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Recent advances in lignins: fundamentals and applications

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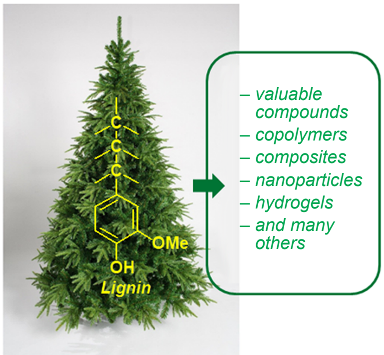
Lignin, one of the most abundant biopolymers on Earth, is a constant object of numerous fundamental and applied studies. Lignin processing is a challenging task of biorefining. Recent publications mainly concern various directions of valorization of technical lignins, as well as applications of lignin in medicine and pharmacology, 3D printing, synthesis of carbon fibres and biofuels. In the field of fundamental research, studies on lignin biosynthesis are of special attention. The review is devoted to the latest advances in the chemistry of lignin. The currently available data on the structure and biosynthesis of lignin are discussed. The trends in lignin valorization, such as pyrolysis and carbonation, production of composites, copolymers and nanoparticles, synthesis of practically valuable low-molecular-weight substances, production of hydro- and aerogels, *etc*., are analyzed in detail. It is noted that at present, the practical application of lignin is developing in two directions: valorization of technical lignins *per se*, without prior depolymerization, and valorization *via* low molecular weight compounds, mainly monomers, formed through lignin degradation by various methods.
The bibliography includes 130 references.



Keywords: lignin, lignin structure, lignin biosynthesis, lignin valorization, biorefining.

Contents

1. Introduction

Being the second most abundant biopolymer on Earth after cellulose, lignin has been and remains an object of ongoing fundamental and applied research. The processing of lignin by chemical, physical and biological methods represents a relevant task of biorefining. The studies of recent years are mainly concerned with different directions of valorization of technical lignins, starting with the review by Ragauskas *et al.*[1] Subsequent publications are devoted to the choice of valorization strategy,[2] the production of polyurethanes,[3] adhesives from lignin,[4,5]

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lignin valorization using enzymes,[6] applications of lignin in medicine and pharmacology, 3D printing, as well as in the synthesis of carbon fibres[7] and biofuels.[8–11]

In the field of fundamental research, the works devoted to lignin biosynthesis attract attention. Comparison of the structure of lignins isolated from transgenic and mutant trees and herbaceous plants has shown that lignin biosynthesis is flexible and can involve other phenolic compounds, in addition to canonical monolignols (coniferyl, synapyl and coumaryl alcohols). Therefore, research is being conducted to reduce the lignin content in plants and to modify its monomeric composition by genetic engineering methods.[12]

The study of so-called ‘stress lignins’ showed that lignin plays an important role in protecting plants from adverse environmental impacts such as mechanical damage, drought, low temperatures, pathogens, *etc.*[12]

The results of studies on lignin gene modification allowed one to identify ways of directed modification of the biosynthesis process to obtain designer lignins, *i.e.* lignins with specified properties. This group includes the so-called zip-lignins. They feature the presence of ester linkages between phenylpropane units.

It is noted that when performing research into genetic engineering, it is necessary to seek a compromise between improving the processability of plant raw materials by modifying lignin and the viability of transgenic plants. This review discusses lignin biosynthesis and structure, as well as directions for valorization of technical lignins, which are not sufficiently covered in the review literature: pyrolysis and carbonization of lignin, preparing composites and copolymers, nanoparticles, practically significant low-molecular-weight substances, hydro- and aerogels from lignin and some other directions.

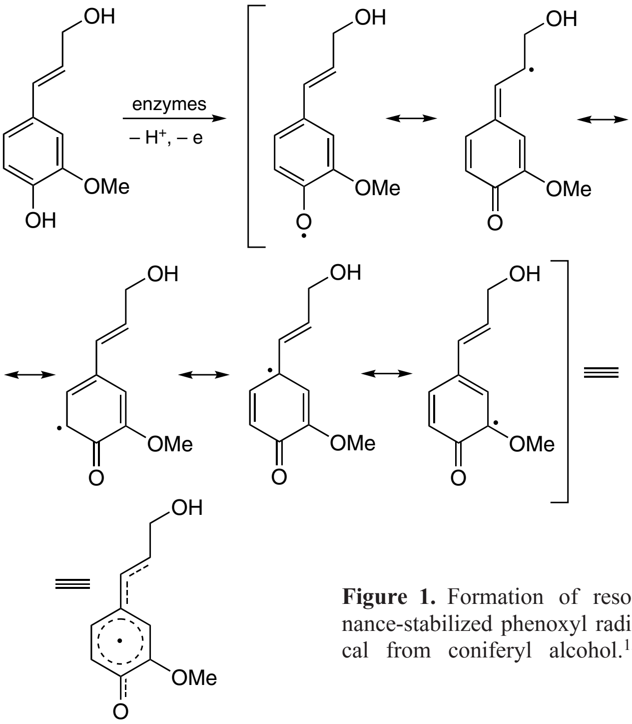


Figure 1. Formation of resonance-stabilized phenoxyl radical from coniferyl alcohol.[13]

2. Biosynthesis and structure of lignin

Lignin biosynthesis is a system of complex biological, biochemical, and chemical processes and includes three stages: synthesis of monolignols in the cytosol, their transport across the plasma membrane, and oxidative polymerization of monolignols to form macromolecules in the cell wall.[12] Traditional views on this process are described in monograph,[13] and modern ideas in reviews.[12,14] In this review, we focus mainly on the last stage of lignin biosynthesis, namely, the assembly of macromolecules from monolignol precursors, since this is the stage at which the views have evolved considerably. Traditionally, coniferyl [3-(4-hydroxy-3-methoxyphenyl)prop-

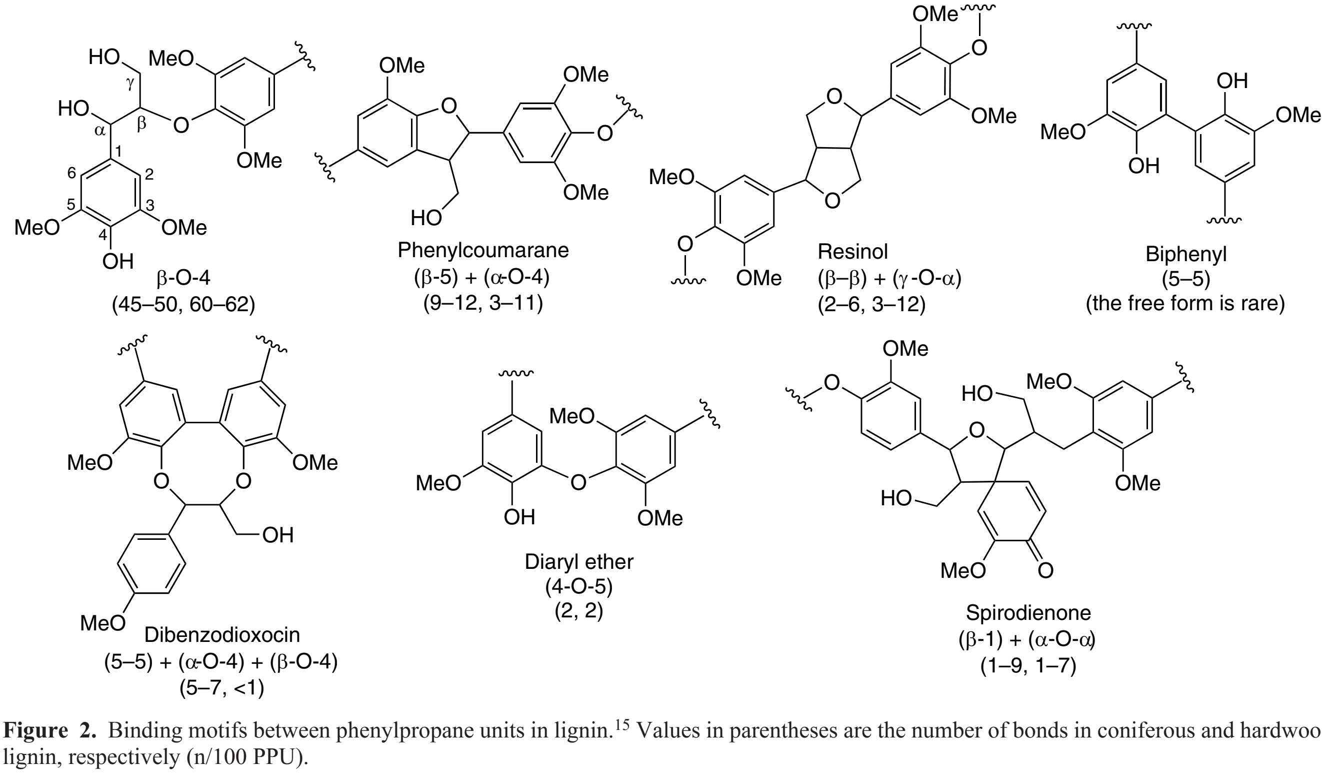


Figure 2. Binding motifs between phenylpropane units in lignin.[15] Values in parentheses are the number of bonds in coniferous and hardwood lignin, respectively (n/100 PPU).

