guaicyl units did not influence brown-rot fungi's biodegradation rate [43]. The understanding of lignin biodegradation mechanism is of interest for biopulping processes. The same wood-decaying fungi can be used to pretreat wood chips to facilitate mechanical, thermomechanical, and chemical pulping. Ligninolytic oxidoreductases mode of action can be upgraded thanks to protein engineering to produce new biocatalysts [45].

3. Supplying industrial lignin

3.1. Overview

Lignin is indubitably an abundant raw material on Earth: for a total lignocellulosic biomass of 10^{13} tons, approximately 100 billion tons of lignin are renewed in the biosphere every year. Industrial lignin produced annually only counts for 1.5-1.8 billion tons. A major production of industrial lignins comes from the pulp and paper industry that extracts alone 50-70 million tons of lignin [46-48]. Today, most of these extracted quantities is used in the form of black liquor for internal energy input in the pulping process. Specialists agree to claim that lignin's potential is under-exploited with a current business of only 300 million US$ [48].

3.2. Industrial sources of lignin

3.2.1. Kraft lignin

Kraft lignin is a product of the sulfate pulping process. The annual worldwide production of Kraft pulp equals to 130 million tons, giving rise to a release of approximately 55-90 million tons of Kraft lignin that is mainly used for energy purposes. Indeed, only 2 % of the lignin production from the Kraft pulp industry is commercially used for value-added products [49]. The production of low sugar content sulfomethylated lignin from wood with a production of around 35 000 tons per year (dry basis) can be cited Although the Kraft process is the most predominant pulping process worldwide, the recovery of Kraft lignin chemicals is not well-developed nowadays [50].

3.2.2. Sulfite lignin

The most commercially available lignin is sulfite lignin produced in the sulfite pulping process that uses calcium or other (bi)sulfites. The development of Kraft lignin production has contributed to sulfite lignin productions decrease from 20 million tons in the 1980s to about 7 million tons nowadays [50]. The production of sulfite lignin decreases in Europe, North America, and Japan but increases in India and China [50]. Note that pulp production *via* the sulfite process is decreasing because of: 1) the high versatility of the Kraft process; and 2) a lower availability of lignosulfonates.

3.2.3. Soda lignin

Soda lignin is a co-product derived from soda anthraquinone process industrialized during the 19th century for non-wood fiber applications (i.e. flax, straw, etc.). These materials are used as sources of pulp and are still used as fiber source for producing papers in developing countries (Asia and South America) and for producing high yield hardwood pulps for packaging papers or boards applications. Non-wood fiber soda pulp mills have a small capacity of production because of the annual variability of the feedstock. The new technologies developed to process the black liquor for energy recovery are more suitable for these mills. Indeed, the removal of the lignin decreases the chemical oxygen demand by about 50 %, leading to a profit stream from an effluent that increases the economic rationale of the mill. Note that the first two soda lignin recovery services were installed in France and India [50,51] but many additional facilities are expected to be added in the next years.

3.2.4. Organosolv lignin

Organosolv lignin is obtained by means of organic solvents in the process [52]. Its structure is closer to native lignin than the other types of technical lignins (i.e. Kraft lignin, lignosulsulfonates). Organosolv lignin is also easily recoverable [52, 53, 54]. Despite these good perpespectives, Organosolv lignin is almost not commercialized due the high capital investments of the implemented technology that has so far not reached the industrial-scale stage [48], with a principal disadvantage of high solvent recovery cost.

3.2.5. Lignin as a by-product from 2nd generation biorefineries

The annual worldwide production of 2nd generation (2G) ethanol from lignocellulosic biomass is evaluated to 316 000 tons. With a mean ratio of 0.5 kg of lignin produced per kg of ethanol, about 200 000 tons of lignin are extracted per year along with the 2G ethanol production [46]. As the focus is made on sugars' extraction, lignin by-product of 2G ethanol biorefineries is poorly studied in terms of chemical structure. The lignocellulosic biomass sources are more suitable for feeding ethanol biorefineries due to their economic and environmental purposes than sugar source feedstock which gets into competing with food and animal feed. In US, for instance, one objective of the Renewable Fuels Standard developed by the US Environmental and Protection Agency was to produce 872 million liters of bioethanol in 2016 with a potential yield of 120 million tons of lignin in 2022. Besides, 60 % of lignin produced (i.e. 72 million tons) is expected to be available for producing high-value products [55]. In 2018, the European Union has updated its Renewable Energy Directive (named RED II) for the period 2021-2030. This updated directive fixed new targets for renewable energy sources in transportation: by 2030, 14 % of the fuel used in road and rail transport must be from renewable sources. 3.5 % of these 14 % must be of lignocellulosic origin with an intermediate milestone of 1 % in 2025 [56]. Knowing all these perspectives, major productions of lignin, as well as bioethanol, are expected in the next few years.

3.2.6. Analysis of the industrial lignin sources

The economic value of each type of lignin depends on the added value of their derivative products. Kraft lignin shows the largest range of applications with middle and high-value products. The availability of this lignin source is guaranteed by pulp and paper producers. Lignin's price obviously depends on its purity: low purity lignin ranges from 50 to 280 US$/ton whereas high purity lignin may reach 750 US$/ton [47]. The cost of the process will influence the price of the different technical lignins as presented in **Table 1**. The two main producers of lignosulfonates are Borregaard LignoTech and Tembec. Borregaard LignoTech has an annual production of 500 000 tons (dry basis) of lignosulfonates obtained from the pulping of woods whereas Tembec produces 570 000 tons of this polymer. Other producers are settled with a much lower production: La Rochette Venizel (France), Nippon Paper Chemicals (Japan), CartiereBurgo (Italy), and DomsjöFabriker AB (Sweden). The production of sulfur-free soda lignin is dominated by GreenValue SA (Switzerland) which has the largest production capacity (10 000 tons per year). Northway Lignin Chemical (North America) produces solids soda liquor from wood pulping that contain soda lignin, ash and sugars and their derivatives [50].

Table 1. Quantities, prices, and main producers of commercial lignin on a global scale. Adapted from [47, 57]

Lignin	Prices (US$/t)	Annual Production (kilotons per annum)	Main producers
Kraft	260-500	90	MeadWestvaco, Domtar (Lignoboost)
Lignosulfonates	180-500	1000	BorregaardLignotech, Tembec, DomsjoFabriker, Nippon paper chemicals, La Rochette Venizel
Soda lignin	200-300	5-10	Green value. Northway Lignin Chemical
Organosolv	280-520	3	CIMv, DECHEMA/Fraunhofer, Dedini

3.3. Obstacles and barriers in lignin productions

Smolarski (2012) exhibited three main barriers for taking lignin's potential to industrial level: *technology maturity, interest from game-changing investors, and funding options* [48].

In terms of *technology maturity*, lignin is mainly used as a macromolecule, whereas there is an economic potential in the production of aromatics. However, production of aromatics requires the development of depolymerization processes that are still in progress in terms of research. Currently, the existing technologies cannot produce fine chemicals (with increased functional groups) and bulk chemicals (with decreased functional groups). Vanillin but no BTX compounds (ie. benzene, toluene and xylene) are available after oxidative depolymerization whereas phenol and benzene are generated by hydro-deoxygenation. The quantities of these products commercially available remain very low compared to the achievements of almost 20 years of research. Supercritical depolymerization producing monomeric phenolic compounds is very costly but seems appealing in terms of economy: (1) this technology has already been used to extract compounds from biological resources, showing its efficiency in other domains; (2) the solvent (CO_2) is an environmentally friendly solution; (3) operating conditions (temperature and pressure) are easier to control compared to other processes.

Another issue is *the interest from game-changing investors*. A huge demand for various chemicals is observed nowadays. They are only supplied by the petrochemical industry. Thus, a progressive switch from oil to biomass refinery is needed. Investments in sugar platforms have favored the production of biofuels, mainly because of government mandates. However, these sugars platforms have clearly slowed down other biomass-based platforms such as wood-based chemicals, including lignin-based chemicals.

The last obstacle relies in *the lack of funding options* for biorefiners. Even if few funding options are available to promote biorefining, their attractiveness is low for investors. Beyond government mandates, investors have no economic incentive to raise money in such emergent technologies. For instance, Gevo introduced its stocks in February 2011 at 15 US$ and it was traded mostly under 6 US$ during June 2012. We may cite other cases like Gevo: Codexis, Amyris, KiOr and Solazyme. This lack of funding may slow down the expansion of biorefineries in the future. Beyond these technico-economic aspects, a key factor for the materialization of the lignin-based bioeconomy potential is the ability to mobilize wood from forests. Nevertheless, Orazio et al (2017) reported that “the largest unused potential of Europe’s wood resources is 'locked' in small and medium privately-owned forests” [58]. Both sociological and institutional are at play to explain the wide diversity of development of the forestry sector across regions and countries [59], and much research is needed to help designing policies adapted to local situations.

