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

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1 **Abstract**

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

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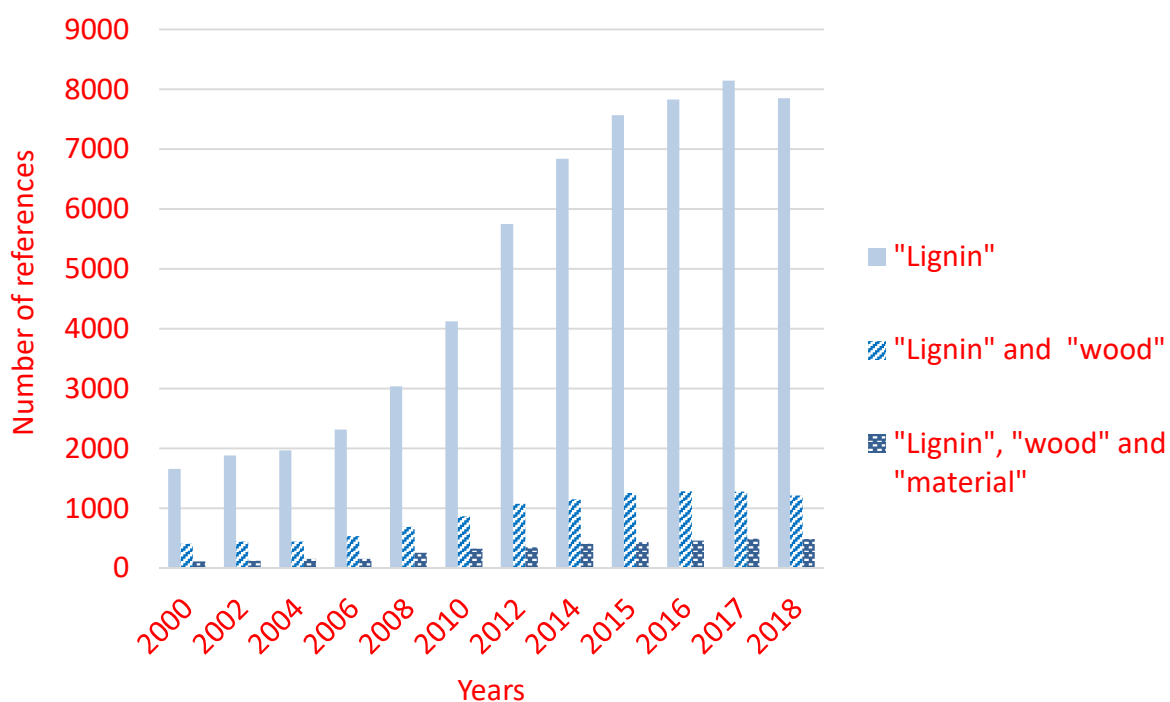
15 **Keywords:** Lignin; wood; extraction process; polymer; bio-based material.

16

1 **1. Introduction**

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

1 Hence, wood-derived lignin has attracted great attention over the past decades due to its
2 availability and versatile properties. Using the word “lignin”, 119360 references are available
3 in the portal of chemistry SciFinder Scholar. Refining this result with the term “wood” gives a
4 score of 27385 references including articles, reviews, patents, books and other. Finally, this
5 data should be compared with the “material” concept leading to 7888 references selected,
6 5050 of them being published after 2000. **Figure 1** clearly illustrates the latest excitement of
7 the industrial and scientific communities for this complex biopolymer often considered as a
8 by-product from biorefinery of second generation or papermaking industry, poorly valorized
9 such as with internal energy production by combustion.



10
11 **Figure 1.** Number of references per year between 2000 and 2018 using the key words
12 “lignin” and the combination “lignin” and “wood” or “lignin” and “wood” and “material”.

13 In 2014, the global lignin market was valued at 775 million US\$ and is expected to be of 900
14 million US\$ in 2020 [6]. The annual growth rate between 2018 and 2020 will probably reach
15 2.5 %. However, lignin is more and more considered as a significant candidate for oil-based
16 products’ replacement in the manufacturing of carbon-based compounds such as chemicals

1 and materials. Indeed, depletion of conventional fuel reserves has prompted the need for the
2 exploration of renewable resources. In this context, the bio-based economy requires the
3 sustainable utilization of bioresources to produce widely consumed products such as plastics,
4 adhesives, chemicals or fuels [7,8]. Therefore, lignin valorization could be economically
5 viable since its low cost and profuse availability as a by-product striking opportunities. The
6 whole process of valorization cannot be fully productive without the development of both
7 cost-effective and green methodologies [9]. Recent advances on traditional or innovative
8 processes for lignin extraction are highlighted in this paper. Over the last decades, lignin was
9 added to various polymers to form blends or composites.

