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Review

Lignin Modifications, Applications, and Possible Market Prices

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Abstract: Lignin is the second most abundant biopolymer in the world. Due to its complex structure, lignin can be considered a valuable source of energy and different chemicals. In addition, using different reactive sites on lignin, it is possible to prepare different value-added products, such as resins, polyurethanes, and many more. Different functional groups are presented on the lignin macromolecule and can be modified via different pathways. Hydroxyl groups are the most promising reactive sites for lignin modifications. Both modified and unmodified lignins could be used for preparing different biomaterials. This paper shows several possible applications of lignin. The main goal of this publication is to show the possible valorization of lignin in different value-added products throughout the actual market prices of non-biobased materials. This review proves that lignin has unquestionable advantages in material technology and can replace different substances which will lead to a higher potential market value of lignins and could create new bio-based materials compared with the actual prices of commercially available materials. Nowadays, it is easier to use lignin as an energy source even though a lot of lignin modifications and conversion processes are still under development and need more time to become more relevant for industrial applications. Information in the presented paper should reveal to the reader the importance and economic benefits of using lignin as a value-added compound in different applications.

Keywords: lignin; modifications; market value; bio-materials; renewable resources; biorefineries; chemicals with added value

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1. Introduction

The current situation in the world is alarming. The amounts of fossil fuels are decreasing, but according to the Statistical Review of World Energy published by British Petrol in 2021, the production of fossil fuels is increasing (see Figure 1) [1]. It is our responsibility to find and use new and modern sources of renewable energy. One of the most promising sources is biomass, especially lignocellulosic materials. It is estimated that dry biomass on Earth represents 550×10^9 tons of C. The representation of plant biomass is approximately 450×10^9 tons of C in the world [2].

In 2019, fossil fuel consumption reached its maximum over the years and stopped at approximately 4.97×10^8 TJ (see Figure 1) [3]. It is the enormous amount of energy created from fossil fuels that is the main reason for global warming and the release of greenhouse gases. That is the reason why it is important to find a new possible, renewable, and sustainable source to produce energy.

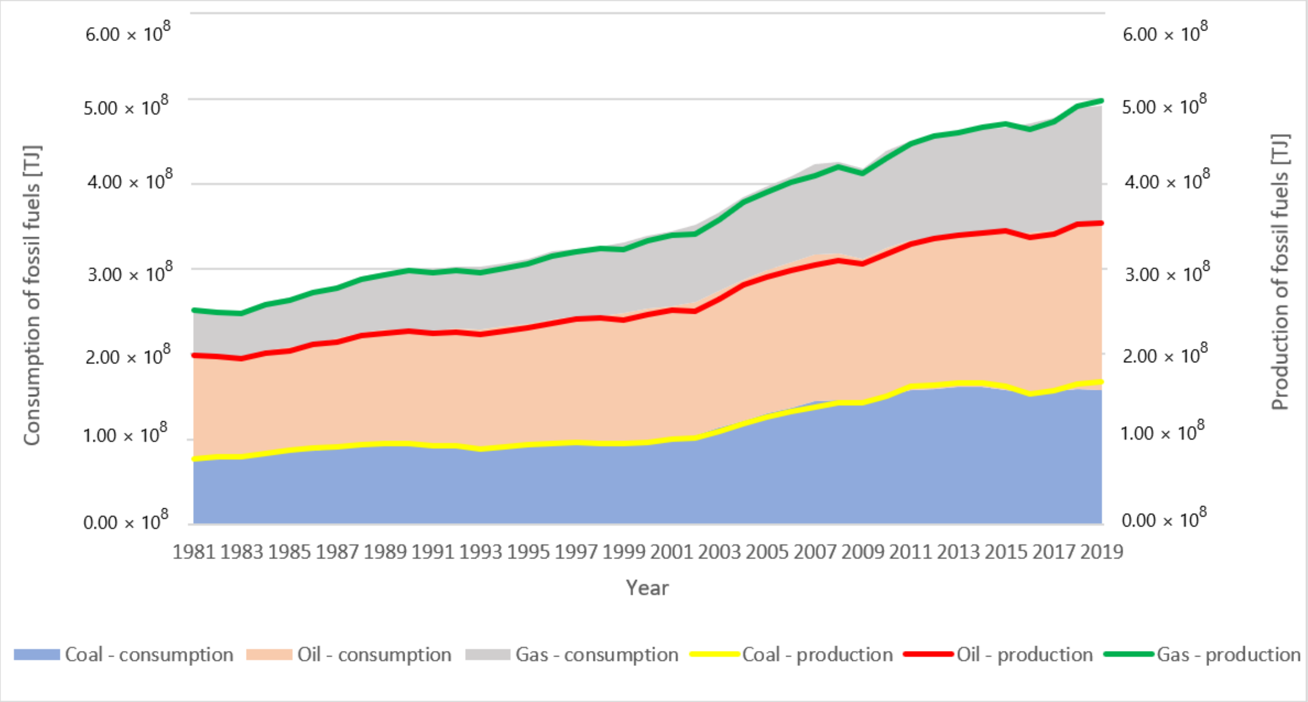

Figure 1. Comparison of fossil fuel production and consumption worldwide.