4. Extraction processes of wood-lignin

As previously mentioned, lignin can be found in different forms and can be isolated by different processes. Usually, lignin is a co-product in the pulp and paper industry as well as a byproduct in lignocellulosic biomass pretreatment and saccharification. These processes make lignin a potential source of value-added products in the chemical, food, pharmaceutical, textile and cosmetic fields [60]. For centuries, several processes such as sulfite, Kraft and soda-anthraquinone processes have been developed and applied in the paper and pulp industries in which lignin is not the target [61]. Nowadays, several alternative developed in the biorefinery concept also called "pretreatment methods", have been subjected to investigation and allow isolation and recovery of lignin from wood. These alternative processes are usually classified into chemical, physicochemical and enzymatic pretreatments [62].

4.1. Industrial wood-lignin extraction processes

4.1.1. Lignin extraction with Kraft process

Kraft process is the most applied (96 % of the market) to isolate lignin from a wood material [63]. Mainly used in the pulp and paper industries, the Kraft process uses significant amounts of aqueous soda (NaOH) and sodium sulfide (Na_2S) at high-temperature (150-180 °C) for about 2 hours. During this treatment, a major part of lignin gets solubilized and captured in the spent pulping liquor called "black liquor". The black liquor contains also a significant quantity of wood hemicelluloses [62,64].

As the Kraft process is highly energetic, the lignin in black liquor serves as a fuel for Kraft plant. In this case, black liquor is first concentrated by evaporators to 40-50 % solids content and then burnt for its heating value. The released heat is used in the one hand for energy recovery, the heat released as high-pressure steam and in the other hand to drive the mill's chemical recuperation of inorganic compounds. For example, this allows also the regeneration of the cooking reactive (sodium sulfite) through a causticization cycle [64]. The amount of lignin produced by cooking plants is greater than for the energy production of factories and could be valorized in other domains. For this purpose, the commercial process (LignoBoost) isolates Kraft lignin from black liquor at high purity by acidification of the liquor with CO_2 [65]. pH lowering is undertaken using mineral acids such as sulfuric or chloridric acids for example. By decreasing the pH, a consequential lignin portion is precipitated and may be recovered by filtering and washing. The plants located respectively at Domtar's Plymouth mill (USA) and at Stora Enso's Sunila mill (Finland) can produce approximately 75 000 tons Kraft lignin per year based on the LignoBoost process [5,50,57].

4.1.2. Lignin extraction with sulfite process

Industrially applied for the very first time by Ekman in 1874, sulfite process is the most ancient pulping method for paper production allowing lignin recovery as a by-product [66]. The sulfite process is now of minor importance compared to the Kraft process, about 7 million tons per year [67]. It is reserved to produce so-called special pulp, most of which being a dissolving pulp for the manufacture of cellulose derivatives. However, it is the most important source of commercially available lignin with a production of 1 million tons per year of lignosulfonates [57]. Sulfite cooking is based on the use of aqueous sulfur dioxide (SO_2) and a sulfite base (calcium, sodium, magnesium or ammonium salts). During cooking, large amounts of sulfur are incorporated into lignin as sulfonate groups -SO_3 linked to the benzylic carbon atom of the lignin phenylpropane (C9) unit. The degree of substitution varies from 0.4 to 0.5 sulfonate per C9 unit [50, 68, 69]. When compared with Kraft lignin, lignosulfonates contain higher sulfur, carbohydrate and inorganic impurities (**Table 2**) [69].

Table 2. Chemical composition of different technical lignins [70].

Lignins	Ash content (%)	Sulfur content (%)	Sugars content (%)	Molecular weight (g/mol)	Polydispersity
Kraft	0.5-3.0	1.0-3.0	1.0-2.3	Up to 25 000	2.5-3.5
Soda	0.7-2.3	0	1.5-3.0	Up to 15 000	2.5-3.5
Lignosulfonates	4.0-8.0	3.5-8.0	-	Up to 15 000	4.2-7.0
Organosolv	1.7	0	1.0-3.0	Up to 5 000	1.5

4.1.3. Lignin extraction with soda-anthraquinone (soda) process

The soda process was developed a few years before the Kraft process. It is quite similar but remains marginal in the paper economy. Practically applied to non-woody biomass such as sugarcane, bagasse and straw, soda lignin isolation process has been industrialized since 1853 [64]. The lignocellulosic material is treated with a high-pressure NaOH solution at a temperature not exceeding 165 °C. The addition of anthraquinone (0.1 %) stabilizes hydrocelluloses, prevents their attack by the alkaline medium and catalyzes delignification [71]. As in the Kraft process, a part of the black liquor containing lignin is concentrated and burnt in a boiler to generate energy and recover the salts of the starting liquor. The other part of black liquor can be treated for lignin recovery, mainly using an acid precipitation process. The advantage of the soda process results in the absence of sulfur in the cooking products which is the major way to get a lignin purer than Kraft lignin [70].

4.2. Alternative wood-lignin extraction processes

As in the methods mentioned above, the so-called alternative wood-lignin extraction processes also known as pretreatment methods, point to split the covalent links bonding the lignin and the carbohydrate components of wood, thus allowing their fractionation [72-74]. The efficiency of these processes derives from the purity of lignin, cellulose, hemicelluloses, the yield of components and the degree to which the structure of the isolated components are altered. Among all these processes, only three are being exposed further.

4.2.1. Alternative chemical lignin extraction processes

4.2.1.1. Acid pretreatment

The primary focus of this process is the isolation and hydrolysis of the cellulose portion of biomass as an ethanol feedstock. The commonly used conditions are high acid concentration with low temperature or low acid concentration with high temperature [75]. This extraction process provides a lignin-containing stream as a by-product. Commercial processes for acid hydrolysis were known in the early part of the 20th century and have the advantage of being inexpensive and straightforward. However, several disadvantages have been reported. Very effective separation can be achieved at high acid concentrations. However, corrosion resistant reactors and an effective acid recovery process are needed for the separation, which raises the overall cost. Both organic and inorganic acids have been used for dilute acid of lignocellulosic biomass. They include hydrochloric, sulfuric, phosphoric, maleic, nitric, formic and acetic acids. Among them, sulfuric acid was the most commonly used [76].

4.2.1.2. Organosolv extraction processes

The principle of this process, derived from the paper industry, is based on the extraction of lignin and hemicelluloses from wood materials using organic solvents (**Figure 4**). Commonly used organic solvents are ethanol, methanol, acetone, or a mixture of water/organic solvent at temperatures ranging from 100 to 250 °C [77]. This extraction can be improved by adding acid catalysts of mineral nature (HCl, H_2SO_4, and H_3PO_4) or organic acid (such as formic or acetic acids) at lower temperatures. The addition of an acid catalyst to the pulping media causes the cleavage of more ether-linkages, but also favors the occurrence of intramolecular condensation reactions, giving rise to a more complex lignin structure [78]. Most of the employed solvents can be easily removed and recycled at their low boiling point. The resulting lignin features are the same to the native lignin ones. The organosolv treatments preferentially cleave the carbohydrate-lignin bonds, leading to high molecular weight lignin without significant chemical modification. Lignin is recovered at the end of the process as a precipitate, after addition of a large amount of acidic water. In the 1990s, some industrial processes were operational: the Organocell process using methanol [79-81], the Alcell process using ethanol [82], and the Milox process using peroxyformic acid [83].