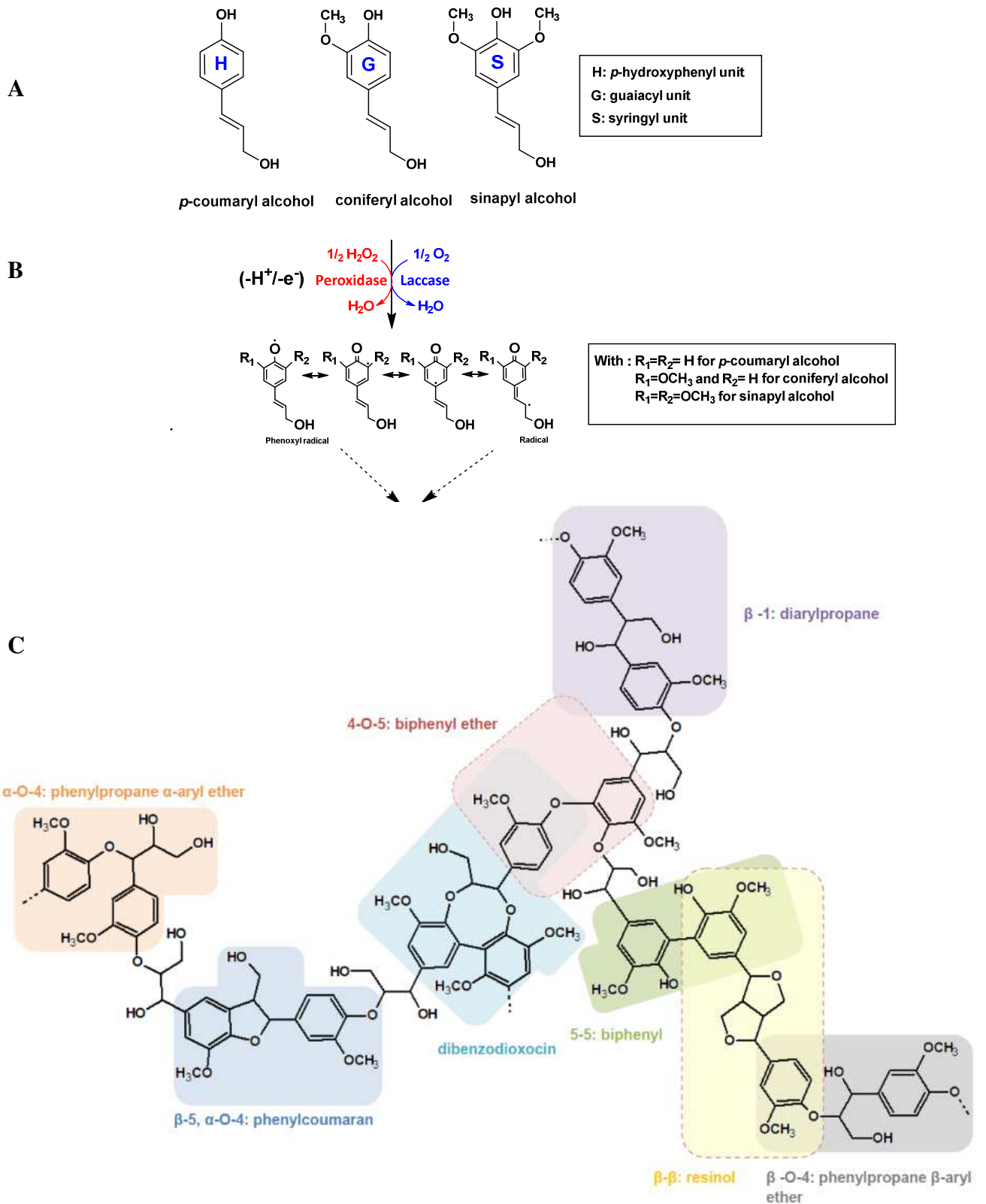
10 **2. Occurrence of native lignin, its structure and its biodegradation**

11 **2.1. Role of lignin in plants evolution**

12 When plants invaded land, they had to adapt specifically their physiology to UV radiations,
13 desiccation, and nutrients rarefaction [10]. Tracheophytes, that include all seed plants like the
14 angiosperm and conifer phylums, were the most successful species in exploiting terrestrial
15 environments [11,12]. This group was the first having a lignified tissue, called xylem, with
16 the function of transporting water and nutrients from roots to leaves. Some characteristic
17 xylem cells are the tracheides that permit water transportation [13]. Lignin precursor
18 metabolism allowed the formation of cuticles to protect plants from drought [14]. Lignin was
19 acting as a waterproofing agent that embedded cellulose microfibrils. Intramolecular
20 hydrogen bonding between cellulose microfibrils was enhanced, resulting in a higher stiffness
21 that prevented cells to collapse when subjected to negative pressures. Presence of lignin can
22 only be proven in Mesozoic plant fossils that lived about 250 million years ago although
23 scientists believe that lignin appeared 440 million years ago during Silurian times since
24 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-OCH₃ groups and are derived from coniferyl alcohol, syringyl units (S) which have two aryl-OCH₃ groups and are derived from sinapyl alcohol, and *p*-hydroxyphenyl units (H) which have no OCH₃ 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].



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3 **Figure 2.** General way toward the synthesis of lignin-hemicellulose complex in

4 lignocelluloses wood matrix. (A) chemical structures of monolignols (lignin monomers), (B)

5 enzymatic synthesis of monolignols radicals, (C) lignin structure with main units.

1 Softwood lignin is mainly composed of G units whereas hardwood structure is governed by a
2 S/G ratio. Nevertheless, in S2 layer of hardwood vessels, G-type lignin is predominant. This
3 latter has a condensed structure that provides strength to the cell walls, subsequently
4 withstanding higher compressive forces from the transportation fluids. Lignin polymer is
5 formed in the wood-cells cytoplasm via a complex enzymatic pathway [18,19]. Biosynthesis
6 of monolignols is initiated via the shikimate pathway, with the deamination of phenylalanine
7 molecule as a starting point. More than 10 enzymes are involved in the formation of the
8 monolignols [20,21]. They are firstly synthesized in the cytosol, then transported to the cell
9 walls, and finally oxidized by laccase, peroxidase or other phenol oxidases enzymes leading
10 to phenoxy radicals [22-24]. The phenoxy radicals are resonance-stabilized thus leading to
11 several forms of radicals that further react to form lignin *via* a polymerization process called
12 lignification. This polymerization begins at the cell corner of the middle lamella and the S1
13 layer of the secondary cell wall before spreading across the secondary wall towards the lumen
14 [25,26]. Lignification cannot be simply impacted by monolignol biosynthesis. The timing
15 between lignin polymerization and lignin deposition in the cell walls, after exportation, is
16 poorly known but determinant for the final lignin structure. The discovery of monolignol
17 transferase (PMT) opened the debate on how many dimers, trimers or oligomers are exported
18 by plant cells for lignification [27,28]. The first product of the lignification process is a dimer
19 of two oxidized monolignols, involving the C- β of one monomer and either the C5 (in G- and
20 H-units) or the C- β of a second monomer [23, 29]. Polymer chain grows with the end-wise
21 addition of a new monolignol radical. Crosslinking points are created by C5-C5 coupling,
22 phenolic hydroxyl-C5 coupling, or the formation of dibenzodioxocin structures [30]. The
23 coupling of the oxidized monolignols gives rise to several covalent bonds' formation, either
24 ether or carbon-carbon bonds namely ether β -O-4, diphenyl ether 4-O-5, 5-5, phenylcoumaran
25 β -5, pinoresinol β - β , dibenzodioxin, and diphenyl methane β -1 most common linkages [31].