As mentioned above, lignocellulosic biomass is one option through which we can accomplish all conditions mentioned above. Lignocellulosic biomass is composed of saccharides (approximately 75%), such as cellulose and hemicelluloses, and the other 20% is composed of a biopolymer named lignin [4]. Today, lignin is mostly considered a renewable source of energy, especially in the pulp and paper industry. Lignin is isolated during the pulping process and is burned in the recovery boilers to obtain heat and energy. The annual global production of lignin in the pulp and papermaking industry is estimated to be approximately 70×10^6 tons. Most of this amount is used as low-value fuel [5]. Instead of this application, lignin has many other possible applications, which will be described below.

According to Keyoumu et al. [6], it can be isolated from 330 to 490 kg of lignin per ton of birch and pine, respectively. In 2020 the production of chemical pulp, which consists mainly of Kraft pulping, represents almost 116 million tons and the estimated capacities for 2025 represent approximately 134.5 million tons of chemical pulp. The rise in the character of chemical pulp production is obvious, which means that the production of lignin will be elevated as well. From the above, it can be calculated that the consumption of wood for chemical pulping can be around 269 million tons (chemical pulping has a yield of around 50%). If we consider that the amount of lignin varies from 25 to 30% (hardwood/softwood), it can be estimated that the yearly supply of lignin could range from 67 to 81 million tons of lignin. Another approach to calculating the approximate supply of lignin is according to Keyoumu et al. [6]. From their results, it can be calculated that in 2025, approximate lignin production can be in the range of 44 to 66 million tons of lignin only from chemical pulping.

The presented review has a role to summarize possible applications of lignin. In addition, this work proves that lignin can fully replace non-renewable materials and has also the economical potential to valorize by-products from the pulp and paper industry. Moreover, this review shows that lignin has unquestionable advantages in material technology and can replace different substances which will lead to a higher potential market value of lignins and could create new bio-based materials compared with the actual prices of commercially available materials. It means that lignin can increase its value, thus it could be more beneficial to use lignin in material production rather than energy production.

Until that time, lignin is suitable to produce clean renewable energy instead of burning fossil fuels.

2. Lignin Structure

Firstly, for a better understanding of possible lignin applications, it is necessary to understand the complex structure of lignin. Lignin is an aromatic biopolymer composed of phenylpropane units. It is an amorphous compound three-dimensional polymer that possesses a structure based on phenyl propane units. In the natural unrefined form, the molecular structure of lignin deviates according to the source and is so complex, and has never been fully described. Lignin is mainly formed by coniferyl alcohol, *p*-cumaryl alcohol, and sinapyl alcohol. In every plant, the proportion of different monolignols is different. It depends on the plant species and the geographical locations of the plant. For example, softwood species contain dominantly coniferyl alcohols compared to sinapyl alcohol, in hardwood species the proportion of these two constituents is almost equal [7,8]. The units resulting from the monolignols, which are linked to the lignin polymer, are called guaiacyl, syringyl, and *p*-hydroxyphenyl units. All these units are shown in Figure 2. The structure of lignin is extremely complex, as monolignols are connected through several linkages in a 3D system [9–12]. As described below (see Figure 2), the lignin structure is composed of phenyl propane units, which are divided into three main building units. They differ in the type of substituent located on the C3 and C5, respectively. If there is one methoxy group on the phenolic part, we are talking about the guaiacyl unit, if there are two methoxyl groups we are talking about the syringyl unit, and if there are no methoxyl group at all, we are talking about the *p*-hydroxyphenyl group.

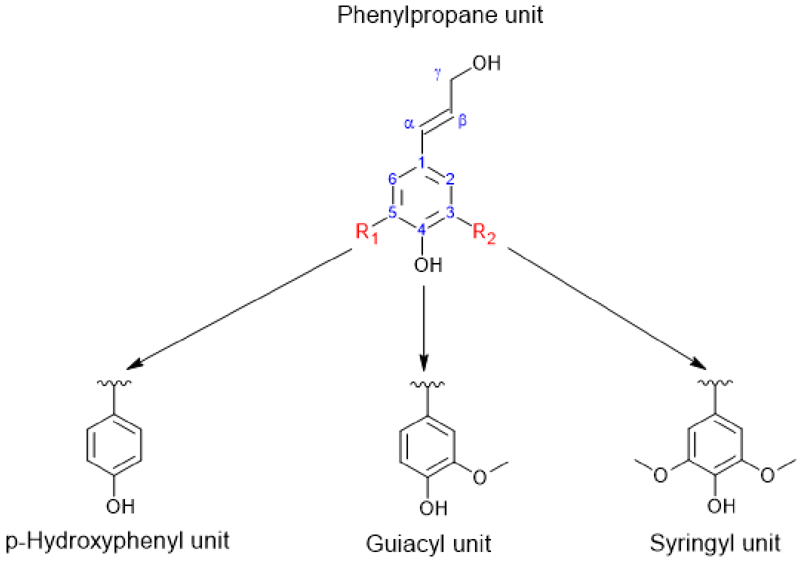

Figure 2. Phenylpropane unit and building units of lignin.