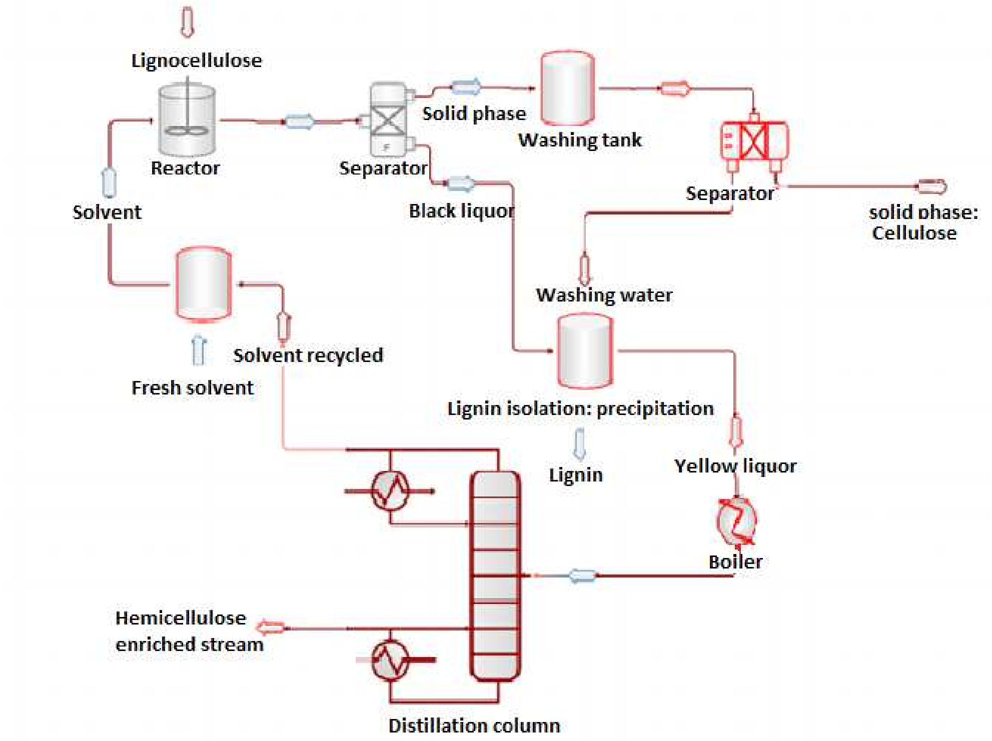

Figure 4. Organosolv process

4.2.1.3. Lignin extraction with ionic liquids

Ionic liquids (ILs) are described as “green solvents” composed of various small inorganic anions and large organic cations. Melting point temperatures of ILs can be below ambient temperature and as low as -100 °C [84]. The ILs can dissolve simultaneously lignin and carbohydrates of wood, or other lignocellulosic biomasses. Various ILs like N-methylmorpholine-N-Oxide monohydrate (NMMO), 1-n-butyl-3-methylimidazolium chloride

(BMIMCl) and 1-allyl-3-methylimidazolium chloride (AMICl) have been used for the pretreatment of lignocellulosic biomass to improve its enzymatic digestibility [75]. It has been also reported that 26.1 % and 34.9 % of initial lignin in the softwood and hardwood lignins respectively, was dissolved by using 1-ethyl-3-methylimidazolium acetate ionic liquid [85]. It should be noted that lignins recovered by ILs are not yet available at an industrial scale due to the price and the availability of ILs. However, due to recent successes in this area, it can be considered as a promising option because lignins obtained with ILs exhibit similar properties to organosolv lignins and can be used in the same applications as soda and organosolv lignins [74].

4.2.2. Physicochemical lignin extraction process

4.2.2.1. Steam explosion

Steam explosion was originally developed in 1924 by Mason to produce chipboard panels [86]. Its application was subsequently extended to the production of ruminant feed in the second half of the 20th century. Steam explosion is a thermochemical process that allows the breakdown of lignocellulosic materials by the combined action of high-pressure steam diffusion within the material structure, hydrolysis of glycosidic bonds by organic acid formed during the process, and shearing forces due to the expansion of the moisture [87]. The process consists of two distinct phases: the steam cracking and the explosive decompression [88]. In the steam explosion, only a small fraction of lignin is solubilized, and alkaline delignification is often used to complete biomass fractionation.

4.2.2.2. Ammonia fiber expansion (AFEX)

AFEX is a physicochemical alkaline pretreatment involving the periodic exposure of lignocellulosic biomass to liquid ammonia at high temperature (90-180 °C) under pressure (7-40 bars) for a very short period before proceeding to a sudden decompression that allows to evaporate the ammonia and explode the substrate [89]. This pretreatment causes a small reduction in the amount of lignins, the elimination of hemicelluloses fraction and the decrystallization of cellulose contained in the wood. Its advantages include high redistribution of lignin, ammonia recovery and recycling [78]. While most of the pretreatments such as steam explosion produce a slurry that can be separated in solid and liquid fractions containing the lignin, ammonia fiber expansion produces only a pretreated solid wood material. However, it has also been shown that the AFEX process was not very efficient for wood with high lignin content such as softwood [76].

4.2.2.3. Liquid hot water

The liquid hot water, also called in other terms hydrothermolysis, hydrothermal pretreatment or aqueous fractionation, is a wood biomass pretreatment like steam pretreatment method but as the name suggests, it uses water at high temperature (170-230 °C) and pressure (up to 5 MPa) instead of steam [90]. In the process, the hot compressed water is put in contact with the woody-biomass for up to a quarter of an hour at a temperature up to 200 °C. The liquid hot water process allows to dissolve between 40 and 60 % of the total biomass, a great quantity of hemicellulose (up to 80 %) and 35-60 % of lignin [76].

4.3. Life cycle analysis of lignin production

Life Cycle Analysis (LCA) of a product is a process that allows to compile and to evaluate the inputs (materials and energy), and the outputs of the product (pollutants, emission, product and by-product) in order to estimate its potential impact on the environment. Investigation about the potential environmental impact of lignin production through four processes (Kraft, Organosolv, soda, and sulfite) was performed [91]. The Organosolv process presents the highest total potential environmental impact (PEI) per kg of lignin with a value of 0.25 PEI per kilogram followed by the Kraft process with approximately 0.09 PEI per kg of product. Finally, the soda process presents the lowest pollution with PEI values of 0.02 per kilogram followed by the sulfite process having a value of 0.03 PEI per kg of lignin. Furthermore, the removal of lignin by different technologies point out several economically and environmentally advantages and disadvantages. Beyond production costs and environmental impact, the extraction method must be selected depending on the use that will be given to lignin. Organosolv methods allow the recovery of high-quality lignin but continue to be a high-cost technology, while Kraft and sulfite processes allow obtaining a lignin at reasonable costs but with impurities. However, the soda extraction process generating lower production costs and low environmental impact is still the more sustainable option of producing lignin for low and high value-added processing [70,91]. To conclude, the toxicological impact of reagents that are being evaluated in the Organosolv and Kraft processes have similar values and are higher compared to the other two processes (soda and sulfite processes).

5. Lignin incorporation in polymeric materials

At present, only 2 % of the lignin production from the pulp industry is used for value-added products [49]. The use of lignin in polymeric materials and as a source of chemicals is considered as solutions towards a more sustainable world. The next sections focus on papers that investigate the use of lignin in polymer-based materials, bearing in mind that fine chemicals can also be obtained from lignin. The reader should be aware that our description is not exhaustive as there are endless possibilities of using lignin or its depolymerized products in many industrial applications.

5.1. Current applications for lignin

Lignosulfonates are used as additives in concrete admixtures for their capacity to retain water. Their surfactant properties are of interest in agrochemicals, dyes, pigments, coatings, textile lubricants, personal care products, or detergent formulations. In the animal feed sector, lignosulfonates are used as animal feed binder, while helping lubrification of the pelletizing equipment and providing the animals with calcium and sodium. Lignosulfonates also find their applications in the formulation of phenol and urea formaldehyde thermosets. They can act as soil stabilizers while increasing soil stiffness [92].

Sulfonated Kraft lignins are currently used as dispersants and rheology agents in dyes, as dispersants for crop protection products, as air entrainment formulations in mortar, as battery expanders, or asphalt emulsifiers. Ethoxylated sulfonated Kraft lignin has been used as doping in the production of conductive polymers, being likely dispersible in water. The production of low molecular weight chemicals from Kraft lignin has been reported. For instance, dimethyl sulfoxide (DMSO) molecule is produced from Kraft black liquor by Gaylord Chemical.

Organosolv and Soda lignins have fewer application fields than Kraft and sulfite lignins because their production is lower (**Table 1**). Nevertheless, their structure, closest to original lignin, is an asset in most cases. For instance, they are used in thermoset adhesives, animal health, and nutrition area because of their low sulfur content.

5.2. Challenges of lignin integration into polymeric materials

Lignin has been considered over the last decades as one of the most interesting raw material to partially substitute materials with fossil origin. It exhibits a good compatibility with other biopolymers (i.e. polylactic acid) or with natural fibers due to its hydrophilic nature, unlike synthetic polymers. Functionalization on lignin polar groups can be imparted in order to enhance compatibility with hydrophobic polymers (i.e. polypropylene). Crosslinking with other polymers is also possible via its hydroxyl groups to give rise to novel materials. Lignin is known for enhancing the biodegradability of polymers where it has been incorporated. However, its large molecular weights and the existence of steric hindrance effects are detrimental to the reactivity of lignin. Many researchers prefer to study depolymerization of lignin that leads to monomer building blocks, instead of working with high molecular weight lignins with heterogenous structure. Aromatic building blocks can be obtained after depolymerization, the latest’s often providing rigidity, hydrophobicity, and fire resistance to materials. With these techniques, bio-based epoxy resins, polyesters and others can be synthetized from lignin depolymerized products, after functionalization [93]. Finally, low-cost carbon fibers are obtained from lignin which is a carbon-rich compound. Figure 5 give the main valorization of lignin into polymer-based material.