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

15 **2.3. Lignin-carbohydrates complex (LCC)**

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

1 *Deuteromycetes* can degrade wood. They are generally grouped into white-rot, brown-rot, and
2 soft-rot fungi according to the color of rooted wood. Among wood-rotting fungi only the
3 white-rot fungi can degrade lignin (e.g. *Daldinia*, *Hypoxylon* and *Xylaria*) [43]. Ligninolytic
4 oxidoreductases secreted by wood-rotting fungi are the only enzymes known to oxidize the
5 phenylpropane units of lignin in nature; namely laccases, lignin-, Mn-, or versatile
6 peroxidases [44]. In the case of lignin- and Mn- peroxidases, H₂O₂ molecule participates in
7 oxidation/reduction mechanism. Wood cell walls components are usually removed
8 simultaneously. However, some white-rot species attack selectively on the lignin and cannot
9 degrade crystalline cellulose. For instance, it was demonstrated that *C. subvermispora* did not
10 produce cellobiohydrolases [45]. Consequently, white-rot fungi lead to a white degraded
11 product of cellulose. High lignified vessel elements with high contents of guaiacyl units are
12 more resistant to white-rot fungi attack probably because they present hindering effects [43].
13 Brown-rot fungi (e.g *Gloeophyllum trabeum*) primarily degrade cellulose and hemicelluloses
14 via Fenton reactions but they also have the ability of slightly modifying lignin. It was noticed
15 that lignin content as well as the amount of guaiacyl units did not influence brown-rot fungi's
16 biodegradation rate [43]. The understanding of lignin biodegradation mechanism is of interest
17 for biopulping processes. The same wood-decaying fungi can be used to pretreat wood chips
18 to facilitate mechanical, thermomechanical, and chemical pulping. Ligninolytic
19 oxidoreductases mode of action can be upgraded thanks to protein engineering to produce
20 new biocatalysts [45].

21 **3. Supplying industrial lignin**

22 **3.1. Overview**

23 Lignin is indubitably an abundant raw material on Earth: for a total lignocellulosic biomass of
24 10¹³ tons, approximately 100 billion tons of lignin are renewed in the biosphere every year.
25 Industrial lignin produced annually only counts for 1.5-1.8 billion tons. A major production of

1 industrial lignins comes from the pulp and paper industry that extracts alone 50-70 million
2 tons of lignin [46-48]. Today, most of these extracted quantities is used in the form of black
3 liquor for internal energy input in the pulping process. Specialists agree to claim that lignin's
4 potential is under-exploited with a current business of only 300 million US\$ [48].

5 **3.2. Industrial sources of lignin**

6 **3.2.1. Kraft lignin**

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

15 **3.2.2. Sulfite lignin**

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

23 **3.2.3. Soda lignin**

24 **Soda lignin is a co-product derived from soda anthraquinone process industrialized during the**
25 **19th century for non-wood fiber applications (i.e. flax, straw, etc.).** These materials are used

1 as sources of pulp and are still used as fiber source for producing papers in developing
2 countries (Asia and South America) and for producing high yield hardwood pulps for
3 packaging papers or boards applications. Non-wood fiber soda pulp mills have a small
4 capacity of production because of the annual variability of the feedstock. The new
5 technologies developed to process the black liquor for energy recovery are more suitable for
6 these mills. Indeed, the removal of the lignin decreases the chemical oxygen demand by about
7 50 %, leading to a profit stream from an effluent that increases the economic rationale of the
8 mill. Note that the first two soda lignin recovery services were installed in France and India
9 [50,51] but many additional facilities are expected to be added in the next years.

10 **3.2.4. Organosolv lignin**

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

17 **3.2.5. Lignin as a by-product from 2nd generation biorefineries**

18 The annual worldwide production of 2nd generation (2G) ethanol from lignocellulosic biomass
19 is evaluated to 316 000 tons. With a mean ratio of 0.5 kg of lignin produced per kg of ethanol,
20 about 200 000 tons of lignin are extracted per year along with the 2G ethanol production [46].
21 As the focus is made on sugars' extraction, lignin by-product of 2G ethanol biorefineries is
22 poorly studied in terms of chemical structure. The lignocellulosic biomass sources are more
23 suitable for feeding ethanol biorefineries due to their economic and environmental purposes
24 than sugar source feedstock which gets into competing with food and animal feed. In US, for
25 instance, one objective of the Renewable Fuels Standard developed by the US Environmental

1 and Protection Agency was to produce 872 million liters of bioethanol in 2016 with a
2 potential yield of 120 million tons of lignin in 2022. Besides, 60 % of lignin produced (i.e. 72
3 million tons) is expected to be available for producing high-value products [55]. In 2018, the
4 European Union has updated its Renewable Energy Directive (named RED II) for the period
5 2021-2030. This updated directive fixed new targets for renewable energy sources in
6 transportation: by 2030, 14 % of the fuel used in road and rail transport must be from
7 renewable sources. 3.5 % of these 14 % must be of lignocellulosic origin with an intermediate
8 milestone of 1 % in 2025 [56]. Knowing all these perspectives, major productions of lignin, as
9 well as bioethanol, are expected in the next few years.