The distribution of lignin differs not only from plant to plant, but it also varies in the layers of plant cell walls. Lignin with its heterogenous structure is unevenly distributed in the matrix. Because of the hydrogen bonds, three main constituents of plants (cellulose, hemicellulose, and lignin) are bonded together and form a lignin-saccharide complex. For example, lignin covalently bonded with hemicellulose forms the majority of the middle lamella, and lignin itself forms around 85% (*w*/*w*) of total middle lamella mass. As we move closer to the middle of the cell wall, called the lumen, the content of lignin decreases, and in the secondary wall (S3 layer), lignin is not formed there at all [13].

There are multiple techniques for lignin isolation. All these techniques could be divided into three main groups:

1. Polysaccharides are removed from the plant and lignin stays as residual compounds (methods according to Klasson, Komarov, Willstätter, Purves, etc.).
2. Lignin is dissolved and removed from the plant, and polysaccharides remain unmodified (Kraft, sulfite, neutral sulfite semi-chemical, soda pulping, etc.).
3. The wood content is mechanically removed, and lignin stays as residual material (milled wood lignin, isolated with enzymes).

Lignin is isolated from plant material for two reasons:

1. For analytical determination of the lignin content.
2. For the preparation of the lignin sample for further investigation.

The most often used process for lignin isolation is the Kraft process. This process has a higher selectivity and produces pulp with higher quality than other pulping methods [14]. Lignin monomers are linked together with different types of bonds that must be cleaved to make lignin soluble in the solution of chemicals used in the pulping process.

Table 1 shows different types of lignin bonds and their approximate percentage in different wood species. From the presented values it is possible to assume that the lignin composition differs according to the plant species. This is the reason why different lignins isolated from different plant materials are used in multiple applications, which is also supported by the data. Before applications of lignins, different linkages between monomeric units can be formed and/or cleaved (see Table 1). Etheric bonds are the most abundant in the lignin structure and are very easily cleaved. The problems with cleavage are repolymerization reactions of lignin which forms C-C bonds which are much stronger and are harder to decompose. For example, the most abundant linkage type in all lignins is the β-O-4 bond. It means that all types of lignins can be cleaved easily until a certain level because ether bonds are easier to cleave than C-C bonds. That is the reason why hardwood lignin could be theoretically better for depolymerization because it has lower concentrations of C-C bonds, such as 5-5, β-5, β-1, β-β, etc. In addition, an important parameter for lignin modifications is the number of functional groups on the lignin structure. There are mostly four main types of functional groups, namely methoxy, aliphatic and phenolic hydroxyl, and carbonyl groups. Among them, hydroxyl groups are the most reactive sites on the lignin structure and also affect the properties of lignin the most.

There are many variable applications of lignin. It is not only in fuel production but also in some specialty materials, pulp, and paper industries, pharmaceuticals, and environmental technologies. Various value-added industrial applications of lignin have been recognized and it is because of its complex structure that a wide range of different applications can be predicted. High-purity lignin can be used in carbon fiber composites. Another possible application of the lignin structure is in the polymer and food industries. Lignin can be valuable in adhesive binders' production, resins and coatings preparation, PU-based foams, films, paints, and plastics. It is also possible to use it as food and beverage additives, or as different nutritional supplements. The use of lignin derivatives has found diverse applications ranging from fuel to biomaterials. Lignin polymers can be created at a low cost, but what is more important is that instead of non-renewable materials, companies can produce bio-based, many times compostable, or bio-degradable polymers. It means that lignin can replace petrochemical resources in the production of various materials [15–17]. Table 2 shows the major material categories, functional products, and their potential applications for Kraft lignins. As already mentioned, this process for lignin isolation is the most common. There are also other pulping processes, which result in different lignin quality, but since the Kraft process is the most common it is relevant to show the most valuable applications of Kraft lignins.

Table 1. Typical bonds of lignin and approximate composition of functional groups for selected lignins.

Linkage Type	Dimer Structure	Approximate Percentage in Grasses	Approximate Percentage in Hardwood	Approximate Percentage in Softwood	References
β-O-4	Phenylpropane β-aryl ether	69–94	50–65	45–50	[18–21]
α-O-4	Phenylpropane α-aryl ether	11–14	1–8	5–8	[18–21]
β-5	Phenylcoumaran	5–11	3–11	9–12	[18,19]
5-5	Biphenyl and dibenzodioxocin	n. i.	1–5	5–25	[18–21]
4-O-5	Diaryl ether	n. i.	6–7	3.5–8	[18–21]
β-1	1,2-Diaryl propane	0–2	1–7	1–10	[18–21]
β-β	β-β-linked structures	1–15	3–12	2–6	[18–21]
		Functional groups of lignin			
Carbonyl [mol/ lignin unit]		-	0.15	0.20	[21]
Aliphatic hydroxyl [mol/ lignin unit]		0.56–1.13	1.10–1.15	1.15–1.20	[21]
Phenolic hydroxyl [mol/ lignin unit]		0.36–0.44	0.10–0.20	0.20–0.30	[21]
Methoxy [mol/ lignin unit]		-	1.40–1.60	0.90–0.95	[21]

Table 2. List of major Kraft lignin-derived materials categories, functional products and their potential applications.