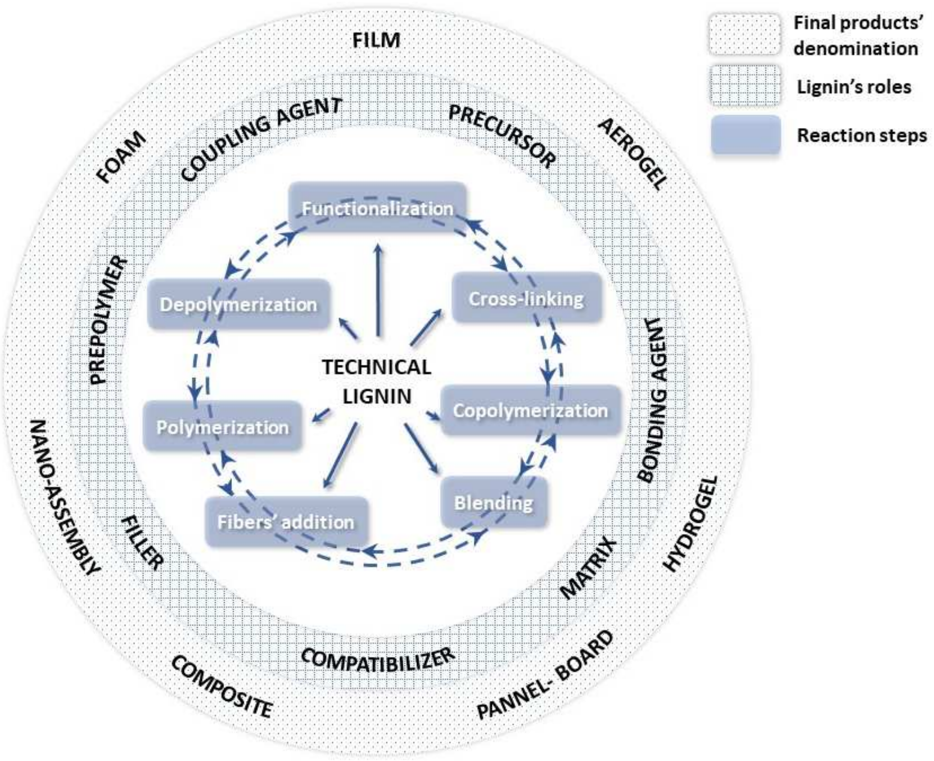

Figure 5. General scheme for valorization of lignin into polymer-based materials. Some common reaction/processing steps, the different roles of lignin, and some common denominations of the final products are presented.

5.3. Lignin incorporation in bioplastics and biocomposites

The main assets of bioplastics and biocomposites materials are their sourcing from renewable raw materials, and their eventual biodegradability.

5.3.1. Unmodified lignin matrix in biocomposites

Composite materials have been developed with a binding matrix of unmodified technical lignin and natural fibers for industrial engineering, industrial goods of mass consumption, electronic or automotive industry applications. Their main advantages are their low density, biodegradability, and wood compatibility. The most striking example of such material is known under the trade name Arborform® (Tecnaro GmbH company), material developed at the Fraunhofer-Institut für Chemische Technologie [94]. This new generation of material is made of natural renewable raw constituents and can be processed by injection molding like thermoplastics. It is constituted of lignin matrix (30-60 %), natural fibers like hemp or flax (10-60 %), and additives such as processing aids, impact modifiers, and flame retardants (0-20 %). Lignin matrix can sometimes be blended with polylactic acid (PLA). Mean tension at break is 18 MPa with a mean Young modulus of 6 GPa, so Arborform® can compete with synthetic thermoplastics in some cases. Rozite et al. (2011) developed composites with similar lignin matrix and 30 % flax fibers focusing on stress-strain curves, temperature behavior, and relative humidity [95]. Domínguez-Robles et al. (2017) described the use of lignin adhesive to produce high-density fiberboards (HDF) [96]. Flexural strength of HDF was higher than commercial ones (96.81 MPa for 15 % lignin amount). Other authors developed composites by compression molding with lignosulfonate matrix, natural fibers, and no additives [97].

5.3.2. Lignin filler in combination with bioplastics

Lignin was tested as filler in bioplastic matrix. The biopolymers PLA, poly(3-hydroxybutyrate) (PHB), and polyamide 10,10 (PA1010) were used by Al Mamun et al. [98]. Lignin incorporation improved stiffness of the material because tensile and flexural moduli increased but the tensile and flexural strength were found to be much lower than the neat polymers. Addition of oleo chemicals plasticizers could improve mechanical properties, and especially the tensile strength but the neat polymers properties could not be reached. Rahman et al. (2013) prepared sheets from ternary system of softwood Kraft lignin, PLA, and polyethylene glycol (PEG) by melt-blending [99]. With 30 % of PEG and 15 % of lignin, a good balance between flexibility and stiffness has been achieved. Spiridon et al. (2015) showed that an addition of lignin to PLA matrix induced an increase of the impact strength and thermal stability of PLA [100]. After accelerated weathering, tensile and impact strengths decreased less than PLA matrix. Commercial PLA/lignin blends are proposed by Modern Plastics under the name PLA-L for polyethylene terephthalate (PET) replacement. They are made with fatty acids and wax as additives. Several blends of lignin with other biopolymers have been reported. For instance starch/lignosulfonates blend films were prepared by Shi and Li (2016) by casting and solvent evaporation method with sorbitol as plasticizer [101]. Hydrophobicity and rigidity were improved but the ultimate tensile strength did not when lignin content increased.

5.4. Lignin in thermoplastics

Lignin can be used as a filler, matrix, coupling agent, or compatibilizer in thermoplastic blends or composites. All technical lignins are suitable for this purpose. Lignin can be blended to other thermoplastics like polyethylene, polypropylene, or polystyrene but the low compatibility between them often requires lignin modification. Frequent lignin modification in thermoplastics is its etherification with maleic anhydride [102,103]. Lignin can also act as a compatibilizer between natural fibers and thermoplastics (coconut-PP, eucalyptus-PP, wood-HDPE, etc.). Processing of such materials is made by extrusion followed by injection or compression molding. In a whole, mechanical properties of synthetic resins are negatively affected when lignin is incorporated in a blend. However, water absorption and swelling have been reported to decrease [104,105]. Antibacterial and biodegradation properties of lignins can be of interest in the preparation of films for food-application [106].When lignin was used as a compatibilizer, thermal properties of materials were most of the time improved.

5.5. Lignin in thermosets

Crude or depolymerized lignins have the ability after optional functionalization to crosslink (i.e. with anhydrides, amines functional groups) to form thermoset resins. Unlike thermoplastics, thermosets cannot be melted again by increasing the temperature because they form a rigid network of polymer chains after crosslinking reaction. The most common lignin-based thermosets are phenol-formaldehyde (PF), polyurethane (PU), and epoxy resins. Adhesives for wood, composite boards, films, and aerogels can be processed with lignin-based thermosets.

5.5.1. Lignin substitute in phenol-formaldehyde (PF) resins and aerogels

It is well known that lignin can substitute to phenol in phenol-formaldehyde resins. However, Dessbesell et al. (2018) predicted with techno-economic and risk analysis that a depolymerized Kraft lignin (DKL) from biorefinery was not price-competitive compared to phenol for resin production [107]. However, they predicted that it is feasible to substitute petroleum-based polyols by DKL for polyurethane production. Experimentally, some high values of lignin replacement have been reported. Akhtar et al. (2009) replaced up to 70 % phenol by lignosulfonates in lignin-phenol-formaldehyde resins for plywood [108] with no significant changes found on the plywood failure. Ghorbani et al. (2018) prepared paper-based laminates with resins containing 40 % (w/w) substituted phenol by pine Kraft lignin. Laminates were tested in terms of water absorption, thickness swelling and mechanical properties, and fulfill test standards requirements for outdoor purposes [109]. Wood adhesives made of lignin-glyoxal instead of toxic formaldehyde were successfully prepared by Mansouri et al. (2007) and applied to panels manufacturing [110]. Lignin can be modified by hydroxymethylation or phenolation to increase its reactivity to produce PF resins. For instance, Taverna et al. (2018) studied the substitution of phenol by hydroxymethylated Kraft lignins in phenol-formaldehyde resols for laminates production [111]. It was possible to replace up to 20 % (w/w) of phenol with no significant changes in the thermal and mechanical laminates properties. Note to mention that these lignin-modified laminates exhibited better water resistance.