10 **3.2.6. Analysis of the industrial lignin sources**

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

1 **Table 1.** Quantities, prices, and main producers of **commercial lignin** on a global scale.

2 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

4 **3.3. Obstacles and barriers in lignin productions**

5 Smolarski (2012) exhibited three main barriers for taking lignin's potential to industrial level:

6 *technology maturity, interest from game-changing investors, and funding options* [48].

7 In terms of *technology maturity*, lignin is mainly used as a macromolecule, whereas there is

8 an economic potential in the production of aromatics. However, production of aromatics

9 requires the development of depolymerization processes that are still in progress in terms of

10 research. Currently, the existing technologies cannot produce fine chemicals (with increased

11 functional groups) and bulk chemicals (with decreased functional groups). Vanillin but no

12 BTX compounds (ie. benzene, toluene and xylene) are available after oxidative

1 depolymerization whereas phenol and benzene are generated by hydro-deoxygenation. The
2 quantities of these products commercially available remain very low compared to the
3 achievements of almost 20 years of research. Supercritical depolymerization producing
4 monomeric phenolic compounds is very costly but seems appealing in terms of economy: (1)
5 this technology has already been used to extract compounds from biological resources,
6 showing its efficiency in other domains; (2) the solvent (CO₂) is an environmentally friendly
7 solution; (3) operating conditions (temperature and pressure) are easier to control compared to
8 other processes.

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

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

1 forestry sector across regions and countries [59], and much research is needed to help
2 designing policies adapted to local situations.

3 **4. Extraction processes of wood-lignin**

4 As previously mentioned, lignin can be found in different forms and can be isolated by
5 different processes. Usually, lignin is a co-product in the pulp and paper industry as well as a
6 byproduct in lignocellulosic biomass pretreatment and saccharification. These processes make
7 lignin a potential source of value-added products in the chemical, food, pharmaceutical,
8 textile and cosmetic fields [60]. For centuries, several processes such as sulfite, Kraft and
9 soda-anthraquinone processes have been developed and applied in the paper and pulp
10 industries in which lignin is not the target [61]. Nowadays, several alternative developed in
11 the biorefinery concept also called “pretreatment methods”, have been subjected to
12 investigation and allow isolation and recovery of lignin from wood. These alternative
13 processes are usually classified into chemical, physicochemical and enzymatic pretreatments
14 [62].

15 **4.1. Industrial wood-lignin extraction processes**

16 **4.1.1. Lignin extraction with Kraft process**

17 Kraft process is the most applied (96 % of the market) to isolate lignin from a wood material
18 [63]. Mainly used in the pulp and paper industries, the Kraft process uses significant amounts
19 of aqueous soda (NaOH) and sodium sulfide (Na₂S) at high-temperature (150-180 °C) for
20 about 2 hours. During this treatment, a major part of lignin gets solubilized and captured in
21 the spent pulping liquor called “black liquor”. The black liquor contains also a significant
22 quantity of wood hemicelluloses [62,64].

23 As the Kraft process is highly energetic, the lignin in black liquor serves as a fuel for Kraft
24 plant. In this case, black liquor is first concentrated by evaporators to 40-50 % solids content
25 and then burnt for its heating value. The released heat is used in the one hand for energy

1 recovery, the heat released as high-pressure steam and in the other hand to drive the mill's
2 chemical recuperation of inorganic compounds. For example, this allows also the regeneration
3 of the cooking reactive (sodium sulfite) through a causticization cycle [64]. The amount of
4 lignin produced by cooking plants is greater than for the energy production of factories and
5 could be valorized in other domains. For this purpose, the commercial process (LignoBoost)
6 isolates Kraft lignin from black liquor at high purity by acidification of the liquor with CO₂
7 [65]. pH lowering is undertaken using mineral acids such as sulfuric or chloridric acids for
8 example. By decreasing the pH, a consequential lignin portion is precipitated and may be
9 recovered by filtering and washing. The plants located respectively at Domtar's Plymouth
10 mill (USA) and at Stora Enso's Sunila mill (Finland) can produce approximately 75 000 tons
11 Kraft lignin per year based on the LignoBoost process [5,50,57].

12 **4.1.2. Lignin extraction with sulfite process**

13 Industrially applied for the very first time by Ekman in 1874, sulfite process is the most
14 ancient pulping method for paper production allowing lignin recovery as a by-product [66].

15 The sulfite process is now of minor importance compared to the Kraft process, about 7
16 million tons per year [67]. It is reserved to produce so-called special pulp, most of which
17 being a dissolving pulp for the manufacture of cellulose derivatives. However, it is the most
18 important source of commercially available lignin with a production of 1 million tons per year
19 of lignosulfonates [57]. Sulfite cooking is based on the use of aqueous sulfur dioxide (SO₂)
20 and a sulfite base (calcium, sodium, magnesium or ammonium salts). During cooking, large
21 amounts of sulfur are incorporated into lignin as sulfonate groups -SO₃ linked to the benzylic
22 carbon atom of the lignin phenylpropane (C9) unit. The degree of substitution varies from 0.4
23 to 0.5 sulfonate per C9 unit [50, 68, 69]. When compared with Kraft lignin, lignosulfonates
24 contain higher sulfur, carbohydrate and inorganic impurities (**Table 2**) [69].