Material Category	Products	Potential Applications	References
Aromatic macromolecules and fine chemicals	Lignin monomers and dimers, aromatic phenols, alkyl phenols, aromatic aldehydes, aromatic alcohols, acids, aryl ketones, antioxidants, dispersants, PU, phenolic resins, vanillin	Industrial chemicals, biobased adhesives, multifunctional materials, building blocks for biobased products	[22–26]
Carbon materials, Biofuels	Biochar, bio-oil, syngas, activated carbon, carbon fibers, carbon black	Light-weight polymer composites, adsorbents, electrochemical devices, automotive	[27,28]
Polymer and nanomaterials	3D Printing resin (anionic surfactant), Scaffolds, lignin nanotubes, hydrogels	Biomedical applications, tissue engineering, drug delivery	[29–31]
Energy Storage	Li-ion, Na-ion batteries (electrodes), super capacitors, solar cells	Energy devices, batteries, fuels cells	[32]
Building Materials	Bitumen, cement additive, dispersant, reinforcement	Construction pavements, cement panels	[22,27]
Specialized Applications	Soil conditioner, in fertilizers and pesticides as controlled release agent, sequestering agent, material absorbing soil contaminants, fire retardant	Agriculture, textiles, soil reclamation, water purification, fire suppression	[22,27,33–36]

There are different well-known procedures for lignin isolation with Kraft lignin the most abundant. That is the reason why Table 2 describes different Kraft lignins' possible applications. There are a lot of products that can be prepared from lignin, e.g., carbon fibers, phenolic resins, dispersants, binders, etc. In addition, some chemicals widely used in organic synthesis can be prepared from lignin as well, especially benzene, vanillin, toluene, xylene, aldehydes, etc. According to the specific lignin application, it is important to obtain desired properties of lignins. For example, lignin used in polyurethanes foams should have a molecular weight from 1180–8020 g/mol and the total hydroxyl content should be around 4.49–6.37 mmol/g [37–39]. In addition, Kraft lignin with M_w between 1000–3000, polydispersity index 2.1–3.5, sulfur content 1.0–3.0%, and ash content 0.5–3% is suitable for many applications, such as fertilizers and pesticide carriers, binders, resins, carbon fibers, additive to thermoplastic polymers, and different chemicals.

3. Modifications of Lignin

Unmodified lignin is used as an additive in the material to improve its properties. There are already a few applications of unmodified lignins. Since there are many active groups in the lignin structure, it could react in different pathways. Because of these reactive spots, lignin can react chemically in different ways, such as halogenation, nitration, phenylation, graft copolymerization, alkylation, dealkylation, sulphomethylation, acylation, ammonisation, esterification, and hydrogenolysis. According to these chemical reactions, it is possible to modify the lignin structure and prepare lignin-modified materials [40]. Different uses of lignin could be divided into three main groups which are as follows: cleavage of different lignin bonds into aromatic compounds or repeating units; use of unmodified polymer extracted from raw material; addition to the lignin biopolymer and use of lignin as a starting material for the production of other useful materials [41].

It exhibits a good compatibility with other biopolymers (i.e., polylactic acid) or with natural fibers because of 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). Cross-linking with other polymers is also possible via its hydroxyl groups to give rise to novel materials. Lignin is known to enhance the biodegradability of polymers where it has been incorporated. However, its large molecular weight and the existence of steric hindrance effects are detrimental to lignin reactivity [42]. Many researchers prefer to study the depolymerization of lignin that leads to monomer building blocks, rather than working with high molecular weight lignins with heterogeneous structures [43]. In recent decades, there is a growing interest in the use of lignin as a feedstock for the synthesis of bioaromatic chemicals (such as vanillin and phenols) and biobased polymeric materials (resins and polymers) due to the following driving forces because of the following reasons [44,45]:

1. The material is sustainable and renewable;
2. There is an immense generation of lignin as a by-product in the pulp/paper industry and the cellulosic ethanol industry;
3. There are various functional groups present in the lignin structure that enable a variety range of chemical reactions;
4. Lignin has intrinsic biodegradability, and it is believed that lignin-incorporated polymers are more biodegradable than petroleum-based polymers.

Aromatic building blocks can be obtained after depolymerization, the latest often providing rigidity, hydrophobicity, and fire resistance to materials. With these techniques, biobased epoxy resins, polyesters, and others can be synthesized from lignin-depolymerized products after functionalization [43].