Lignin is used as a substitute for phenol and resorcinol polymer precursor in aerogels preparations. Guaiacyl units in addition to unconjugated ketones and carbonyl groups in lignin are involved in condensation reactions with phenol and formaldehyde. Lignin-based aerogels are mesoporous foams with high surface area and low density obtained after solvent evaporation in hydrogels. They can be used for energy storage applications or acoustic insulator. It is possible to incorporate up to 80 % (w/w) lignin in phenol-formaldehyde aerogels [112]. Lignin has an impact on porous structure morphology (mesopores formation) and gelation time of the material.

5.5.2. Lignin substitute in polyurethane (PU) resins

Lignin is a good candidate for crosslinking with diisocyanate in PU resins. PU with unmodified lignins exhibits brittle behavior. Therefore, authors recommend the use of lignin in combination with other polyols to create some soft segments via the crosslinking reaction. Polyethylene glycol (PEG), polybutadiene glycol (PBG), hydroxyl terminated polybutadiene, or poly(ethyleneadipate) (PEA) are frequently used. Ciobanu et al. (2004) studied the properties of lignin-PU films prepared with 4.2-23.2 % (w/w) of soda lignin and containing soft segments of PEA and PEG [113]. The tensile strength lignin-PU film can be improved compared to pure PU film, but the elasticity and the decomposition temperatures did not increase. To improve reactivity with isocyanates, numerous authors have studied modification of lignin including etherification (e.g. hydroxypropyl lignin) and esterification. The use of low contents of nitrified lignin for PU synthesis has also been reported. In addition to films, rigid or flexible foams were prepared and characterized in various studies. For instance, Luo et al. (2018) successfully applied a one-pot method to obtain foams from lignin powder, bio-based soy polyols, and polymeric methyldiphenyldiisocyanate [114]. Covalent bonds were formed between lignin and polyols. The foams were rigid, biodegradable, and exhibited improved thermal and mechanical properties up to 218.1 MPa.g^{-1}.cm^{-3} with 5 % (w/w) lignin powder.

5.5.3. Lignin substitute in epoxy resins

From depolymerized products of lignin such as 4-(1-propenyl)guaiacol, 4-propylguaiacol, vanillyl alcohol, guaiacol, or vanillin various routes to epoxy resins have been proposed [93]. Such monomers can be obtained directly during deconstruction of lignocellulosic biomass. The lignin-based molecule is made to react, with epichlorohydrin for instance, to form epoxy functionality [115]. Lignin-based epoxy-resins are obtained by subsequent polymerization with amines or anhydrides. These materials possess high performance in terms of mechanical, thermal, and adhesive properties as well as chemical resistance.

5.6. Lignin for carbon fibers and activated carbon

Lignin-derived from wood has been of interest as an alternative precursor since it naturally contains a six-membered ring aromatic structure and is abundantly available at low cost [116]. One interesting lignin valorization results in carbon fiber synthesis. Carbon fibers are one of the most important engineering materials in various industrial fields, having light-weight properties while providing them strong mechanical strength [117]. Lignin-based carbon fibers have been studied for nearly 50 years [118]. Initially, carbon fibers have been produced from polyacrylonitrile (PAN), and the precursor alone costs as much as the half of the production cost of the carbon fibers [119]. Low-cost carbon fibers made from non-petroleum precursors could enable the application of carbon fibers in large scale. Lignin is expected to result in savings between 37-49 % of the final cost of producing carbon fiber [120]. Nevertheless, lignin is a brittle bio-based polymer that cannot be spun and stretched into fibers without modification. Carbon fibers were synthesized from different lignin either by thermal processing, chemical modification, or mixing lignin with other polymers compounds [121]. Note that carbon fibers were produced from Kraft lignin, without any chemical modification through a thermal spinning process followed by carbonization [122]. The University of Iowa developed a robust process for producing high quality, low-cost carbon fine-diameter fiber from a lignin precursor. The lignin precursor was produced, spun and stretched before being pyrolyzed into the carbon fiber. To obtain a carbon fiber derived from lignin, this polymer is usually first converted into fibers by extruding a molten or solvent-swollen gel. Then, the spun fibers are oxidized in the air. At this point, the filaments become pyrolyzable without fusion. During pyrolysis under nitrogen or inert atmosphere, the fibers are carbonized with removal of volatile hydrocarbons, oxidized derivatives, carbon monoxide and moisture [123]. More specifically, carbon electrodes are being developed for batteries and electrochemical capacitor devices. Lignin can be used as a precursor of activated carbon for electrodes preparation, and especially for carbon anodes. Tenhaeff et al. (2014) developed, with a novel synthesis method, interconnected three-dimensional architectures of carbonized lignin for lithium insertion [124]. This anode material, with its high specific capacity and its stable cycling is suitable for high power and high energy applications.

6. Conclusion

Lignin is a not classical biopolymer, with its non-defined and complex structure, and its high level of heterogeneity depending of numerous factors. Approximately 95 % of lignin's worldwide production is used to save energy through cogeneration systems, while the remaining 5 % has been marketed for the formulation of adhesives, dispersants, surfactants and rubbers mainly. Lignin shows a huge economic potential, especially if the oil price is seen to increase. The main key-issue for promoting the development of lignin-based products remains the economic incentives in terms of lignin sources and lignin-based products. Beyond subsidies, investors must be aware of the potential growth of the lignin especially for high-value products (BTX, vanillin, phenol, carbon fiber). The second issue relies in promoting these high value-products in a first step, but it would be necessary to promote other innovative lignin-based products such as bio-based materials (bioplastics, composites, etc.). However, this will only be possible when the first issue is overcome and when robust, affordable and environmental friendly extraction processes are available. Then, the stabilizing of lignin sources will decrease their price and open new perspectives for the lignin-based industry. Utilization of lignin as material could be of great interest as the sole limitations in this field of application is the imagination. In the future bioeconomy, wood should be biorefined to produce biofuel but also carbon fiber, bioplastics, hydrogels, biofoams, elastomers, and others. These products need to be competitive with oil-based ones. The multifunctionalities of lignin have been the subject of a lot of publications and patents but rather not associated with economic success on the market; although small companies with high level of technology for the extraction and purification of several grades of lignins recently emerged. The plant enginery using the new genetic tools and a better understanding of lignin biosynthesis pathways could lead to wood more adapted to biorefinery processes with a control of lignin structures, and above all, the control of covalent linkages between lignin and polysaccharides of the cell wall. Moreover, note that even if lignin is a biodegradable polymer, its lifetime in the environment is long when formulated into materials. So, they can be considered as carbon trap to store carbon dioxide. Lignin could then be a sustainable solution to support new bio-based materials in a context of depleting non-renewable fossil resources.

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References

[1] D. Kun, B. Pukánszky, Polymer/lignin blends: Interactions, properties, applications, Eur. Polym. J. 93 (2017) 618–641.

[2] G. Chatel, R.D. Rogers, Review: Oxidation of lignin using ionic liquids—An innovative strategy to produce renewable chemicals, ACS Sustain. Chem. Eng. 2 (2014) 322–339.

[3] D. Fengel, G. Wegener, Wood—Chemistry, Ultrastructure, Reactions, Walter de Gruyter, Berlin, 1984, pp. 56–58.

[4] H. dos Santos Abreu, M.A. Maria, J.L. Reis, Dual oxidation ways toward lignin evolution, Floresta e Ambiente. 8 (2001) 207-210.

[5] J. Hu, Q. Zhang, D.-J. Lee, Kraft lignin biorefinery: A perspective, Bioresour. Technol. 247 (2018) 1181–1183.

[6] https://globenewswire.com/news-release/2015/11/20/789059/0/en/Global-Lignin-Market-is-Expected-to-Reach-US-900-Million-by-2020-Growing-at-2-5-CAGR.html (accessed 21st December 2018)

[7] W. Xu, X. Wang, N. Sandler, S. Willför, C. Xu, Three-dimensional printing of wood-derived biopolymers: a review focused on biomedical applications, ACS Sustain. Chem. Eng. 6 (2018) 5663–5680.

[8] G. Brodeur, E. Yau, K. Badal, J. Collier, K.B. Ramachandran, S. Ramakrishnan, Chemical and physicochemical pretreatment of lignocellulosic biomass: A Review, Enzyme Res. 2011 (2011) 1–17.

[9] S.-H. Li, S. Liu, J.C. Colmenares, Y.-J. Xu, A sustainable approach for lignin valorization by heterogeneous photocatalysis, Green Chem. 18 (2016) 594–607.