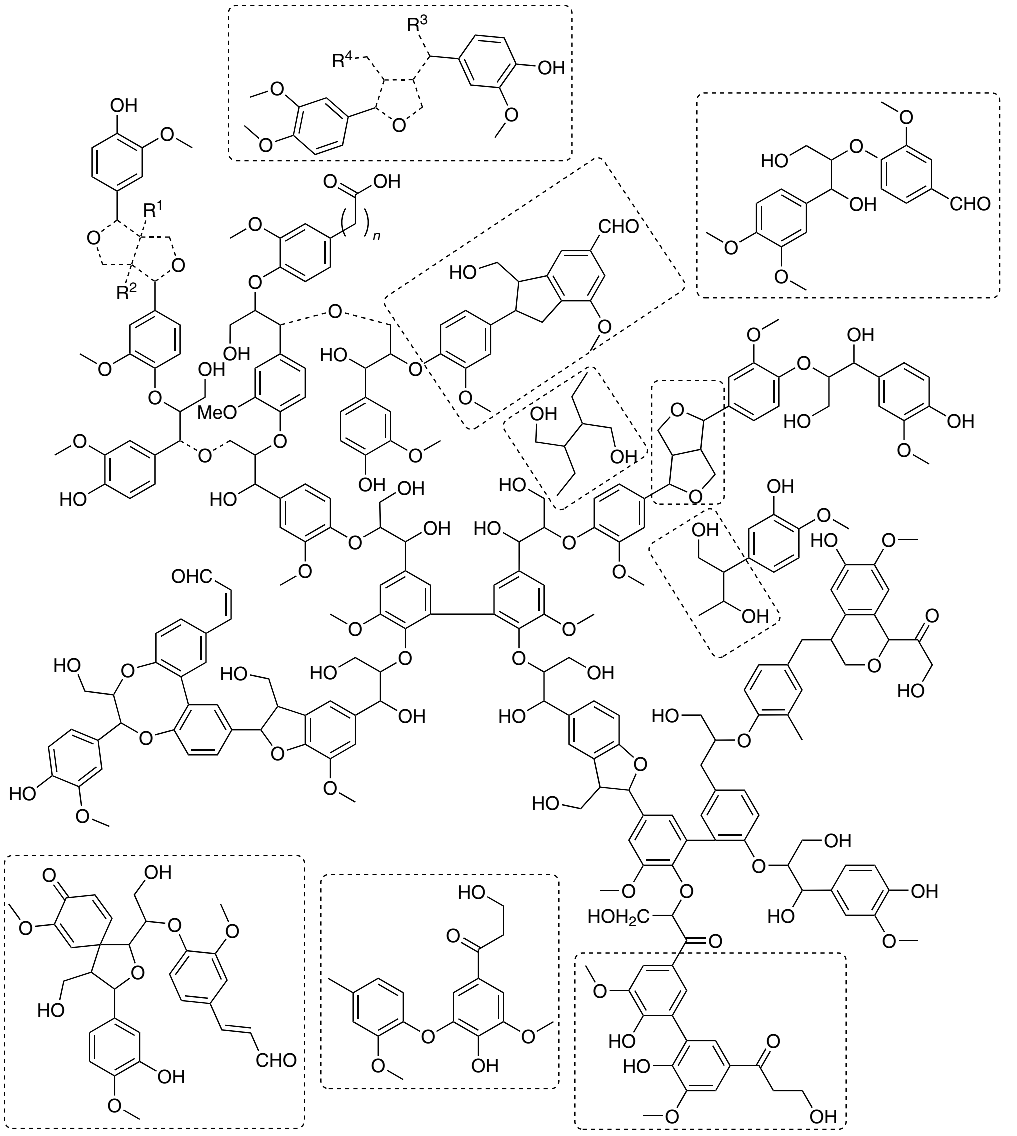


Figure 3. Proposed scheme for the structure of the spruce milled wood lignin.[17] Minor structures (content below 4 structures per 100 aromatic units) are marked with dashed lines.

2-en-1-ol], synapyl [3-(4-hydroxy-3,5-dimethoxyphenyl)prop-2-en-1-ol] and *p*-coumaryl [3-(4-hydroxyphenyl)prop-2-en-1-ol] alcohols were considered to be the precursor monolignols. Later, caffeyl [3-(3,4-dihydroxyphenyl)prop-2-en-1-ol] and 5-hydroxyconiferyl [3-(3,4-dihydroxy-5-methoxyphenyl)prop-2-en-1-ol] alcohols joined this group.[12]

The formation of lignin macromolecules from monolignol precursors is currently considered as dehydrogenation polymerization under the action of peroxidases, laccases, and hydrogen peroxide. Figure 1 illustrates the formation of a resonance-stabilized phenoxyl radical from coniferyl alcohol by deprotonation and one-electron transfer.

Then, recombination of phenoxyl radicals and stabilization of intermediate dimeric quinonmethides with the formation of bonds of various types occur. Due to the noted peculiarities of the biosynthesis process, lignin features a diversity of bonds between phenylpropane units (PPU) (Fig. 2), as this process is essentially combinatorial, in which all available ways of combination are possible, but they are not equally probable.[16] The monolignol supply and polymerization conditions are carefully controlled in the cell. However, this control should not be confused with control of lignin polymer assembly. The actual structure of the lignin macromolecule is controlled only by the on-going chemical reactions, the availability of monomers, the ability to generate radicals, and conditions in the cell wall. According to Ralph and co-workers,[14] to date there is no convincing evidence for any control of the primary structure of lignin by an organized assembly process.

The combinatorial nature of the biosynthesis process results in lignin not being an individual compound but a mixture of related compounds. Therefore, its structure is represented by schemes rather than structural formulas used to describe cellulose, proteins, and other biopolymers. At present, the

Table 1. Number average molecular weights ($\bar{M}_n$), weight average molecular weights ($\bar{M}_w$) and polydispersity indices (D) of milled wood lignin derived from wood and other biomass sources.[18]

Lignin source	$\bar{M}_n$	$\bar{M}_w$	D
Norway Spruce	6400	23500	3.7
Douglas Fir	2500	7400	3.0
Redwood	2400	5900	2.5
White Fir	2800	8300	3.0
E. globulus	2600	6700	2.6
Southern Pine	4700	14900	3.2
Bamboo	5410	12090	2.23
Miscanthus	8300	13700	1.65