Lignin can be used as a filler or it can substitute around 20–30% (*w*/*w*) of some reactive components in polymeric materials. For example, it can replace phenols in phenolic resins, polyols in polyurethane, bisphenol-A in epoxy resins, etc [46–48]. Because of the unique physical and chemical properties of lignin, the first attempts at adding value to it focused on physical blending as a bulk material. Properties such as hydrophobicity, thermal stability, thermo-oxidation resistance, UV-absorption, and the presence of a highly crosslinked structure were the major ones that made lignin a suitable component as a filler in such blends [49]. Of course, there are certain limitations, which originate in the structure of the lignin complex, such as large M_w with steric hindrance effect, poor solubility in organic solvents, and low reactivity. The greater substation ratio of lignin in polymer materials is challenging but can be achieved by modification of its structure [44]. Different lignin modification technologies have been explored, including chemical [49,50], biological [51], photochemical [52,53], and electrochemical [52,54] methods. Among these methods, chemical modification processes have attracted significant interest. It is well known that lignin is a natural polydisperse phenolic polymer, as shown in Figure 2 and Table 1. Lignin contains both polar (hydroxyl) groups and nonpolar hydrocarbon and benzene rings; therefore, it is expected to act as a compatibilizer between natural hydrophilic fibers and a hydrophobic matrix polymer [55–58]. The presence of phenolic hydroxyl groups in lignin has also enabled its use in the synthesis of various polymers such as phenolic resins [59,60], epoxy resins [59,61], polyurethanes [45,47], and polyesters [62,63]. Due to its hindered phenol structure, lignin can be used directly with elastomers or polyolefins as an antioxidant [64–66], ultraviolet light stabilizer [67], and possibly also as a flame retardant [68]. Several studies have investigated the incorporation of lignin into a polymeric matrix such as industrial thermoplastics (polyesters, polyamides, polycaprolactone, and polyhydroxy butyrate) to reduce polymer production [69–71]. Although lignin has potential direct applications in the polymer industry, it can only be incorporated in small amounts, taking into account its thermal degradation and mechanical properties. Modification of lignin seems to be the best way to use this renewable product as a starting material for polymer and chemical synthesis [72].

4. Lignin Fractionation

Fractionation is a physico-chemical modification technique, which allows the separation of low-molecular-weight fractions from high-molecular-weight lignin chains. There are multiple techniques for fractionation e.g., enzymatic treatment, partial suspension in organic solvents [73,74], selective precipitation at reduced pH, and membrane-assisted ultrafiltration [75,76]. Regarding enzymatic and ultrafiltration, these methods are efficient for molecular weight distribution control but are costly and difficult to use at an industrial level [77].

Ultrafiltration is a process used to separate lignin according to different molecular weights or to separate lignin from black liquor in pulp mills. The main benefit of membrane processes in lignin extraction is the ability to be removed from any pulping mill without the need to adjust the pH or temperature. In addition, there is a possibility of controlling the molecular weight of the lignin fractions by the membrane cut-off [78,79].

The fractionation technique seems to hold promise for upgrading technical lignins into homogenous polyaromatic macromolecules, which are suitable for further conversion, especially for the products that need lignins with very high purity, e.g., carbon fibers, adhesives, etc. On the one hand, this is a good method to obtain high purity [75,80,81].

4.1. Depolymerisation/Fragmentation of Lignin

Depolymerisation is the thermochemical conversion of lignin, which includes the decomposition of organic matter at high temperatures with or without the presence of the catalyst. In the case of lignin, it is a very complicated conversion process, where many different reactions are presented at the same time. The mechanism of lignin depolymerization is affected by many factors, such as lignin type, reaction temperature and time, catalyst concentration, and reaction medium [82]. Figure 3 represents a simplified diagram of lignin depolymerization and production of different chemical substances. There are multiple pathways for lignin reaction which lead to multiple products. One of the well-known depolymerization techniques is the liquefaction of lignin. The resulting products of liquefaction are chemicals such as catechol, guaiacol, and phenol. The other depolymerization process is pyrolysis which will lead us to the pyrolytic products, especially bio-char, toluene, benzene, xylene, and bio-oil.