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

	Ash	Sulfur	Sugars	Molecular	
Lignins	content	content	content	weight	Polydispersity
	(%)	(%)	(%)	(g/mol)	
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

1

2

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

3

The soda process was developed a few years before the Kraft process. It is quite similar but

4

remains marginal in the paper economy. Practically applied to non-woody biomass such as

5

sugarcane, bagasse and straw, soda lignin isolation process has been industrialized since 1853

6

[64]. The lignocellulosic material is treated with a high-pressure NaOH solution at a

7

temperature not exceeding 165 °C. The addition of anthraquinone (0.1 %) stabilizes

8

hydrocelluloses, prevents their attack by the alkaline medium and catalyzes delignification

9

[71]. As in the Kraft process, a part of the black liquor containing lignin is concentrated and

10

burnt in a boiler to generate energy and recover the salts of the starting liquor. The other part

11

of black liquor can be treated for lignin recovery, mainly using an acid precipitation process.

12

The advantage of the soda process results in the absence of sulfur in the cooking products

13

which is the major way to get a lignin purer than Kraft lignin [70].

14

4.2. Alternative wood-lignin extraction processes

15

As in the methods mentioned above, the so-called alternative wood-lignin extraction

16

processes also known as pretreatment methods, point to split the covalent links bonding the

17

lignin and the carbohydrate components of wood, thus allowing their fractionation [72-74].

18

The efficiency of these processes derives from the purity of lignin, cellulose, hemicelluloses,

1 the yield of components and the degree to which the structure of the isolated components are
2 altered. Among all these processes, only three are being exposed further.

3 **4.2.1. Alternative chemical lignin extraction processes**

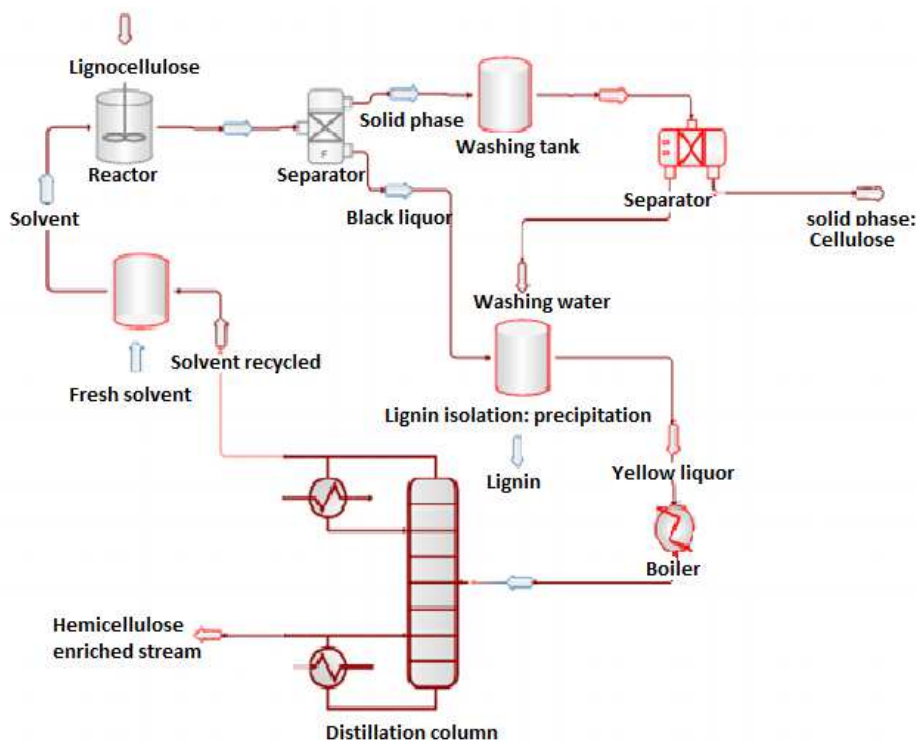
4 **4.2.1.1. Acid pretreatment**

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

16 **4.2.1.2. Organosolv extraction processes**

17 The principle of this process, derived from the paper industry, is based on the extraction of
18 **lignin** and hemicelluloses from wood materials using organic solvents (**Figure 4**). Commonly
19 used organic solvents are ethanol, methanol, acetone, or a mixture of water/organic solvent at
20 temperatures ranging from 100 to 250 °C [77]. This extraction can be improved by adding
21 acid catalysts of mineral nature (HCl, H₂SO₄, and H₃PO₄) or organic acid (such as formic or
22 acetic acids) at lower temperatures. The addition of an acid catalyst to the pulping media
23 causes the cleavage of more ether-linkages, but also favors the occurrence of intramolecular
24 condensation reactions, giving rise to a more complex lignin structure [78]. Most of the
25 employed solvents can be easily removed and recycled at their low boiling point. The

1 resulting lignin features are the same to the native lignin ones. The organosolv treatments
 2 preferentially cleave the carbohydrate-lignin bonds, leading to high molecular weight lignin
 3 without significant chemical modification. Lignin is recovered at the end of the process as a
 4 precipitate, after addition of a large amount of acidic water. In the 1990s, some industrial
 5 processes were operational: the Organocell process using methanol [79-81], the Alcell process
 6 using ethanol [82], and the Milox process using peroxyformic acid [83].



7

8 **Figure 4. Organosolv process**

9

10 **4.2.1.3. Lignin extraction with ionic liquids**

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

1 (BMIMCl) and 1-allyl-3-methylimidazolium chloride (AMICl) have been used for the
2 pretreatment of lignocellulosic biomass to improve its enzymatic digestibility [75]. It has been
3 also reported that 26.1 % and 34.9 % of initial lignin in the softwood and hardwood lignins
4 respectively, was dissolved by using 1-ethyl-3-methylimidazolium acetate ionic liquid [85]. It
5 should be noted that lignins recovered by ILs are not yet available at an industrial scale due to
6 the price and the availability of ILs. However, due to recent successes in this area, it can be
7 considered as a promising option because lignins obtained with ILs exhibit similar properties
8 to organosolv lignins and can be used in the same applications as soda and organosolv lignins
9 [74].