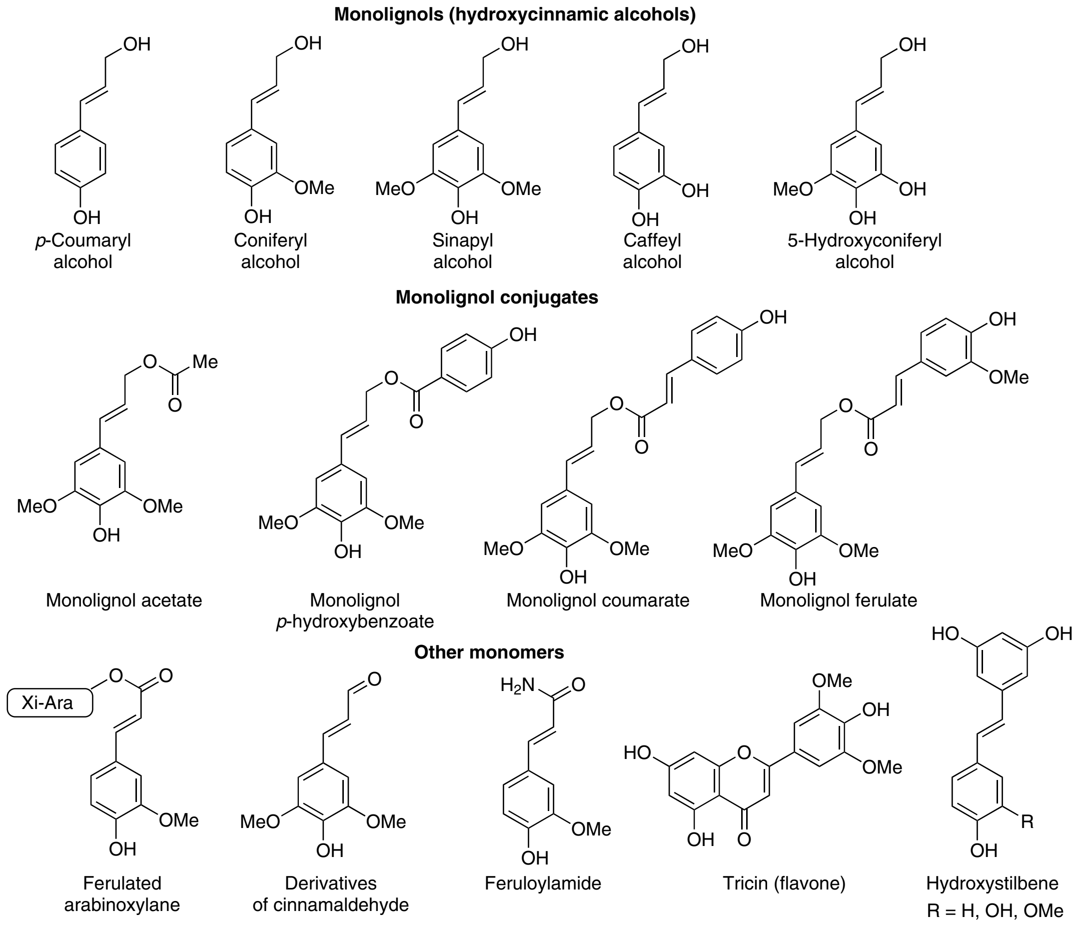


Figure 4. Canonical monolignols and other compounds able to participate in the lignin biosynthesis.[22]

scheme proposed by Balakshin *et al.*[17] (Fig. 3) is probably the most consistent with the known data on the lignin structure. The values of molecular weights and polydispersity of isolated lignin preparations are given in Table 1. Coupled with the scheme in Fig. 3, these data show that lignin is a polyfunctional, polydisperse, irregular heteropolymer. The topological structure of lignin remains a matter of debate: it is considered both as a linear, branched, and cross-linked polymer (this issue is discussed in more detail in Ref. 17).

A detailed study of the composition of lignins derived from transgenic and mutant trees, as well as herbaceous plants, showed that in addition to canonical monolignols (coniferyl, synapyl and coumaryl alcohols), other compounds may participate in the lignin biosynthesis (Fig. 4).

The biosynthesis of monolignols turned out to be very flexible, which allows plants to replace monolignols when the expression of one or more genes is misregulated, so that the composition and amount of lignin often change simultaneously. For example, suppression of one of the genes in hybrid poplar resulted in a 60% decrease in lignin content and a shift in biosynthesis towards the formation of *p*-hydroxyphenylpropane units.[19]

5-Hydroxyconiferyl alcohol was detected in the lignin of poplar *P. tremula* × *P. alba*,[20] and caffeyl alcohol was detected in *Pinus radiata* tracheal cell cultures.[21] Notable among the non-canonical monolignols are their conjugates: acetate, ferulate, *p*-hydroxybenzoate and *p*-coumarate (see Fig. 4). In fact, any compatible phenolic compounds present at the polymerization site in the cell wall are candidates for radical transfer, radical-radical coupling and lignin polymerization.[23]

As views on the lignification process of plant cells have evolved, terms for lignins have emerged to reflect this evolution.

2.1. Stress lignins

The placticity of the biosynthesis of lignin is also manifested in the protection of plants against adverse environmental effects. In response to an external stress, plants modulate lignin biosynthesis to eliminate its negative impact. Plants respond to external stresses in a generally similar way – by increasing lignin content. For example, this occurs under water shortage in the basal zone of *Eucalyptus urograndis* and apical zone of *E. globulus*, and in both cases the ratio of syringylpropane to guaiacylpropane units in lignin increases.[24] Some herbaceous plants respond to cold stress in a similar way.[25,26] Increased lignification also occurs in response to pathogen attack. For example, *Eucalyptus* and *Ulmus* species with increased resistance to fungal diseases had higher lignin content than less resistant species.[27]

The monomer composition of stress lignins depends on the type and intensity of stress and the plant species, but some common properties are observed: such lignins comprise more *p*-hydroxyphenylpropane units, which have the shortest biosynthetic pathway, allowing the plant to respond to stress more rapidly.[28]

2.2. Designer lignins

Designer lignins are lignins that are not native but can be synthesized by exploiting the plasticity of lignin biosynthesis to improve the processability of plant raw materials.

For example, ferulic [3-(4-hydroxy-3-methoxyphenyl) propenoic] acid is incorporated into the lignin of plants deficient in certain enzymes to form acid-labile acetals,[29] and overexpression of ferulate-5-hydroxylase in hybrid poplar produces a lignin containing almost 98% syringylpropane units and characterized by high levels of β-O-4 bonds that are unstable in alkaline environments.[30]

Designer lignins also includes the so-called zip lignins (from the word zip fastener). They are characterized by the presence of ester linkages between PPUs. Transgenic poplars with such genetically engineered lignin are more easily delignified under mild alkaline treatment and kraft pulping conditions compared to the control group.[31,32] When only caffeyl or 5-hydroxyconiferyl alcohol is involved in biosynthesis, homogeneous linear lignin molecules consisting exclusively of benzodioxane units connected by β-O-4 linkages are formed.[33,34]

The above literature data indicate some progress in gene engineering of lignin, but such interference in the biosynthesis processes developed in the course of natural plant evolution has negative consequences. Transgenic plants often exhibit developmental defects ranging from stem lodging to dwarfism. Reduced lignin content is thought to alter structural integrity and impair water transport, and such plants often have destroyed xylem cells.[35] They are also characterized by increased susceptibility to disease.[36,37] Therefore, when conducting research into lignin gene engineering, a compromise needs to be reached between improving the processing of plant material and the viability of transgenic plants.

3. Pyrolysis and carbonization of lignin

One of the important directions of lignin utilization is pyrolysis to produce gaseous (CO, CO_2, CH_4 and H_2), liquid (bio-oil containing aromatic benzene derivatives) and solid (biochar) products. Most of the published works are focused on obtaining biochar and products derived therefrom. The second direction of research is to improve the yield of bio-oil in general and the yield of arenes while decreasing the yield of phenols in particular. Due to the problems associated with the depletion of fossil natural resources and environmental pollution, the considered directions are promising for the production of organic substances from lignin.

Qi *et al.*[38] prepared cobalt catalysts on a carbon support obtained from the pyrolysis of Co/Zn-containing lignin at temperatures of 550 and 1000 °C. The catalyst was used to activate potassium peroxymonosulfate, which in turn decomposes organic pollutants (antibiotics, endocrine disruptors, pesticides) into low-toxic intermediates or even to the final oxidation products such as CO_2 and H_2O.

Chen *et al.*[39] explored pyrolysis of all three biomass components (cellulose, hemicelluloses, alkaline lignin) in a wide temperature range (311.5–800 °C). The main pyrolytic volatile products are H_2O, CO, CO_2, CH_4 and carbonyl-containing compounds. The yields of CH_4 and H_2 increase significantly with increasing temperature. The maximum yield of bio-oil (28.7%) is reached at 550 °C, while the yield of biochar gradually declined with increasing temperature.

It was found that at lower temperature (200 °C), the yield of gas and liquid is rather low (4%), while the char yield is 95%.[40] The yields and composition of liquid products and biochar are close to the findings of the above-mentioned study.[39] At pyrolysis temperature below 500 °C, the phenolic compounds are mainly methoxyphenols, the yield of which is maximum (81.7%) at 450 °C and decreases with decreasing temperature. As the pyrolysis temperature raises from 200 to 600 °C, the yield of phenols, alkylphenols and gaseous products (H_2, CH_4 and CO) increases. The major gaseous product is carbon dioxide, maximum content (95%) of which is observed at 200 °C and decreases with increasing temperature, but only at 600 °C it is formed less than hydrogen. The hydrogen and methane content increases with increasing temperature, with hydrogen only beginning to be produced at 350 °C. The content of aliphatic compounds in the liquid pyrolysis products is the highest (~87%) at 250 °C and decreases to ~ 10% at temperatures above 350 °C.