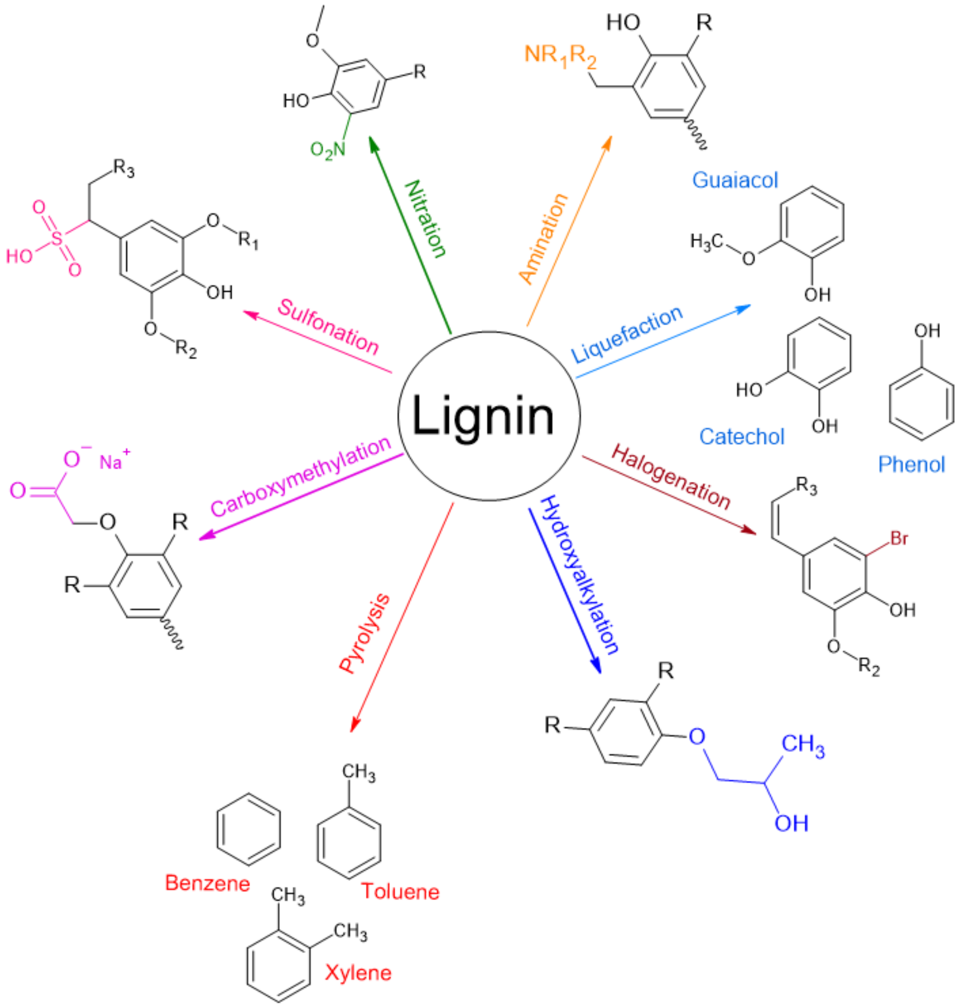

Figure 3. Different pathways of depolymerization and modifications of lignin and its final products.

Oxidation cleavage of the C-C and C-O-C bonds in the lignin structure is possible to form vanillin and different acyclic organic acids. The disadvantage of lignin oxidation is that during this conversion it is hard to eliminate free radicals, which are formed. These radicals lead to the repolymerization reaction and the creation of carbon residue. The reduction cleavage of mentioned bonds is much more effective, and the products are monomer compounds, such as phenols, benzene, toluene, xylene, etc [83].

4.2. Modification of Functional Groups

Lignin contains many different ending groups, such as hydroxyl, methoxyl, carbonyl, and carboxyl. These groups could be modified to prepare new products and increase the application range of lignin. Due to the complex structure of lignin, it is very difficult to reach a wide range of possible lignin utilization [84].

One possible approach is alkylation. This process usually refers to reactions with alcohols in the presence of catalysts. According to Lai et al. [85], ethanol organosolv lignin was alkylated with ethanol, leading to the etherification of C_α of the lignin fraction. Alkylated lignins are, according to the different results, hydrophobic due to the ether and ester bonds [84].

Another promising modification is carboxylation and carboxymethylation. Lignin can be modified with enzymatic treatment (laccase and peroxidase) [86]. It was discovered that different lignin bonds, especially β-O-4′ and β-β′, can be cleaved in the laccase-violuric acid solution. The final product has a lower amount of methoxyl; vice versa, the amount of phenolic hydroxyl and carboxyl groups increases [87]. Carboxyl groups show good adsorption capability for heavy-metal ions. Adsorption capacity can be increased by grafting the carboxylic groups. Carboxymethylated lignin is possible to prepare nanocomposites via surface modification. It is proposed to use these composites in wastewater treatment and biofilter packaging material for environmental protection due to the possible removal of Ni^{2+} and Cd^{2+} ions [84,88,89].

5. Lignin Products

In addition to fuel production, many variable applications of lignin can be found in chemical production, specialty materials, pulp and paper industries, pharmaceuticals, and environmentally. Because of the versatile properties of lignin, various value-added industrial applications have been recognized. High-purity lignin can be used in carbon fiber composites. Another possible application of the lignin structure is in adhesive binders, food and beverage additives, resins and coatings, nutritional supplements, PU-based foams, films, paints, and plastics. The use of lignin derivatives has found diverse applications in applications ranging from fuel to biomaterials. Lignin polymers can be created at low cost and can be used as a replacement for feedstocks developed from fossil fuel or petrochemical resources in the production of various products [15–17].

Figure 4 represents the summary of the selected lignin prices and the prices of different chemicals that can be derived from the lignin structure throughout the depolymerization reactions. It can be assumed that lignin has a great potential to increase its actual market value. Every compound created from any of the presented lignins has a higher price than the original lignin. Prices of the lignins depend on their purity, and the origin of the lignin e.g., low purity lignin has prices ranging between USD 100–300 MT, but the prices for high purity lignin for laboratory scale can be USD 66.50 up to 153.00 for only 100 g. Such big differences in the prices are because of the purity and possible applications. High purity lignins can be used in laboratory analyses as a standard, but low purity lignins are more suitable for low-cost industrial applications. It means that if the procedure for lignin conversions is developed deeper, it will be possible to rapidly increase the price of lignins according to the product derived from it. However, conversion reactions are still under development and need to be examined further for possible industrial applications.