10 **4.2.2. Physicochemical lignin extraction process**

11 **4.2.2.1. Steam explosion**

12 Steam explosion was originally developed in 1924 by Mason to produce chipboard panels
13 [86]. Its application was subsequently extended to the production of ruminant feed in the
14 second half of the 20th century. Steam explosion is a thermochemical process that allows the
15 breakdown of lignocellulosic materials by the combined action of high-pressure steam
16 diffusion within the material structure, hydrolysis of glycosidic bonds by organic acid formed
17 during the process, and shearing forces due to the expansion of the moisture [87]. The process
18 consists of two distinct phases: the steam cracking and the explosive decompression [88]. In
19 the steam explosion, only a small fraction of lignin is solubilized, and alkaline delignification
20 is often used to complete biomass fractionation.

21 **4.2.2.2. Ammonia fiber expansion (AFEX)**

22 AFEX is a physicochemical alkaline pretreatment involving the periodic exposure of
23 lignocellulosic biomass to liquid ammonia at high temperature (90-180 °C) under pressure (7-
24 40 bars) for a very short period before proceeding to a sudden decompression that allows to
25 evaporate the ammonia and explode the substrate [89]. This pretreatment causes a small

1 reduction in the amount of lignins, the elimination of hemicelluloses fraction and the
2 decrystallization of cellulose contained in the wood. Its advantages include high redistribution
3 of lignin, ammonia recovery and recycling [78]. While most of the pretreatments such as
4 steam explosion produce a slurry that can be separated in solid and liquid fractions containing
5 the lignin, ammonia fiber expansion produces only a pretreated solid wood material.
6 However, it has also been shown that the AFEX process was not very efficient for wood with
7 high lignin content such as softwood [76].

8 **4.2.2.3. Liquid hot water**

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

16 **4.3. Life cycle analysis of lignin production**

17 Life Cycle Analysis (LCA) of a product is a process that allows to compile and to evaluate the
18 inputs (materials and energy), and the outputs of the product (pollutants, emission, product
19 and by-product) in order to estimate its potential impact on the environment. Investigation
20 about the potential environmental impact of lignin production through four processes (Kraft,
21 Organosolv, soda, and sulfite) was performed [91]. The Organosolv process presents the
22 highest total potential environmental impact (PEI) per kg of lignin with a value of 0.25 PEI
23 per kilogram followed by the Kraft process with approximately 0.09 PEI per kg of product.
24 Finally, the soda process presents the lowest pollution with PEI values of 0.02 per kilogram
25 followed by the sulfite process having a value of 0.03 PEI per kg of lignin. Furthermore, the

1 removal of lignin by different technologies point out several economically and
2 environmentally advantages and disadvantages. Beyond production costs and environmental
3 impact, the extraction method must be selected depending on the use that will be given to
4 lignin. Organosolv methods allow the recovery of high-quality lignin but continue to be a
5 high-cost technology, while Kraft and sulfite processes allow obtaining a lignin at reasonable
6 costs but with impurities. However, the soda extraction process generating lower production
7 costs and low environmental impact is still the more sustainable option of producing lignin for
8 low and high value-added processing [70,91]. To conclude, the toxicological impact of
9 reagents that are being evaluated in the Organosolv and Kraft processes have similar values
10 and are higher compared to the other two processes (soda and sulfite processes).

11 **5. Lignin incorporation in polymeric materials**

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

19 **5.1. Current applications for lignin**

20 Lignosulfonates are used as additives in concrete admixtures for their capacity to retain water.
21 Their surfactant properties are of interest in agrochemicals, dyes, pigments, coatings, textile
22 lubricants, personal care products, or detergent formulations. In the animal feed sector,
23 lignosulfonates are used as animal feed binder, while helping lubrication of the pelletizing
24 equipment and providing the animals with calcium and sodium. Lignosulfonates also find

1 their applications in the formulation of phenol and urea formaldehyde thermosets. They can
2 act as soil stabilizers while increasing soil stiffness [92].

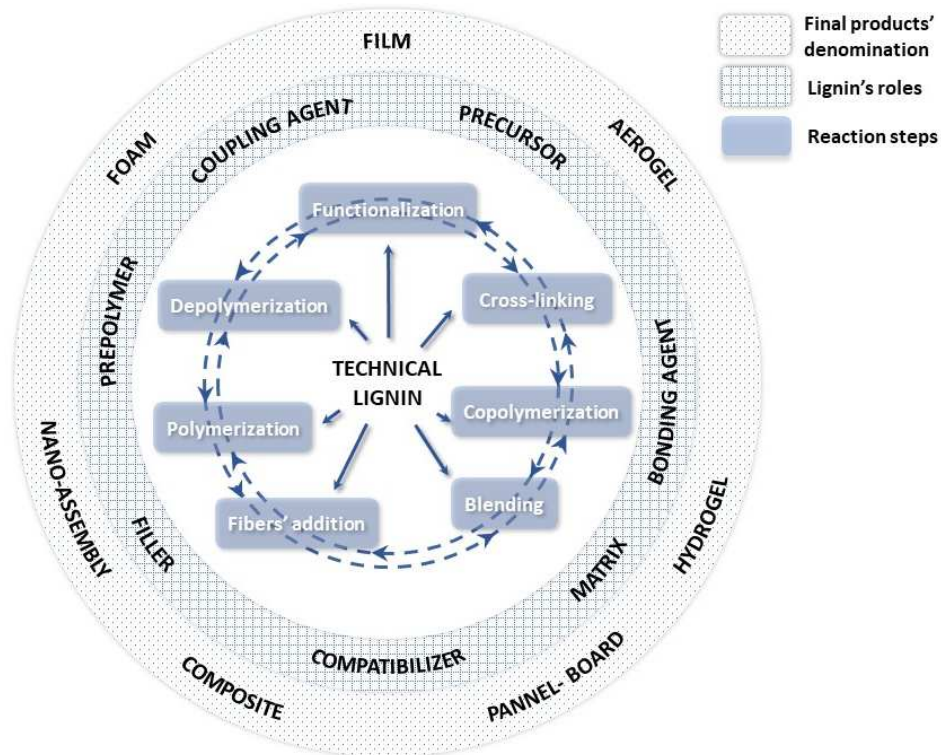
3 Sulfonated Kraft lignins are currently used as dispersants and rheology agents in dyes, as
4 dispersants for crop protection products, as air entrainment formulations in mortar, as battery
5 expanders, or asphalt emulsifiers. Ethoxylated sulfonated Kraft lignin has been used as doping
6 in the production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