Biswas *et al.*[41] studied hydrothermal liquefaction of alkaline lignin catalyzed by activated carbon-supported metals (Ni, Co, Ni–Co, 5–20 wt.%) at 260, 280, 300 °C in various solvents (water, ethanol, methanol). The same authors prepared biochar support for the catalyst by pyrolysis of the rice straw at 450 °C.[42] It was found that using ethanol and methanol as solvents and catalysts containing Ni, Co, Ni–Co at 280 °C, the maximum yield of bio-oil, consisting mainly of methoxyphenols, was 25.6, 70.5 and 72 wt.%, respectively, with a maximum vanillin content of 36.2%.

A good yield of bio-oil (79.75–85.25%) was achieved by using SO_4^{2-}/TiO_2 solid acid catalyst in the liquefaction of sodium lignosulfonate in a methanol–glycerol mixture at 160–180 °C for 1 h.[43] The obtained bio-oil varieties have better lubricating properties than commercial polyethylene glycol-200.

A higher yield of bio-oil (90%) was achieved using $H-NiFe_2O_4$ as a catalyst.[44] In this case, depolymerization of kraft lignin in combination with demethoxylation was carried out at 320 °C for 24 h in a hydrogen atmosphere (2.0 MPa) to provide 90 wt.% yield of liquid products with a minimum amount of coke (3.4 wt.%). The main monomeric products of pyrolysis at 300 °C for 3 h were guaiacol and methoxyphenols (up to 73.7%). When increasing the temperature to 320 °C, the yields of alkylphenols and solids improved to 50 and 26%, respectively.

Huang *et al.*[45] explored catalytic fast pyrolysis of milled wood lignin (MWL) from coniferous (Chinese fir), hardwood (poplar) and herbaceous biomass (corn straw) to produce a mixture of benzene, toluene and xylenes. Various microporous and mesoporous zeolites and bifunctional Zn/zeolite systems were used as catalysts when heated up to 650 °C. The maximum bio-oil yield was observed for poplar lignin.

Table 2 presents the yields of lignin pyrolysis products depending on the catalyst used in the process. The studies were focused on minimizing the yield of solid and gaseous products and maximizing the yield of bio-oil, especially aromatic hydrocarbons (benzene, toluene, xylene[44,45]). The lowest yield of bio-oil was obtained from alkaline lignin using Ni/C[41] (25.6%, see Table 2, line 3) or no catalysts[39] (27.8%, see Table 2, line 2) in short time (10–40 min). With increasing reaction time, the yield of bio-oil increased. The maximum yield (90%) was achieved by carrying out pyrolysis at 320 °C for 24 h using $H-NiFe_3O_4$ (Ref. 44) as a catalyst (see Table 2, line 12). The yield of arenes in this case was also maximum (70%).

Biswas *et al.*[41] tried to obtain vanillin, another important product of lignin processing, in maximum yield. A yield of 36% was achieved by liquefaction of alkaline lignin at 280 °C for 15 min on Co/C catalyst (see Table 2, line 4).[41]

Microporous zeolites are more efficient for aromatic hydrocarbons production (maximum yield 56.56% using HZSM-5) than mesoporous ones. The yields of arenes increased with increasing zeolite acidity and catalyst/lignin ratio, and with increasing pyrolysis temperature from 550 to 850 °C. Previously,

Table 2. Yields of lignin pyrolysis products depending on the catalysts and conditions used.

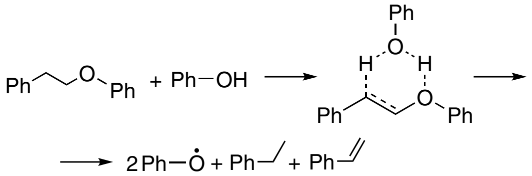
№	Lignin	Pyrolysis conditions			Pyrolysis products, yield (%)			Ref.
		catalyst	temperature, °C	time	liquid	solid	gaseous	
1	Alkaline lignin	No	800	10–40 min	–	–	24.8	39
2	Alkaline lignin	No	500	10–40 min	27.8	–	–	39
3	Alkaline lignin	Ni/C	280	15 min	25.6	–	–	41
4	Alkaline lignin	Co/C	280	15 min	70.5 (vanillin, 36.2)	–	–	41
5	Alkaline lignin	Ni–Co/C	280	15 min	72 (vanillin, 34.8)	–	–	41
6	Sodium lignosulfonate	SO_4^{2-}/TiO_2	160–180	1 h	79.75–85.25	–	–	43
7	Kraft lignin	Нет	300	3 h	45.3	54.6	–	44
8	Kraft lignin	Fe_2O_3/Prussian blue	300	3 h	54.1	42.7	–	44
9	Kraft lignin	H–$NiFe_3O_4$	300	3 h	73.7	22.0	–	44
10	Kraft lignin	Ni/Fe_2O_3/Prussian blue	300	3 h	54.7	39.4	–	44
11	Kraft lignin	Ni/Fe_2O_3	300	3 h	52.5	42.3	–	44
12	Kraft lignin	H–$NiFe_3O_4$	320	24 h	90 (arenes, 70)	3.4	–	44
13	MWL	HZSM-5 zeolite	160–180	1 h	arenes 56.56	9.50–11.75	3.60–9.00	45

similar studies were carried out for masson pine lignin[46] and palm kernel shells.[47]

Li *et al.*[48] used a fixed bed reactor for lignin pyrolysis at temperatures up to 1000 °C with different heating rates in a nitrogen atmosphere. With increasing heating rate, the yield of biochar gradually decreased, and the yield of gaseous products increased accordingly. The maximum yield of bio-oil was 28%; besides phenols, it included carboxylic acids and furfural.

Based on thermal transformations of model lignin compounds (phenylethyl phenyl ether, phenol, and ethylbenzene) with the use of quantum chemical calculations, a mechanism of lignin pyrolysis has been proposed.[49] Phenols promote the processes of bond cleavage in lignin under pyrolysis conditions due to the generation of six-membered transition states between the hydroxyl group of phenol and ether linkages in lignin. As a result, phenoxyl radicals, alkyl- and alkenylbenzenes are formed, as it was established for the model compounds (Scheme 1).

Scheme 1



Runeberg *et al.*[50] examined thermal transformations occurring in polyphenols, in particular, during thermal processing of food products. The transformations of a wide range of polyphenolic lignans (hydroxymatairesinol, matairesinol, α-conidendrin, resveratrol, *etc.*) were studied at temperatures between 200 and 250 °C (Fig. 5).

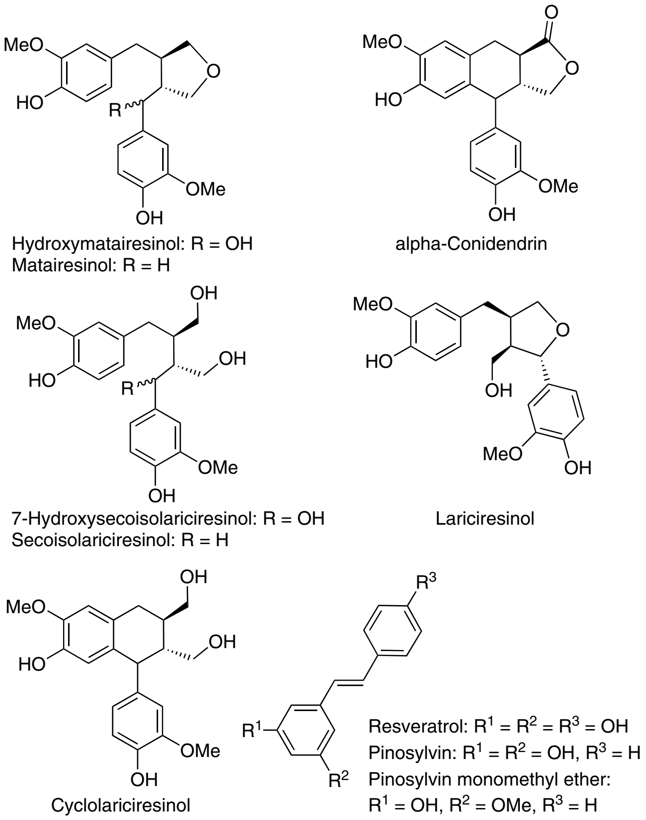


Figure 5. Polyphenols subjected to thermal transformations.[50]

The lignans showed high stability at temperatures between 150 and 180 °C. At typical food processing temperatures within these intervals, the polyphenols investigated are quite stable and safe. Interconversions between some lignans were detected, but the formation of toxic substances was not observed. The antioxidant activity of the investigated substrates was maintained at 200 °C in air. In the presence of oxygen at temperatures above 220 °C, lignans were oxidized to give oligomerization products, especially substrates containing phenolic hydroxyl groups in combination with aliphatic or benzyl hydroxyl substituents. Matairesinol and pinosylvin monomethyl ether were the most resistant to oxidative oligomerization.