5.1. High Purity Lignin

High-purity lignin is the first step in the valorization of lignin. The separation of lignin from other biomass constituents is a major process in producing value-added unconverted lignin. This product could be used directly as a raw material in some applications, such as carbon fibers, or can be modified toward specific properties and further applications as a low molecular material. Actual prices for pure lignin on a laboratory scale are USD 66.50–153.00 for 100 g of the product [90,91]. According to the work supported by the European Commission [92], this product is already at TRL 5 and is in development. The applications of both sources are currently in the laboratory stage of development and seem to work properly with non-sulfur lignins. The main parameters observed in the case of purity of lignin are the ash content and the metal content (e.g., sodium content). Prices are very variable and differ according to many different parameters, such as ash content, sulfur content, metal content, and other impurities content.

5.2. Lignin Biocomposites Reinforced with Plant Fibres

Lignin fibers composites are materials that combine different properties of lignin with plant fibers, some additives with or without fossil-based or biobased plastic compounds, to create material with specific and desired properties. Lignin is used as a stabilizing additive and properties aid. The main role of lignin in this application is to improve the mechanical-physical properties of the final product. Actually, this application is under development at

TRL 6 [92]. Lignin biocomposites reinforced with plant fibers have the main application as thermoplastics, and their uses depend on different industries. In the automotive sector, this material can be used as acoustic and thermal insulators [93]. The other possible uses are for technical parts, furniture, sports and leisure equipment, packaging, and clothing [92].

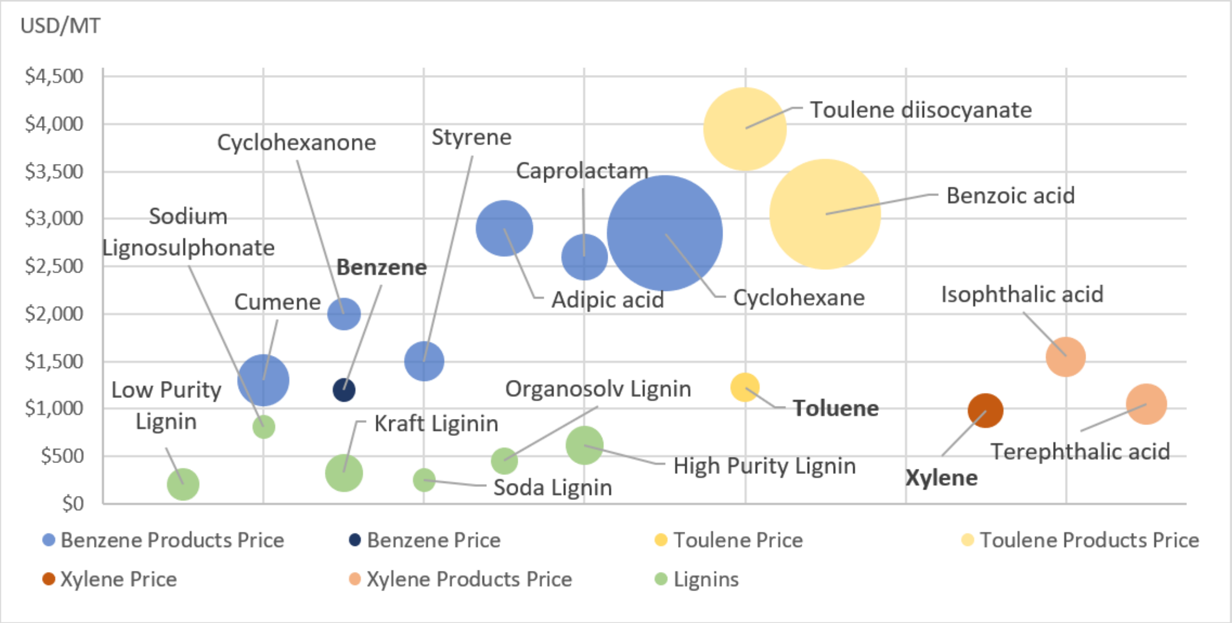

Figure 4. Lignin prices and prices of different chemicals potentially derived from lignin. *Individual bubbles represent minimum and maximum price of compounds.*

Lignin biocomposites have great potential because, nowadays, bioplastic materials from all sources, except soybean plastics, are two–five times more expensive than oil-based plastics. Lignin price can be a positive factor that could influence the final price of bioplastic materials.

5.3. Benzene, Toluene, Xylene

Selective catalytic hydrogenation of lignin and similar compounds is used predominantly for bio-oil and fuel production. These reactions could be used for the preparation of intermediate products which are used to produce new substances. The main products which can be prepared using catalytic hydrogenations are benzene, toluene, xylene (BTX), and phenol [5]. BTX are basic aromatics that represent approximately 60% of all industrially prepared aromatic chemicals [94]. This enormous amount of consumption predicts that lignin has great potential in this application [95]. However, this application has a lower price than carbon fibers, for example, xylene is USD 865–1100/ton, toluene is USD 1150–1300/ton, and benzene is USD 1100–1300/ton. The prices are relevant for non-renewable raw materials and it is possible that the same chemicals produced from renewable resources could be even more expensive. Currently, all BTX preparation procedures from lignin are still under development. The TRL for this application is 6. Research is focused on improving the yields and specificity of the preparation procedure [92].