[10] B. Becker, B. Marin, Streptophyte algae and the origin of embryophytes., Ann. Bot. 103 (2009) 999–1004.

[11] M.J. Oliver, Z. Tuba, B.D. Mishler, The evolution of vegetative desiccation tolerance in land plants, Plant Ecol. 151 (2000) 85–100.

[12] K.G. Karol, R.M. McCourt, M.T. Cimino, C.F. Delwiche, The closest living relatives of land plants, Science 294 (2001) 2351–2353.

[13] W.E. Friedman, M.E. Cook, The origin and early evolution of tracheids in vascular plants: integration of palaeobotanical and neobotanical data., Philos. Trans. R. Soc. Lond. B. Biol. Sci. 355 (2000) 857–68.

[14] H. Renault, A. Alber, N.A. Horst, A. Basilio Lopes, E.A. Fich, L. Kriegshauser, G. Wiedemann, P. Ullmann, L. Herrgott, M. Erhardt, E. Pineau, J. Ehlting, M. Schmitt, J.K.C. Rose, R. Reski, D. Werck-Reichhart, A phenol-enriched cuticle is ancestral to lignin evolution in land plants, Nat. Commun. 8 (2017) 14713.

[15] A. Bjorkman, Studies on finely divided wood. Part I. Extraction of lignin with neutral solvents, Sven. Papperstidning. 59 (1956) 477–485.

[16] S. Laurichesse, L. Avérous, Chemical modification of lignins: Towards biobased polymers, Prog. Polym. Sci. 39 (2014) 1266–1290.

[17] E. Adler, Lignin chemistry-past, present and future, Wood Sci. Technol. 11 (1977) 169–218.

[18] Q. Zhao, R.A. Dixon, Transcriptional networks for lignin biosynthesis: more complex than we thought?, Trends Plant Sci. 16 (2011) 227–233.

[19] J. Grima-Pettenati, M. Soler, E.L.O. Camargo, H. Wang, Transcriptional regulation of the lignin biosynthetic pathway revisited-new players and insights, Adv. Bot. Res. 61 (2012) 173–218.

[20] K.M. Herrmann, L.M. Weaver, The Shikimate Pathway, Annu. Rev. Plant Physiol. Plant Mol. Biol. 50 (1999) 473–503.

[21] P. Rippert, J. Puyaubert, D. Grisollet, L. Derrier, M. Matringe, Tyrosine and phenylalanine are synthesized within the plastids in Arabidopsis., Plant Physiol. 149 (2009) 1251–60.

[22] K., Freudenberg, Biosynthesis and constitution of lignin, Nature. 183, (1959) 1152–1155.

[23] J. Ralph, K. Lundquist, G. Brunow, F. Lu, H. Kim, P.F. Schatz, J.M. Marita, R.D. Hatfield, S.A. Ralph, J.H. Christensen, W. Boerjan, Lignins: Natural polymers from oxidative coupling of 4-hydroxyphenyl- propanoids, Phytochem. Rev. 3 (2004) 29–60.

[24] L.B. Davin, M. Jourdes, A.M. Patten, K.-W. Kim, D.G. Vassão, N.G. Lewis, Dissection of lignin macromolecular configuration and assembly: Comparison to related biochemical processes in allyl/propenyl phenol and lignan biosynthesis, Nat. Prod. Rep. 25 (2008) 1015.

[25] L.A. Donaldson, Lignification and lignin topochemistry - an ultrastructural view., Phytochemistry 57 (2001) 859–73.

[26] R. Moller, G. Koch, B. Nanayakkara, U. Schmitt, Lignification in cell cultures of *Pinus radiata*: activities of enzymes and lignin topochemistry, Tree Physiol. 26 (2006) 201–210.

[27] D.L. Petrik, S.D. Karlen, C.L. Cass, D. Padmakshan, F. Lu, S. Liu, P. Le Bris, S. Antelme, N. Santoro, C.G. Wilkerson, R. Sibout, C. Lapierre, J. Ralph, J.C. Sedbrook, p-Coumaroyl-CoA: monolignol transferase (PMT) acts specifically in the lignin biosynthetic pathway in *Brachypodiumdistachyon,* Plant J. 77 (2014) 713–726.

[28] C.G. Wilkerson, S.D. Mansfield, F. Lu, S. Withers, J.-Y. Park, S.D. Karlen, E. Gonzales-Vigil, D. Padmakshan, F. Unda, J. Rencoret, J. Ralph, Monolignol ferulate transferase introduces chemically labile linkages into the lignin backbone, Science 344 (2014) 90–3.

[29] Y. Katayama, T. Fukuzumi, Enzymatic synthesis of three lignin-related dimers by an improved peroxidase-hydrogen peroxide system, J. Japan Wood Soc. 24 (1978) 664-667.

[30] L. Zhang, G. Gellerstedt, J. Ralph, F. Lu, NMR Studies on the occurrence of spirodienone structures in lignins, J. Wood Chem. Technol. 26 (2006) 65–79.

[31] C. Crestini, M. Crucianelli, M. Orlandi, R. Saladino, Oxidative strategies in lignin chemistry: A new environmental friendly approach for the functionalisation of lignin and lignocellulosic fibers, Catal. Today 156 (2010) 8–22.

[32] J.-L. Faulon, P.G. Hatcher, Is There Any Order in the Structure of Lignin?, Energy & Fuels 8 (1994) 402–407.

[33] P.G. Hatcher, R.D. Minard, Comparison of dehydrogenase polymer (DHP) lignin with native lignin from gymnosperm wood by thermochemolysis using tetramethylammonium hydroxide (TMAH), Org. Geochem. 24 (1996) 593–600.

[34] O. Eriksson, D.A.I. Goring, B.O. Lindgren, Structural studies on the chemical bonds between lignins and carbohydrates in spruce wood, Wood Sci. Technol. 14 (1980) 267–279.

[35] O. Karlsson, U. Westermark, Evidence for chemical bonds between lignin and cellulose in Kraft pulps, J. Pulp Pap. Sci. 22 (1996) 397-401.

[36] M. Lawoko, G. Henriksson, G. Gellerstedt, Structural differences between the lignin-carbohydrate complexes present in wood and in chemical pulps, Biomacromol. 6 (2005) 3467–3473.

[37] M. Lawoko, Unveiling the structure and ultrastructure of lignin-carbohydrate complexes in softwoods, Int. J. Biol. Macromol. 62 (2013) 705-713.

[38] R. Deshpande, N. Giummarella, G. Henriksson, U. Germgård, L. Sundvall, H. Grundberg, M. Lawoko, The reactivity of lignin carbohydrate complex (LCC) during manufacture of dissolving sulfite pulp from softwood, Ind. Crops Prod. 115 (2018) 315–322.

[39] N. Terashima, M. Yoshida, J. Hafrén, K. Fukushima, U. Westermark, Proposed supramolecular structure of lignin in softwood tracheid compound middle lamella regions, Holzforschung 66 (2012) 907–915.

[40] M. Lawoko, R. Berggren, F. Berthold, G. Henriksson, G. Gellerstedt, Changes in the lignin-carbohydrate complex in softwood Kraft pulp during Kraft and oxygen delignification, Holzforschung 58 (2004) 603-610.

[41] L. Salmen, A.-M. Olsson, Interaction between hemicelluloses, lignin and cellulose: Structure property relationships, J. Pulp Pap. Sci. 24 (1998) 99-103.

[42] M. Petit-Conil, C. de Choudens, T. Espilit, Ozone in the production of softwood and hardwood high-yield pulps to save energy and improve quality, Nord. Pulp Pap. Res. J. 13 (1998) 16-22.

[43] G. Henriksson, T. Teeri, Biotechnology in the forest industry, in: M. Ek, G. Gellerstedt, G. Henriksson, (Eds.), Pulp and Paper Chemistry and Technology Volume 1. Wood Chemistry and Wood Biotechnology, de Gruyter, 2009, pp. 273-300.

[44] R. Zhang, C. Li, J. Wang, Y. Yan, Microbial Ligninolysis: Toward a Bottom-Up Approach for Lignin Upgrading, Biochem. (2018)

[45] S. Camarero, M. J. Martínez, A. T. Martínez, Understanding lignin biodegradation for the improved utilization of plant biomass in modern biorefineries, Biofuels, Bioprod. Bioref. 8 (2014) 615–625.

[46] P. Bruijnincx, B. Weckhuysen, G-J. Gruter, A. Westenbroek, E. Engelen-Smeets, Lignin valorization, the importance of a full chain approach. Utrecht University, 2016.