Y.Sun *et al.*[51] prepared biochar from iron-modified ($FeCl_3 \cdot 6H_2O$) lignin at 800 °C for 2 h. Such carbon material is characterized by high adsorption capacity (200 mg g^{-1}) towards methylene blue in the pH range from 2 to 12, as well as towards high salt and multiple dye systems.

Carbonization of alkaline hydrolyzed lignin from corn cob residues at 400 °C in the presence of $MnCl_2$, $KMnO_4$, $MnSO_4$ solutions yields manganese-modified biochar with a maximum adsorption capacity of 248.96 mg g^{-1}, and a removal rate of

99.73% compared to 234.65 mg g^{-1} and 94% for unmodified biochar.[52]

A method of self-propagating high-temperature synthesis of carbon nanomaterials from technical lignosulfonates, Pepper lignins, isolated from the cow parsnip biomass, wheat straw and red bilberry is described.[53] Such carbon materials showed excellent sorption capacity towards uranium-238 isotope and mycotoxin T-2.

X.Chen *et al.*[54] presented a systematic study of synthetic and photo-Fentone-like catalytic properties of $LaFeO_3$/lignin-biochar composites. The $LaFeO_3$/lignin – biochar catalysts were prepared by sol-gel method at 600 °C for 4 h. They showed highly efficient degradation of ofloxacin under visible light irradiation. The degradation efficiency was improved from 53.4% for pure $LaFeO_3$ to 95.6% for the composite photocatalyst.

Ma *et al.*[55] prepared ultra-fine porous carbon nanofibres by initial electrospinning using a mixture of lignin with polyvinylpyrrolidone and $Zn(NO_3)_2 \cdot 6H_2O$, followed by oxidation and carbonization at 800 °C. Such fibres have good flexibility, which opens up the possibility of their direct use as electrodes in supercapacitors.

Hérou *et al.*[56] described a new generation of lignin-derived carbon nanofibre electrodes. The nanofibres were first formed by electrospinning from an aqueous alkaline solution of a mixture of hardwood lignin and polyethylene oxide. After electrospinning, the fibres were compressed at pressures between 40 and 120 bar, then stabilized at 200 °C and carbonized at 800 °C. These materials are good candidates for the production of high-density electrodes.

Hybrid nanostructures of silicon-containing carbon nanofibres for use as high-performance anodes in lithium-ion batteries were fabricated from hardwood lignin by electrospinning with polylactic acid followed by carbonization at 900 °C.[57] High capacitance values of up to 921 mA H g^{-1} were obtained for nanofibres made from precursors containing 15% silicon. Oxidation of sodium lignosulfonates and carbonization at 600 °C also yields hard carbon anodes with a boosted capacity of 584 mA H g^{-1} for lithium ion storage.[58]

Cao *et al.*[59] obtained ultralight honeycomb-like multilayer carbon by electrospraying and one-step carbonization. Poplar wood lignin and methyl methacrylate were mixed in DMF, then subjected to electrospraying and carbonization at temperatures from 250 to 800 °C. The specific capacitance of 348 F g^{-1} of such material, when tested as electrodes for supercapacitors in aqueous electrolytes, was higher than that of most previously described lignin carbon materials.

Spherical carbon particles were prepared from kraft lignin with different KOH content.[60] This mixture was subjected to spray drying at 200 °C and carbonized at 700 – 900 °C. The specific surface area of the resulting particles (1233 $m^2\ g^{-1}$) is much higher than that of irregularly shaped carbon particles. It should be noted that in the absence of KOH, carbonization does not provide spherical structures.

Rechargeable wet Zn-air batteries using a catalyst based on Fe-containing carbon derived from lignosulfonate were described.[61] The batteries are characterized by high power density (216.88 mW cm^{-2}), small charge-discharge voltage gap (0. V), significant reversibility and long cycle time (stable run for 93 h).

Wu *et al.*[62] compared adsorption properties of alkaline lignin and its biochar derivative towards Pb^{II} ions. It was found that the temperature of biochar production significantly affects its ability to bind Pb^{II}. The adsorbent obtained at 400 °C was significantly superior to the pristine lignin in sorption rate and almost twofold in terms of maximum adsorption capacity.

Chen *et al.*[63] pyrolyzed kraft lignin at 700 °C to produce biochar for further efficient extraction and removal of tetracycline hydrochloride.

A Ru – MoS_2 hybrid catalyst on alkaline lignin carbonized at 900 °C was designed.[64] The synergistic effect and interfacial interaction between Ru, MoS_2 and carbon provided an excellent catalytic performance: electrochemical activity with a low onset overvoltage (25 mV) and a very low Tafel slope (46 mV dec^{-1}) in the hydrogen evolution reaction.

4. Composites and copolymers from lignin

The chemical structure of lignin containing reactive functional groups allows it to become a part of complex composites. As a result, materials with superior or completely new practically relevant properties can be achieved.

A composite membrane with low vanadium ion permeability for use in high-efficiency vanadium redox flow batteries was created by casting a solution of perfluorosulfone polymer Nafion 212 and lignin in DMF.[65] Compared to a pristine Nafion 212 membrane, a single cell with an optimized Nafion/lignin composite membrane exhibits superior performance: high Coulombic efficiency (97.4%), energy capacity (82.7%), and slower capacity decay of *ca*. 52.8% capacity retention after 1000 cycles, whereas the pristine polymer membrane retains 34.8% capacity after only 150 cycles. Partial replacing of the expensive polymer with affordable lignin in large-scale production would reduce the cost of the composite membrane while maintaining the stability of the conductive material.

A certain correlation between the composite structure and its properties was shown on the example of a polymer membrane obtained by copolymerization of pre-oxidized kraft lignin with poly(ethylene glycol)diglycidyl ether.[66] The glass transition temperature of the material decreased with increasing ether content in its composition. Thus, the polyethylene glycol chains act as flexible segments, increasing the molecular mobility of the three-dimensional polymer chain. Swelling in a liquid electrolyte increases with decreasing amount of lignin. A number of optimizations led to a biocomposite identical to quasi-solid electrolytes in solar cells.

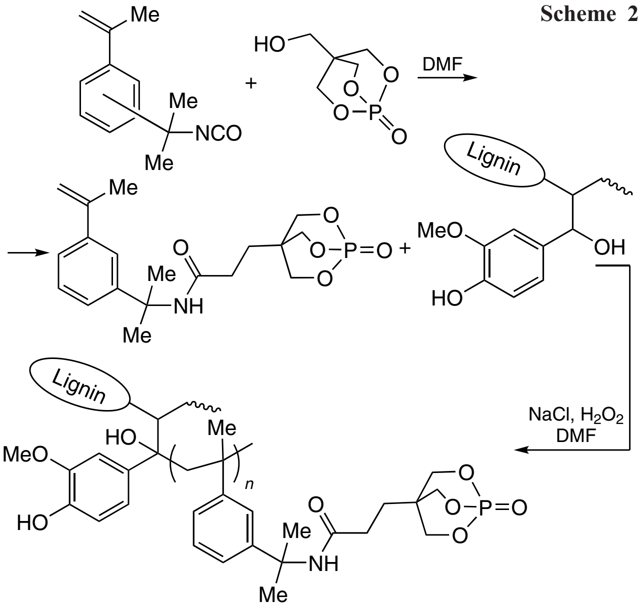
Beverage straws, made by rolling up a thin, wet film consisting of homogenized micro- and nanofibres of cellulose and washed alkaline lignin, are an excellent alternative to plastic straws.[67] Analogous to such products are paper straws, which, when placed in soil and waste, can be completely degraded by microorganisms over time. However, they have poorer mechanical properties and less water resistance.