5.4. Phenol Resins

Phenol is commonly produced from petroleum-derived benzene by a cumene process. It is widely used as a precursor to drugs (especially aspirin), many herbicides, and pharmaceuticals. All reaction processes include demethylation, phenylation, and methylation. Different studies suggest that the substitution of 70–100% of the phenolic portion of phenolic adhesives is possible if Kraft lignins or lignin by-products of second-generation biorefineries are used. Phenols are extremely interesting as building blocks of new synthetic bioplastics, phenol-formaldehyde, epoxy, or PU materials [24,25,96–100]. Phenolic resins are used mainly in different coatings, composites, adhesives, insulations, lamination, wood bonding, in molded parts, and as plywood adhesives [101]. The TRL of lignin-based phenolic resins is very developed and is actually in number 8. Nowadays, the price for phenolic or phenyl formaldehyde resins is USD 1600–2400/MT [102].

5.5. Lignin Bio-Oil

Bio-oil is the fluid product of the thermochemical conversion of biomass, mostly through fast pyrolysis. Bio-oil has great potential as a renewable source of chemical compounds for resin synthesis, polymers, or adhesives. Compounds of pyrolysis bio-oil are mostly coniferylalcohol, sinapylalcohol, isoeugenol, vanillin, catechol, guaiacol, vinylguaiacol, methylguaiacol, and many more. Different products of bio-oil depend on the time and/or temperature of pyrolysis, for example, longer times are for bio-oils for fuel production, and shorter times are characteristic of optimal yields of valuable compounds [103,104]. Bio-oil as a product is interesting for fuel preparation, different chemical isolation, and as oil-based products. In 2018, the TRL for the isolation of lignin bio-oil was 6 and it has a big growth potential [92].

5.6. Lignin-Based Carbon Nanofibers

According to materials technology publications, in 2011 the global demand for carbon fibers (CF) was estimated at 46,000 tonnes and is forecasted to rise to 140,000 tonnes by 2020. The actual production of carbon nanofibers is highly dependent on polyacrylonitrile (PAN). PAN makes carbon fibers very expensive and that is the reason why they are not so widely used in industrial applications [105]. The actual price of carbon fibers varies from USD 5 to 44/kg [106]. Lignin has great potential to decrease this price and make carbon fibers more accessible for different industrial applications. However, to prepare carbon fibers from different lignins, it is necessary to have a very low amount of impurities (less than 1000 ppm). This amount corresponds to an ash content of less than 1% [107]. Another advantage of lignin-based carbon fibers is to increase energy efficiency and reduce environmental emissions and in addition use renewable resources. Today, the level of technology readiness for lignin-based carbon nanofibers is 5–6 [92,108].

5.7. Lignin-Based Polyurethane and Polyurethanes Foams

Polyurethanes can be defined as block copolymers that are made of two components varying in blocks. The first constituents are low molecular weight polyesters or polyethers. The second is a urethane group (-NHCO-O-). Both constituents are bonded together by covalent bonds. Polyurethanes are prepared throughout the reactions of comprised polyisocyanate; polyhydroxyl containing polymer (i.e., polyether or polyester); a chain extender, which is usually a low molecular weight diol (e.g., 1,4-dibutylamine). Due to the inherent versatility of polyurethane syntheses, this polymer could have properties exactly suited to the various applications. Polyurethanes have unique properties. They are valuable because of their low density, high strength-to-weight ratio, low thermal conductivity and moisture permeability, and high dimensional stability. Polyurethane foams are defined as flexible materials. Depending on their mechanical performance and core densities, we classify polyurethane foams in two categories, namely rigid or semi-rigid polymers [109–112].

According to Mahmood et al. [113], hydrolytic depolymerization of Kraft lignin and hydrolysis lignin could be a viable method to prepare depolymerized products with low molecular weights and acceptably high hydroxyl numbers. These products could be involved in the preparation of rigid PU foams at higher replacement ratios (50%) without compromising the properties of the final foams. The actual price for polyurethane foams is USD 900–1420/ton [114].

6. Conclusions

Lignin has a great potential to become a valuable replacement for non-renewable resources. Nowadays, lignin is used for energy production in the pulp and paper industry which is also relevant to today's problems with fossil fuels. In this review, we summarized possible lignin applications not only for energy production but also as a valuable raw material to produce different chemicals and/or bio-based materials. There are still a lot of challenges in lignin development to fully replace non-renewable materials, for example, the lignin conversion mechanisms are still very expensive compared to fossil fuel processing, lignin must be isolated and purified which also increases its price. When the technology development will be at a level suitable for industrial processing, lignin will be a very interesting material because of its structure and multiple applications. Nowadays, we know that there are many products that can be obtained from lignin (chemicals, materials, energy) and that is only because of the complex lignin structure. Actual prices for products and chemicals which are produced from non-renewable resources are very interesting for companies that have lignin as a by-product of their technology e.g., paper mills.

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