[47] L. Hodásová, M. Jablonsky, A. Škulcová, A. Ház, Lignin, potential products and their market value, Wood Research. 60 (2015) 973-986.

[48] N. Smolarski, High-value opportunities for lignin: unlocking its potential. Frost and Sullivan, 2012.

[49] L.P. Christopher, Integrated forest biorefineries: current state and development potential, in: L. P. Christopher (Ed.), Integrated Forest Biorefineries: Challenges and Opportunities, Royal Society of Chemistry, Cambridge, 2012, pp 1-66.

[50] J. Lora, Chapter 10 - Industrial Commercial Lignins: Sources, Properties and Applications, in: M.N. Belgacem, A. Gandini, (Eds.), Monomers, Polymers and Composites from Renewable Resources. Elsevier, Amsterdam, 2008, pp. 225–241.

[51] J.H. Lora, Biorefinery non-wood lignins: Potential commercial impact, 92nd Annual Meeting Preprints – Book C, Pulp and Paper Technical Association of Canada, Montreal, 2006, pp. C3–C6.

[52] C. Hallberg, D. O'Connor, M. Rushton, E.K. Pye, G. Gjennestadt, Continuous counter-current organosolv processing of lignocellulosic feedstocks, US20080299628A1, 2008. https://patents.google.com/patent/US20080299628A1/en (accessed December 2018).

[53] M.J. de la Torre, A. Moral, M.D. Hernández, E. Cabeza, A. Tijero, Organosolv lignin for biofuel, Ind. Crops. Prod. 45 (2013) 58–63.

[54] I. Cybulska, G. Brudecki, J.E. Schmidt, M.H. Tomsen, Organosolv Fractionation of Palm Tree Residues, Energy Procedia. 75 (2015) 742–747.

[55] P.F.H. Harmsen, W.J.J. Huijgen, L.M. Bermúdez Lopez, R.R.C. Bakker. Literature review of physical and chemical pretreatment processes for lignocellulosic biomass, Food & Biobased Research, Wageningen UR, 2010.

[56] https://www.theicct.org/sites/default/files/publications/EU_Fuels_Policy_Update_20180719.pdf (accessed December 2018)

[57] Z. Strassberger, S. Tanase, G. Rothenberg, The pros and cons of lignin valorization in an integrated biorefinery, RSC Adv. 4 (2014) 25310–25318.

[58] C. Orazio, U. Kies, D. Edwards, Handbook for wood mobilization in Europe, European Forest Institute, 2017.

[59] T. Schulz, Comparison of integrative nature conservation in forest policy in Europe: a qualitative pilot study of institutional determinants, Biodivers. Conserv. 23 (2014) 3425-3450.

[60] B. Kamm, M. Kamm, P.R. Gruber, Biorefinery Systems – An Overview, in: Biorefineries-Industrial Processes and Products. Wiley-Blackwell, 2008, pp. 1-40.

[61] F. Cotana, G. Cavalaglio, A. Nicolini, M. Gelosia, V. Coccia, A. Petrozzi, L. Brinchi, Lignin as co-product of second generation bioethanol production from ligno-cellulosic biomass, Energy Procedia, ATI 2013 - 68th Conference of the Italian Thermal Machines Engineering Association, 45 (2014) 52–60.

[62] J. Zakzeski, P.C.A. Bruijnincx, A.L. Jongerius, B.M. Weckhuysen, The catalytic valorization of lignin for the production of renewable chemicals, Chem. Rev. 110 (2010) 3552–3599.

[63] M.T. Holtzapple, LIGNIN, in: B. Caballero (Ed.), Encyclopedia of Food Sciences and Nutrition (Second Edition). Academic Press, Oxford, 2003, pp. 3535–3542.

[64] J.E. Holladay, J.F. White, J.J. Bozell, D. Johnson, Top Value-Added Chemicals from Biomass - Volume II—Results of Screening for Potential Candidates from Biorefinery Lignin (No. PNNL-16983). Pacific Northwest National Lab. (PNNL), Richland, WA (United States), 2007.

[65] P. Tomani, The lignoboost process, Cellul. Chem. Technol. 44 (2010) 53–58.

[66] F.G. Calvo-Flores, J.A. Dobado, J.I. García, F.J. Martín-Martínez, Lignin and lignans as renewable raw materials: Chemistry, Technology and Applications, Wiley, 2015.

[67] H. Sixta, Introduction, in: Handbook of Pulp. Wiley-Blackwell 2008, pp. 2–19.

[68] S.M. Braaten, P.B.E. Christensen, G.E. Fredheim, Comparison of molecular weight and molecular weight distributions of softwood and hardwood lignosulfonates, J. Wood Chem. Technol. 23 (2003) 197–215.

[69] G.E. Fredheim, S.M. Braaten, B.E. Christensen, Molecular weight determination of lignosulfonates by size-exclusion chromatography and multi-angle laser light scattering, J. Chromatogr. A. 942 (2002) 191–9.

[70] A.G. Vishtal, A. Kraslawski, Challenges in industrial applications of technical lignins, BioResources 6 (2011) 3547–3568.

[71] R.C. Francis, T.S. Bolton, N. Abdoulmoumine, N. Lavrykova, S.K. Bose, Positive and negative aspects of soda/anthraquinone pulping of hardwoods, Bioresour. Technol. 99 (2008) 8453–8457.

[72] V. Chaturvedi, P. Verma, An overview of key pretreatment processes employed for bioconversion of lignocellulosic biomass into biofuels and value added products, 3 Biotech. 3 (2013) 415-431.

[73] P.R. Seidl, A.K. Goulart, Pretreatment processes for lignocellulosic biomass conversion to biofuels and bioproducts, Curr. Opin. Green Sustain. Chem. 2 (2016) 48–53.

[74] T. Shahzadi, S. Mehmood, M. Irshad, Z. Anwar, A. Afroz, N. Zeeshan, U. Rashid, K. Sughra, Advances in lignocellulosic biotechnology: A brief review on lignocellulosic biomass and cellulases, Adv. Biosci. Biotechnol. 5 (2014) 246–251.

[75] D. Kumari, R. Singh, Pretreatment of lignocellulosic wastes for biofuel production: A critical review, Renew. Sustain. Energy Rev. 90 (2018) 877–891.

[76] P. Alvira, E. Tomás-Pejó, M. Ballesteros, M.J. Negro, Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review, Bioresour. Technol. 101 (2010) 4851–4861.

[77] X. Zhao, K. Cheng, D. Liu, Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis, Appl. Microbiol. Biotechnol. 82 (2009) 815-827.

[78] Y. Sun, J. Cheng, Hydrolysis of lignocellulosic materials for ethanol production: a review, Bioresour. Technol. 83 (2002) 1–11.

[79] A. Linder, G. Wegener, Characterization of Lignins from Organosolv Pulping According to the Organocell Process Part 2. Residual lignins, Journal of Wood Chemistry and Technology 4 (1989) 443-465.

[80] A. Lindner, G. Wegener, Characterization of Lignins from Organosolv Pulping According to the Organocell Process Part 1. Elemental Analysis, Nonlignin Portions, Journal of Wood Chemistry and Technology 3 (1988) 323-340.

[81] A. Lindner, G. Wegener, Characterization of Lignins from Organosolv Pulping According to the Organocell Process. Part 3. Permanganate Oxidation and Thioacidolysis, Journal of Wood Chemistry and Technology 3 (1990) 331-350.

[82] E.K. Pye, The ALCELL process: a proven alternative to Kraft pulping. Pulping Conf. Proc. USA, 1990.

[83] A. Seisto, K. Poppius-Levlin, T. Jousimaa, Peroxyformic acid pulping of non-woody plants by the Milox method, TAPPI Journal 80 (1997) 215-221.

[84] N. Muhammad, Z. Man, M.A. Bustam, Ionic liquid - a future solvent for the enhanced uses of wood biomass, Eur. J. Wood Prod. 70 (2012) 125–133.

[85] N. Sun, M. Rahman, Y. Qin, M.L. Maxim, H. Rodríguez, R.D. Rogers, Complete dissolution and partial delignification of wood in the ionic liquid 1-ethyl-3-methylimidazolium acetate, Green Chem. 11 (2009) 646–655.

[86] W.H. Mason, Process and apparatus for disintegration of wood and the like (1924) US1578609A.

[87] B.K. Avellar, W.G. Glasser, Steam-assisted biomass fractionation, I. Process considerations and economic evaluation, Biomass Bioenergy 14 (1998) 205–218.

[88] X.F. Sun, F. Xu, R.C. Sun, Z.C. Geng, P. Fowler, M.S. Baird, Characteristics of degraded hemicellulosic polymers obtained from steam exploded wheat straw, Carbohydr. Polym. 60 (2005) 15–26.