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

13 **5.2. Challenges of lignin integration into polymeric materials**

14 Lignin has been considered over the last decades as one of the most interesting raw material
15 to partially substitute materials with fossil origin. It exhibits a good compatibility with other
16 biopolymers (i.e. polylactic acid) or with natural fibers due to its hydrophilic nature, unlike
17 synthetic polymers. Functionalization on lignin polar groups can be imparted in order to
18 enhance compatibility with hydrophobic polymers (i.e. polypropylene). Crosslinking with
19 other polymers is also possible via its hydroxyl groups to give rise to novel materials. Lignin
20 is known for enhancing the biodegradability of polymers where it has been incorporated.
21 However, its large molecular weights and the existence of steric hindrance effects are
22 detrimental to the reactivity of lignin. Many researchers prefer to study depolymerization of
23 lignin that leads to monomer building blocks, instead of working with high molecular weight
24 lignins with heterogenous structure. Aromatic building blocks can be obtained after
25 depolymerization, the latest's often providing rigidity, hydrophobicity, and fire resistance to

1 materials. With these techniques, bio-based epoxy resins, polyesters and others can be
 2 synthesized from lignin depolymerized products, after functionalization [93]. Finally, low-cost
 3 carbon fibers are obtained from lignin which is a carbon-rich compound. Figure 5 give the
 4 main valorization of lignin into polymer-based material.



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

9

10 5.3. Lignin incorporation in bioplastics and biocomposites

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

13 5.3.1. Unmodified lignin matrix in biocomposites

14 Composite materials have been developed with a binding matrix of unmodified technical
 15 lignin and natural fibers for industrial engineering, industrial goods of mass consumption,

1 electronic or automotive industry applications. Their main advantages are their low density,
2 biodegradability, and wood compatibility. The most striking example of such material is
3 known under the trade name Arborform® (Tecnaro GmbH company), material developed at
4 the Fraunhofer-Institut für Chemische Technologie [94]. This new generation of material is
5 made of natural renewable raw constituents and can be processed by injection molding like
6 thermoplastics. It is constituted of lignin matrix (30-60 %), natural fibers like hemp or flax
7 (10-60 %), and additives such as processing aids, impact modifiers, and flame retardants (0-
8 20 %). Lignin matrix can sometimes be blended with polylactic acid (PLA). Mean tension at
9 break is 18 MPa with a mean Young modulus of 6 GPa, so Arborform® can compete with
10 synthetic thermoplastics in some cases. Rozite et al. (2011) developed composites with
11 similar lignin matrix and 30 % flax fibers focusing on stress-strain curves, temperature
12 behavior, and relative humidity [95]. Domínguez-Robles et al. (2017) described the use of
13 lignin adhesive to produce high-density fiberboards (HDF) [96]. Flexural strength of HDF
14 was higher than commercial ones (96.81 MPa for 15 % lignin amount). Other authors
15 developed composites by compression molding with lignosulfonate matrix, natural fibers, and
16 no additives [97].

17 **5.3.2. Lignin filler in combination with bioplastics**

18 Lignin was tested as filler in bioplastic matrix. The biopolymers PLA, poly(3-
19 hydroxybutyrate) (PHB), and polyamide 10,10 (PA1010) were used by Al Mamun et al. [98].
20 Lignin incorporation improved stiffness of the material because tensile and flexural moduli
21 increased but the tensile and flexural strength were found to be much lower than the neat
22 polymers. Addition of oleo chemicals plasticizers could improve mechanical properties, and
23 especially the tensile strength but the neat polymers properties could not be reached. Rahman
24 et al. (2013) prepared sheets from ternary system of softwood Kraft lignin, PLA, and
25 polyethylene glycol (PEG) by melt-blending [99]. With 30 % of PEG and 15 % of lignin, a

1 good balance between flexibility and stiffness has been achieved. Spiridon et al. (2015)
2 showed that an addition of lignin to PLA matrix induced an increase of the impact strength
3 and thermal stability of PLA [100]. After accelerated weathering, tensile and impact strengths
4 decreased less than PLA matrix. Commercial PLA/lignin blends are proposed by Modern
5 Plastics under the name PLA-L for polyethylene terephthalate (PET) replacement. They are
6 made with fatty acids and wax as additives. Several blends of lignin with other biopolymers
7 have been reported. For instance starch/lignosulfonates blend films were prepared by Shi and
8 Li (2016) by casting and solvent evaporation method with sorbitol as plasticizer [101].
9 Hydrophobicity and rigidity were improved but the ultimate tensile strength did not when
10 lignin content increased.

11 **5.4. Lignin in thermoplastics**

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

1 **5.5. Lignin in thermosets**

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

9 **5.5.1. Lignin substitute in phenol-formaldehyde (PF) resins and aerogels**

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

1 replace up to 20 % (w/w) of phenol with no significant changes in the thermal and mechanical
2 laminates properties. Note to mention that these lignin-modified laminates exhibited better
3 water resistance.