When ramie (Chinese nettle) fibres and lignin were added to the chitosan matrix, mechanical, water-resistant, thermal and antioxidant properties of the film composites were improved.[68] Compared to their polyethylene counterpart, such films contributed to better preservation of meat products by keeping pH within the acceptable range and allowing less contamination of food by microorganisms due to the antibacterial properties of chitosan.

Polylactic acid food packaging materials containing 1 to 3 wt.% citric acid-modified lignin nanoparticles showed antioxidant, antibacterial and UV-protective properties.[69]

The introduction of enzymatic hydrolyzed lignin into polylactide composites helps to achieve excellent fire resistance.[70] Lignin was pre-modified by grafting with a vinyl monomer containing nitrogen and phosphorus atoms (Scheme 2). The presence of even 5 wt.% of such an additive in the polylactide biocomposite increases the elastic modulus by

Scheme 2



26%, fully preserves the mechanical strength and imparts excellent UV-protective properties to the polymer. Such modifier allows to change the characteristics of polylactic acid and use the new material in the field of packaging, electronics, automotive industry, *etc*., allowing to improve the properties of the pristine polymer material.

Wasti *et al.*[71] proposed to replace polylactic acid used in extrusion of composite filaments with organosolv lignin up to 20 wt.%. A 5 wt.% lignin significantly reduces the elongation of the polymeric material. The addition of polyethylene glycol as a plasticizer to the composite blend decreases the internal stress of the material and promotes elongation of the filaments, facilitating the 3D printing process.

Alkaline lignin modified by condensation with ammonium vinyl salt excellently cleans wastewater.[72] Similar flocculants and coagulants were shown to be insensitive to pH conditions, and the high molecular weight and branched structure of the macromolecules have made the material effective in removing industrial dyes from solutions.

Bamboo lignin modified with amino-functionalized magnetic iron nanoparticles and cyanuric chloride as a chemoselective crosslinking agent showed selective sorption properties towards Pb^{II} ions.[73] Two materials differing in the content of lignin were produced. The first material contained 2.5 times more bamboo lignin and exhibited higher adsorption affinity (111.23 mg g^{-1}) and better selectivity to Pb^{II} ions than the second one (81.97 mg g^{-1}). The presence of magnetic cores in the sorbent network favors its rapid recovery after the adsorption process due to its good superparamagnetic properties of 40.06 and 26.95 emu g^{-1} (electromagnetic units per gram), respectively.

Free-radical copolymerization of lignosulfonates with acrylic and citric acids affords a copolymer with excellent adsorption properties towards Cu^{2+} and Pb^{2+} ions.[74] The as-resulting adsorbent had the adsorption capacity of 276 mg g^{-1} (Cu^{2+}) and 323 mg g^{-1} (Pb^{2+}), exhibiting maximum efficiency even after 5 runs of sorption–desorption cycles.

Grafting polyethyleneimine onto alkaline lignin by an inverse suspension polymerization method using polyethylene glycol as a porogen produces bifunctional lignin microspheres.[75] The porous structure of the material promotes effective capture of the reference herbicide, 2,4-dichlorophenoxyacetic acid, over a wide pH range (4–10). Beyond the above range, under acidic (pH = 2) and alkaline (pH = 11) conditions, up to 57% and 88% of the herbicide is released in 72 h, respectively. The maximum adsorption capacity of the material was 909.09 mg g^{-1} at 45 °C, which is much higher than that of activated carbon (515.46 mg g^{-1}) and metal organic framework like MIL-53 (556 mg g^{-1}).

Based on a mechanical mixture of lignin (isolated by enzymatic hydrolysis from plant raw materials) and carbon nanotube-modified polyurethane foam, a photothermal sorbent with good adsorption capacity for heavy-oil products was prepared.[76] The modified foam demonstrated complete sunlight absorption (97%), and its surface temperature reached 90.3 °C within the first 500 s due to the excellent photothermal effect of nanotubes.

Under solar irradiation, the foam is heated, the viscosity of oil decreases over the entire surface of the material, increasing the absorption of oil products more than six times relative to the weight of the sorbent.

An environmentally friendly method for the preparation of polyurethane–lignin composites, free of isocyanates, solvents and catalysts, based on the interaction of a bis-derivative of 1,3-dioxan-2-one, a long-chain diamine and lignin is described.[77] The resultant materials possess dual networks: dynamic covalent network and hydrogen bonding network, demonstrating high thermal stability, mechanical strength and ‘smart’ properties, such as shape memory effect and self healing. Such natural lignin copolymer can be further combined with paper to fabricate materials with high tensile strength, impact strength and good electromagnetic properties.

5. Lignin nanoparticles

The complex structure and high reactivity of individual lignin fragments is the main challenge in the search for the application of this natural material in knowledge-intensive technologies. Lignin nanoparticles (LNPs) are produced to adjust and control the homogeneity of its structure and size of macromolecules. LNPs have proven themselves as special additives to various polymer compounds, as well as reinforcing particles in copolymerization with monomers having superior mechanical, thermal and biocompatible properties compared to the pristine lignin.

Lignin nanoparticles derived from alkaline poplar lignin by self-assembly at room temperature shows a stable photothermal effect (22%).[78] The photothermal conversion of solar energy into NLP electricity is attributed to intermolecular π–π stacking of lignin macromolecules. The resultant material was successfully used to power a thermoelectric generator and drive a solar steam generator under standard solar irradiation (100 mW cm^{-2}).

Coprecipitation of NLPs derived from softwood kraft lignin with bisphenol A diglycidyl ether promotes cross-linking of lignin macromolecules to give a new hybrid material.[79] Varying the content of a cross-linking agent, it was possible to obtain products with different properties and areas of technical application. At a bisphenol ether content of $\leqslant$ 20 wt.%, structural stabilization of the material is observed due to intraparticle cross-linking while preserving the surface charge and colloidal stability in aqueous medium. Increasing the content of the bisphenol A derivative to a mass fraction of $\geqslant$30% leads to additional interparticle cross-linking, which allows the use of such material as waterborne wood adhesives.

Lignin content significantly affects the morphology and rheology of cellulose nanofibres.[80] Lignocellulosic nanofibres were formed from chemi-thermo-mechanical wood pulp (maple and birch mixture) with different degrees of bleaching with glacial acetic acid and sodium chlorite by mechanical processing in a high-pressure microfluidizer. The nanofibre suspensions with high lignin content (23.79 wt.%) exhibited high viscosity, negligible resistance to deformation, low gelling and reducing ability and low yield strength. At low lignin content (up to 6.52 wt.%), the fibril bundles were sensitive to defibrillation and the lignocellulosic material contained long and flexible fibres with a high tendency to tangle, while the suspensions were characterized by high viscosity and significant gelation.

The recyclable deep eutectic solvents intensify the pretreatment of lignocellulosic samples of Radiata Pine, allowing improved delignification and removal of hemicelluloses while preserving most of the cellulose.[81] Lignin recovered from deep eutectic solvents was obtained in high yield; its structure was assigned to the nanoscale range based on the results of studies.

Calcining lignin macromolecules with melamine cyanuric acid derivatives gave rise to a graphite photocatalyst based on carbon nitride (g-C_3N_4).[82] This nanomaterial had an increased conductivity zone and increased light absorption in the visible range. The study was able to improve the performance of the hydrogen evolution reaction by a factor of 3.5 compared to a material obtained by calcining melamine cyanuric acid without the addition of lignin using carbon nitride calcined in the absence of lignin. The authors attribute the results to the synergistic effect occurring between the layers of the nanostructured material. In the future, such a material can be considered as an effective photocatalyst for scaling up hydrogen production using solar energy.

Immunomodulatory drugs used to target tumour-associated macrophages present side effects when administered systemically, which limits their clinical use. A biocompatible polymer modified with a toll-like receptor agonist, resiquimod, was created on the basis of NLPs.[83] The use of the active drug-loaded lignin even in extremely low doses promotes an antitumour immune response in cells by increasing the number of macrophages, cytotoxic T cells and activated dendritic cells. Softwood kraft lignin, acting as a carrier for the compound resiquimod, is a promising candidate for chemotherapeutic use in very aggressive tumours, such as triple-negative breast cancer.