[89] F. Teymouri, L. Laureano-Perez, H. Alizadeh, B.E. Dale, Optimization of the ammonia fiber explosion (AFEX) treatment parameters for enzymatic hydrolysis of corn stover, Bioresour. Technol. 96 (2005) 2014–2018.

[90] A.K. Kumar, S. Sharma, Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review, Bioresour. Bioprocess. 4 (2017) 7-26.

[91] J.C. Carvajal, Á. Gómez, C.A. Cardona, Comparison of lignin extraction processes: Economic and environmental assessment, Bioresour. Technol. 214 (2016) 468–476.

[92] B. Ta'negonbadi, R. Noorzad, Stabilization of clayey soil using lignosulfonate, Transportation Geotechnics 12 (2017) 45-55.

[93] Z. Sun, B. Fridrich, A. de Santi, S. Elangovan, K. Barta, Bright side of lignin depolymerization: toward new platform chemicals, Chem. Rev. 118 (2018) 614–678.

[94] H. Naegele, J. Pfitzer, N. Eisenreich, P. Eyerer, P. Elsner, W. Eckl, Method for producing a fiber-reinforced plastic substance (2000) WO2000027925.

[95] L. Rozite, J. Varna, R. Joffe, A. Pupurs, Nonlinear behavior of PLA and lignin-based flax composites subjected to tensile loading, J. Thermoplast Compos. Mater. 26 (2011) 476-496.

[96] J. Domínguez-Robles, Q. Tarrés, M. Delgado-Aguilar, A. Rodríguez, F.X. Espinach, P. Mutjé, Approaching a new generation of fiberboards taking advantage of self lignin as green adhesive, Int. J. Biol. Macromol. 108 (2018) 927–935.

[97] E. Privas, P. Navard, Preparation, processing and properties of lignosulfonate-flax composite boards, Carbohydr. Polym. 93 (2013) 300-306.

[98] A. Al Mamun, M.A. Nikousaleh, M. Feldmann, A. Rüppel, V. Sauer, S. Kleinhans, H.-P. Heim, Lignin Reinforcement in Bioplastic Composites, in: O. Faruk, M. Sain (Eds), Lignin in Polymer Composites, William Andrew, 2016, pp. 153–165

[99] M.A. Rahman, D. De Santis, G. Spagnoli, G. Ramorino, M. Penco, V.T. Phuong, A. Lazzeri, Biocomposites based on lignin and plasticized poly(L-lactic acid), J. Appl. Polym. Sci. 129 (1) (2013) 202–214.

[100] I. Spiridon, K. Leluk, A.M. Resmerita, R.N. Darie, Evaluation of PLA–lignin bioplastics properties before and after accelerated weathering, Compos. Part B Eng. 69 (2015) 342–349.

[101] R. Shi, B. Li, Preparation and characterization of corn starch and lignosulfonate blend film with a high content of lignosulfonate, BioResources 11 (2016) 8860–8874.

[102] L. Hu, T. Stevanovic, D. Rodrigue, Unmodified and esterified Kraft lignin-filled polyethylene composites: Compatibilization by free-radical grafting, J. Appl. Polym. Sci. 132 (2015) 414-484

[103] A. V. Maldhure, J.D. Ekhe, E. Deenadayalan, Mechanical properties of polypropylene blended with esterified and alkylated lignin, J. Appl. Polym. Sci. 125 (2012) 1701–1712.

[104] H.D. Rozman, K.W. Tan, R.N. Kumar, A. Abubakar, Z.A. Mohd. Ishak, H. Ismail, The effect of lignin as a compatibilizer on the physical properties of coconut fiber–polypropylene composites, Eur. Polym. J. 36 (2000) 1483–1494.

[105] T. Liu, Q. Wang, Y. Xie, Q. Fu, Incorporation effect of enzymatic hydrolysis lignin on the mechanical and rheological properties of the resulting wood flour/high-density polyethylene composites, Polym. Compos. 37 (2016) 379–384.

[106] L.B. Tavares, N.M. Ito, M.C. Salvadori, D.J. dos Santos, D.S. Rosa, PBAT/kraft lignin blend in flexible laminated food packaging: Peeling resistance and thermal degradability, Polym. Test. 67 (2018) 169–176.

[107] L. Dessbesell, Z. Yuan, S. Hamilton, M. Leitch, R. Pulkki, C.C. Xu, Bio-based polymers production in a kraft lignin biorefinery: techno-economic assessment, Biofuels, Bioprod. Biorefining 12 (2018) 239–250.

[108] T. Akhtar, G. Lutfullah, R. Nazli, Synthesis of lignin-based phenolic resin and its utilization in the exterior grade plywood, J. Chem. Soc. Pak. 31, (2009) 304-308.

[109] M. Ghorbani, J. Konnerth, H.W.G. van Herwijnen, G. Zinovyev, E. Budjav, A. Requejo Silva, F. Liebner, Commercial lignosulfonates from different sulfite processes as partial phenol replacement in PF resole resins, J. Appl. Polym. Sci. 135 (2018) 45893.

[110] N.-E. Mansouri, A. Pizzi, J. Salvadó, Lignin-based wood panel adhesives without formaldehyde, HolzRohWerkst. 65 (2007) 65-70.

[111] M.E. Taverna, O. Tassara, J. Morán, M. Sponton, P. Frontini, V. Nicolau, D. Estenoz, Effect of Kraft lignin from hardwood on viscoelastic, thermal, mechanical and aging performance of high pressure laminates, Waste Biomass Valor. (2017) 1–13.

[112] L.I. Grishechko, G. Amaral-Labat, A. Szczurek, V. Fierro, B.N. Kuznetsov, A. Celzard, Lignin–phenol–formaldehyde aerogels and cryogels, Microporous Mesoporous Mater. 168 (2013) 19–29.

[113] C. Ciobanu, M. Ungureanu, L. Ignat, D. Ungureanu, V.I. Popa, Properties of lignin–polyurethane films prepared by casting method, Ind. Crops Prod. 20 (2004) 231–241.

[114] X. Luo, Y. Xiao, Q. Wu, J. Zeng, Development of high-performance biodegradable rigid polyurethane foams using all bioresource-based polyols: Lignin and soy oil-derived polyols, Int. J. Biol. Macromol. 115 (2018) 786-791.

[115] R. Auvergne, S. Caillol, G. David, B. Boutevin, J.-P. Pascault, J.-P, Biobased thermosetting epoxy: present and future, Chem. Rev. 114 (2014) 1082-1115.

[116] A.J. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, B.H. Davison, R.A. Dixon, P. Gilna, M. Keller, P. Langan, A.K. Naskar, J.N. Saddler, T.J. Tschaplinski, G.A. Tuskan, C.E. Wyman, Lignin valorization: Improving lignin processing in the biorefinery, Science 344 (2014) 1246843.

[117] W. Qu, Y. Xue, Y. Gao, M. Rover, X. Bai, Repolymerization of pyrolytic lignin for producing carbon fiber with improved properties, Biomass Bioenergy. 95 (2016) 19–26.

[118] D.A. Baker, T.G. Rials, Recent advances in low-cost carbon fiber manufacture from lignin, J. Appl. Polym. Sci. 130 (2013) 713–728.

[119] M. Thunga, K. Chen, D. Grewell, M.R. Kessler, Bio-renewable precursor fibers from lignin/polylactide blends for conversion to carbon fibers, Carbon N. Y. 68 (2014) 159–166.

[120] C. Eberle, D.C. Webb, T. Albers, C. Chen, Commercialization of New Carbon Fiber Materials Based on Sustainable Resources for Energy Applications, United States, https://www.osti.gov/servlets/purl/1072149, 2013 (accessed December 2018).

[121] J. Luo, J. Genco, B.J.W. Cole, R.C. Fort, Lignin recovered from the near-neutral hemicellulose extraction process as a precursor for carbon fiber, BioResources 6 (2011) 4566–4593.

[122] J.F. Kadla, S. Kubo, R.A. Venditti, R.D. Gilbert, A.L. Compere, W. Griffith, Lignin-based carbon fibers for composite fiber applications, Carbon N. Y. 40 (2002) 2913–2920.

[123] U. Zielke, K.J. Hüttinger, W.P. Hoffman, Surface oxidized carbon fibers: II. Chemical modification, Carbon N. Y. 34 (1996) 999–1005.

[124] W.E. Tenhaeff, O. Rios, K. More, M.A. McGuire, Highly robust lithium ion battery anodes from lignin: an abundant, renewable, and low-cost material, Adv. Funct. Mater. 24 (2014) 86-94.

Graphical Abstract