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

12 **5.5.2. Lignin substitute in polyurethane (PU) resins**

13 Lignin is a good candidate for crosslinking with diisocyanate in PU resins. PU with
14 unmodified lignins exhibits brittle behavior. Therefore, authors recommend the use of lignin
15 in combination with other polyols to create some soft segments via the crosslinking reaction.
16 Polyethylene glycol (PEG), polybutadiene glycol (PBG), hydroxyl terminated polybutadiene,
17 or poly(ethyleneadipate) (PEA) are frequently used. Ciobanu et al. (2004) studied the
18 properties of lignin-PU films prepared with 4.2-23.2 % (w/w) of soda lignin and containing
19 soft segments of PEA and PEG [113]. The tensile strength lignin-PU film can be improved
20 compared to pure PU film, but the elasticity and the decomposition temperatures did not
21 increase. To improve reactivity with isocyanates, numerous authors have studied modification
22 of lignin including etherification (e.g. hydroxypropyl lignin) and esterification. The use of
23 low contents of nitrified lignin for PU synthesis has also been reported. In addition to films,
24 rigid or flexible foams were prepared and characterized in various studies. For instance, Luo
25 et al. (2018) successfully applied a one-pot method to obtain foams from lignin powder, bio-

1 based soy polyols, and polymeric methyldiphenyldiisocyanate [114]. Covalent bonds were
2 formed between lignin and polyols. The foams were rigid, biodegradable, and exhibited
3 improved thermal and mechanical properties up to 218.1 MPa.g⁻¹.cm⁻³ with 5 % (w/w) lignin
4 powder.

5 **5.5.3. Lignin substitute in epoxy resins**

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

13 **5.6. Lignin for carbon fibers and activated carbon**

14 Lignin-derived from wood has been of interest as an alternative precursor since it naturally
15 contains a six-membered ring aromatic structure and is abundantly available at low cost [116].
16 One interesting lignin valorization results in carbon fiber synthesis. Carbon fibers are one of
17 the most important engineering materials in various industrial fields, having light-weight
18 properties while providing them strong mechanical strength [117]. Lignin-based carbon fibers
19 have been studied for nearly 50 years [118]. Initially, carbon fibers have been produced from
20 polyacrylonitrile (PAN), and the precursor alone costs as much as the half of the production
21 cost of the carbon fibers [119]. Low-cost carbon fibers made from non-petroleum precursors
22 could enable the application of carbon fibers in large scale. Lignin is expected to result in
23 savings between 37-49 % of the final cost of producing carbon fiber [120]. Nevertheless,
24 lignin is a brittle bio-based polymer that cannot be spun and stretched into fibers without
25 modification. Carbon fibers were synthesized from different lignin either by thermal

1 processing, chemical modification, or mixing lignin with other polymers compounds [121].
2 Note that carbon fibers were produced from Kraft lignin, without any chemical modification
3 through a thermal spinning process followed by carbonization [122]. The University of Iowa
4 developed a robust process for producing high quality, low-cost carbon fine-diameter fiber
5 from a lignin precursor. The lignin precursor was produced, spun and stretched before being
6 pyrolyzed into the carbon fiber. To obtain a carbon fiber derived from lignin, this polymer is
7 usually first converted into fibers by extruding a molten or solvent-swollen gel. Then, the
8 spun fibers are oxidized in the air. At this point, the filaments become pyrolyzable without
9 fusion. During pyrolysis under nitrogen or inert atmosphere, the fibers are carbonized with
10 removal of volatile hydrocarbons, oxidized derivatives, carbon monoxide and moisture [123].
11 More specifically, carbon electrodes are being developed for batteries and electrochemical
12 capacitor devices. Lignin can be used as a precursor of activated carbon for electrodes
13 preparation, and especially for carbon anodes. Tenhaeff et al. (2014) developed, with a novel
14 synthesis method, interconnected three-dimensional architectures of carbonized lignin for
15 lithium insertion [124]. This anode material, with its high specific capacity and its stable
16 cycling is suitable for high power and high energy applications.

17 **6. Conclusion**

18 Lignin is a not classical biopolymer, with its non-defined and complex structure, and its high
19 level of heterogeneity depending of numerous factors. Approximately 95 % of lignin's
20 worldwide production is used to save energy through cogeneration systems, while the
21 remaining 5 % has been marketed for the formulation of adhesives, dispersants, surfactants
22 and rubbers mainly. Lignin shows a huge economic potential, especially if the oil price is seen
23 to increase. The main key-issue for promoting the development of lignin-based products
24 remains the economic incentives in terms of lignin sources and lignin-based products. Beyond
25 subsidies, investors must be aware of the potential growth of the lignin especially for high-

1 value products (BTX, vanillin, phenol, carbon fiber). The second issue relies in promoting
2 these high value-products in a first step, but it would be necessary to promote other innovative
3 lignin-based products such as bio-based materials (bioplastics, composites, etc.). However,
4 this will only be possible when the first issue is overcome and when robust, affordable and
5 environmental friendly extraction processes are available. Then, the stabilizing of lignin
6 sources will decrease their price and open new perspectives for the lignin-based industry.
7 Utilization of lignin as material could be of great interest as the sole limitations in this field of
8 application is the imagination. In the future bioeconomy, wood should be biorefined to
9 produce biofuel but also carbon fiber, bioplastics, hydrogels, biofoams, elastomers, and
10 others. These products need to be competitive with oil-based ones. The multifunctionalities of
11 lignin have been the subject of a lot of publications and patents but rather not associated with
12 economic success on the market; although small companies with high level of technology for
13 the extraction and purification of several grades of lignins recently emerged. The plant
14 engineering using the new genetic tools and a better understanding of lignin biosynthesis
15 pathways could lead to wood more adapted to biorefinery processes with a control of lignin
16 structures, and above all, the control of covalent linkages between lignin and polysaccharides
17 of the cell wall. Moreover, note that even if lignin is a biodegradable polymer, its lifetime in
18 the environment is long when formulated into materials. So, they can be considered as carbon
19 trap to store carbon dioxide. Lignin could then be a sustainable solution to support new bio-
20 based materials in a context of depleting non-renewable fossil resources.

21

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25

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Graphical Abstract