The combination of non-toxic silver nanoparticles and LNPs in a single preparation resulted in a drug with antibacterial activity against a wide range of bacterial cultures.[84]

Yang *et al.*[85] explored antioxidant, antibacterial and UV-absorbing activities of nanoparticles of alkaline lignin (derived from corn stalks), the surface of which was modified by Mannich amination using ethylenediamine and formaldehyde. Modification of lignin with amino groups gives the resultant material an additional dark colour, which increases its UV resistance. However, the investigated lignin has reduced antibacterial ability against *S. aureus*, possibly due to difficulties in penetration of the compound through the bacterial cell wall. In scavenging tests with reactive oxygen species, the similarly modified lignin performed better than the pristine lignin and the commercial antioxidant 2,6-di-*tert*-butyl-4-methylphenol. A possible mechanism of radical scavenging by aminated NLPs is associated with a decrease in the enthalpy of dissociation of the Ar–O···H bond, which provided electron transfer due to the electron-donor effect of substituents in the *ortho*-position to the phenolic hydroxyl group of PPU.

6. Synthesis of low-molecular-weight compounds from lignin

An important area in lignin chemistry and technology is the production of low-molecular-weight practically valuable substances from lignin: arenes, including phenols, various functional compounds (alcohols, aldehydes, ketones, carboxylic acids, amines, *etc.*). At the same time, lignin macromolecules can be cleaved by chemical methods under reducing (hydrogenolysis) or oxidizing conditions, as well as by biotechnological approaches.

One of the most relevant and intriguing tasks of biorefining is the conversion of lignin to aromatic hydrocarbons as a direct alternative to petrochemical methods. It has recently been found that catalytic transformations of lignin can produce benzene in yields of up to 18.8 wt.%.[86] This was achieved using a catalyst consisting of a ruthenium-tungsten (RuW) alloy deposited onto a silicon-rich zeolite. The zeolite induces the degradation of C(sp^2) to C(sp^3) bonds between aromatic rings and their pendant chains in the PPU. RuW alloy promotes hydrogenolysis of C(sp^2)-O bonds in lignin, while the hydrogen necessary for this reaction is formed from lignin itself in the process of its catalytic transformation.

Wang *et al.*[87] studied the selective hydrogenolysis of catechol lignin, which was extracted from the seed coats of some plants and contained a significant amount of benzodioxane moieties. Hydrogenolysis of such lignin with hydrogen (3 MPa) over Ru–ZnO–C catalyst in methanol at 200 °C for 4 h produces catechols (4-substituted 1,2-dihydroxybenzenes) with a total yield up to ~26 wt.%, with the major product being 1,2-dihydroxy-3-(*E*-prop-1-en-1-yl) benzene (yield 18 wt.%).

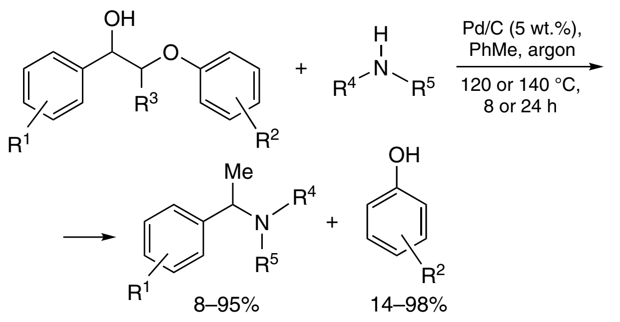
Direct abies wood hydrogenation (H_2, 9 MPa, 250 °C, 3 h, ethanol) produces up to 42 wt.% of liquid products in which significant amounts of 4-propanolguaiacol [3-(4-hydroxy-3-methoxyphenyl)propan-1-ol, 16.1 wt.%] and 4-propylguaiacol (2-methoxy-4-propylphenol, 11.9 wt.%) derived from lignin were identified.[88]

A number of studies are devoted to the search for novel catalysts for lignin hydrogenolysis, among which ruthenium compounds are the most effective. Thus, the example of hydrogenolysis of benzyl phenyl ether, used as a model lignin compound, over the ruthenium catalyst loaded on activated carbon (H_2 0.1–2 MPa, 80–220 °C, 2 h, methanol or other alcohols) shows that the C–O bond is cleaved to form methylcyclohexane and cyclohexanol.[89] Nickel catalyst supported on mixed metal oxides displayed excellent catalytic activity in various hydrodeoxygenation processes (H_2 1 MPa, 130 °C, 2 h, methanol–water) for model lignin compounds such as vanillin, *ortho*-vanillin, isoeugenol, cinnamaldehyde, *etc.*[90] However, despite promising results obtained on model compounds, when transferring these processes to real lignin, it is often impossible to achieve the same efficiency due to technical difficulties related to poor solubility of lignin, inhomogeneity of its structure, heterogeneity of reactions, *etc.*

The study of reactions of lignin model compounds with amines catalyzed by palladium on charcoal showed the possibility of cleavage of the β-O-4 ether linkage of lignin accompanied by reductive amination to give benzylamines and phenols in high yields (Scheme 3).[91]

To produce benzylamines directly from lignin, a two-step cleavage strategy was used.[91] First, in the presence of a rhodium bidentate complex, lignin was converted into low-molecular-weight carbonyl-containing depolymerization products, which were then subjected to amination using pyrrolidine. As a result,

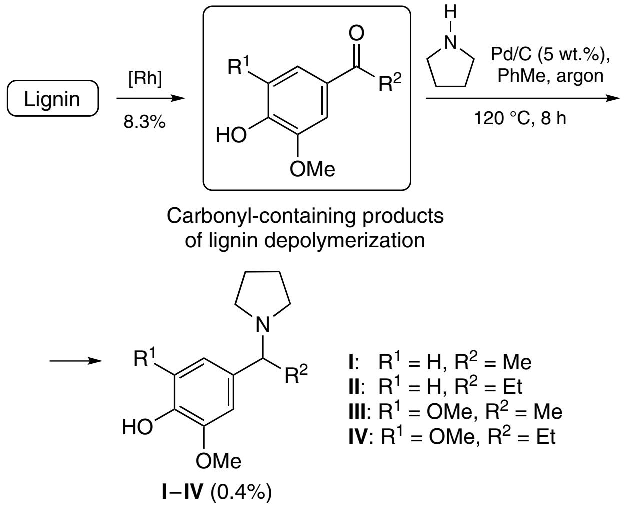
Scheme 3



R^1 = H, 4-MeO, 3,4-$(MeO)_2$; R^2 = H, 2-MeO, 2,6-$(MeO)_2$;
R^3 = H, CH_2OH; $R^4 = R^5$ = $(CH_2)_4$, $(CH_2)_5$, Pr^n;
R^4 = H; R^5 = Bu^n, n-C_7H_{15}, $(CH_2)_3OMe$, cyclo-C_6H_{11}, Ph, $(CH_2)_3Ph$

a mixture of four benzylamines **I**–**IV**, which are of interest for medicinal chemistry, was isolated with a minor total yield (0.4%) over all reaction steps (Scheme 4).

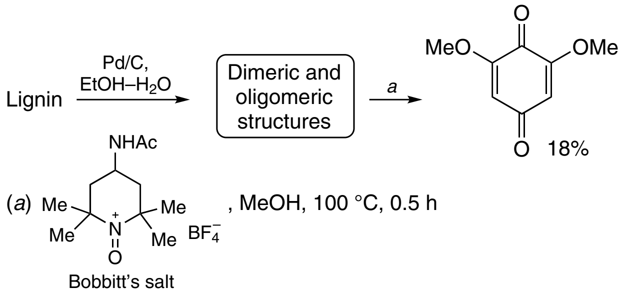
Scheme 4



The oxidative cleavage of chemical bonds in lignin also yields valuable individual compounds. One of the most developed areas in this field is the synthesis of vanillin (4-hydroxy-3-methoxybenzaldehyde) for the food industry, as well as other aromatic aldehydes (see review[92]).

Subbotina *et al.*[93] carried out oxidation of lignin oligomers obtained *via* preliminary reductive catalytic fractionation of birch wood lignin using palladium on charcoal in the presence of Bobbitt's salt (Scheme 5). As a result, 2,6-dimethoxy-1,4-benzoquinone was selectively formed in 18 wt.% yield. This procedure provides an approach to benzoquinone derivatives of great importance for chemistry, biology, medicine and materials science, which is an alternative to petrochemical production.

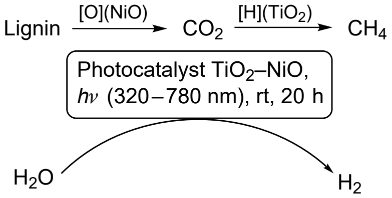
Scheme 5



Electrochemical oxidation of model lignin compounds containing motifs of benzyl alcohol (1-phenylethanol, *etc.*) and aromatic ketones (3,4-dimethoxyacetophenone, *etc.*) carried out at room temperature in an alkaline aqueous solution on an anode comprising manganese-doped cobalt oxyhydroxide MnCoOOH on a nickel foam support, affords the corresponding benzoates in 84–99% yields.[94] Under similar conditions, cyclohexanol and cyclohexanone, used as model compounds of products of oxidative cleavage of lignin, gave adipates in 64% yield. The authors believe that their method developed for the synthesis of practically relevant benzoic and adipic acids from lignin can replace the current petrochemical processes.

Redox transformations of kraft lignin under photocatalysis conditions using TiO_2–NiO nanocomposite result in significant depolymerization of lignin and proceed as its initial oxidation to CO_2 (on NiO particles), which is further reduced to methane (on TiO_2 particles). Also, photocatalytic water splitting occurs to produce hydrogen (Scheme 6).[95] The higher fatty acids (palmitic and stearic acids) detected in the lignin oxidation products are probably external impurities from the pristine lignin.

Scheme 6



Various biotechnological processes are actively used for lignin valorization. Such an important compound as itaconic (3-carboxybut-3-enoic) acid was obtained in 56 mol.% yield from lignin isolated from corn stalks under the action of genetically engineered saprophytic bacteria *Pseudomonas putida*.[96] The importance of preliminary lignin depolymerization to improve its water solubility before microbiological treatment was highlighted.[97]

Depolymerization pretreatment of lignin includes its treatment with hot water, dilute sulfuric acid, aqueous NaOH solution or ammonia, and steam explosion.[98]

Other methods of lignin conversion to low-molecular weight-compounds are also known, which allow the α-O-4 and β-O-4 bonds to be cleaved, namely, electrochemical reduction, photochemical and enzymatic degradation, as well as some other methods. It was found that selective catalytic cleavage of these bonds occurs to provide the maximum yield of monomeric aromatic compounds of 23% using natural softwood lignin and 51% using hardwood lignin.[99]

7. Lignin-based hydro- and aerogels

Hydrogels belonging to swellable polymer matrices have attracted wide attention due to their ability to swell in various media, as well as their sensitivity to pH and temperature changes. Hydrogels are characterized by their ability to adsorb various compounds, including biologically active drugs, dyes, heavy metal ions, *etc.*, and can therefore be used in medicine and water remediation applications.[100]

In recent years, new trends have emerged in the production and application of lignin-based hydrogels. For example, a method was developed to produce a double-layer hydrogel for use in wearable bioelectrodes and self-powered sensors. The bottom layer of the hydrogel, made with sodium lignosulfonate, exhibits high softness and skin-adhesion, while the top layer, which includes hydroxyethylcellulose, provides high mechanical strength.[101]

A new cross-linked lignin–agarose/fibroin/$ZnCr_2O_4$ nanobiocomposite material was designed. The cross-linking reaction of lignin and agarose biopolymers to form a lignin–agarose hydrogel was carried out using epichlorohydrin as a cross-linking agent. It was found that after three days, the toxicity of the cross-linked nanobiocomposite was less than 13%. Moreover, according to the *in vivo* assay, the wounds of mice treated with this material healed almost completely within five days.[102]

Demethylated alkaline lignin was tested as a component of hydrogels for bioelectronics. Traditional silicon-based sensors for physiological signal transmission feature brittleness and hardness, which limits their application. The first step in the synthesis of the new hydrogel involves the interaction of alkaline lignin with oxidized graphene. Then the resultant mixture, along with some additives, is introduced into a hydrogel based on sodium alginate and polyacrylamide, transferred into a special mould and mixed at 50 °C. The developed hydrogel is a promising material for the manufacture of long-acting flexible sensors characterized by good conductive and adhesive properties.[103]

A hydrogel based on sodium lignosulfonate was tested as a biosensor capable of operating at low temperatures. Polyacrylic acid, polyvinyl alcohol, LiCl, $FeCl_3$ were used as additional synthesis components. The hydrogel is formed rapidly (in a few minutes) without external heating and UV radiation due to the participation of ammonium persulfate in the reaction. A hydrogel-based sensor allows fast, accurate and reliable recording of electrical signal changes for monitoring various physiological activities (*e.g.*, limb activity and breathing).[104]

The use of a catalyst representing silver nanoparticles immobilized on a lignin hydrogel was proposed for the hydrogenation of *p*-nitrophenol.[105] A lignin-based hydrogel was prepared using glycine, formaldehyde, acrylamide and ammonium persulfate. Further, $AgNO_3$ is reduced with sodium borohydride in the presence of this gel. High rate and efficiency of hydrogenation as well as high stability of the catalyst were observed.

It was found that hydrogels can be produced *in situ* when lignin interacts with heavy metals such as lead, iron and copper.[106] Ionic, coordination and hydrogen bonds are involved in the formation of lignin hydrogel (Fig. 6).

Aerogels are gels in which the liquid phase is completely replaced with the gaseous one. To improve the properties of graphene-based aerogel, enzymatic lignin and sodium ascorbate were introduced into the gel composition. As a result, a 3D porous structure with homogeneous distribution of lignin was formed, giving the aerogel skeleton shrinkage resistance. The modified aerogel showed high polyethylene glycol absorption capacity (~99 wt.%). Considering the ability of the new aerogel to absorb light in the whole range from infrared to ultraviolet radiation and to improve the conversion of solar energy into thermal energy, it is considered to be a promising material for solar energy storage and conversion.[107]

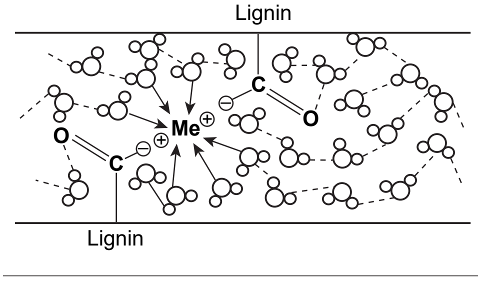


Figure 6. Proposed scheme of intermolecular bonding in lignin hydrogels.[106]

The properties of aerogel based on silica and lignosulfonates, such as pore volume and specific surface area, depend on the delignification method used (sulfite or modified bisulfite process).[108]

8. Valorization of hydrolysis lignin

A significant obstacle to the development of biotechnology towards biofuel production is the formation of large amounts of hydrolysis lignin (HL) waste at the stage of wood hydrolysis. Hydrolysis of 1 tonne of coniferous wood yields 160–175 kg of ethanol, while 350–400 kg of lignin is produced. In Russia, HL reserves are estimated at *ca*. 95 million tonnes.[109]

The heterogeneity of the structure, insolubility in conventional solvents and low reactivity make the chemical processing of HL quite challenging. There are many fundamental solutions and patents in this area, but they have not yet been commercialized.[7] Nevertheless, in recent years, a number of new pioneering innovations have emerged that contribute to producing new high value-added products from HL.

Oxidation of HL with hydrogen peroxide in acidic medium improves both its solubility and reactivity. Oxidized hydrolysis lignin (OHL) has physico-chemical properties that offer new opportunities for valorization of this large-tonnage waste product of the hydrolysis industry.[110]

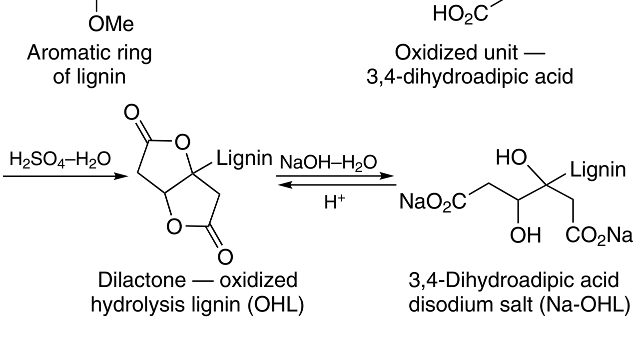
For example, the surface-active properties of OHL allow it to be considered as an equivalent replacement for lignosulfonates, the production of which is constantly decreasing due to environmental problems. The sorption properties of OHL allows carrying out research to produce a new enterosorbent.[111,112] The high surface-active properties of OHL made it possible to develop a reagent based thereon for the treatment of drilling fluids.[113]

The mesoporosity of such catalysts as zeolites is increased at the stage of their formation in the presence of OHL; the resultant zeolites showed high catalytic activity in the synthesis of coumarins.[114]

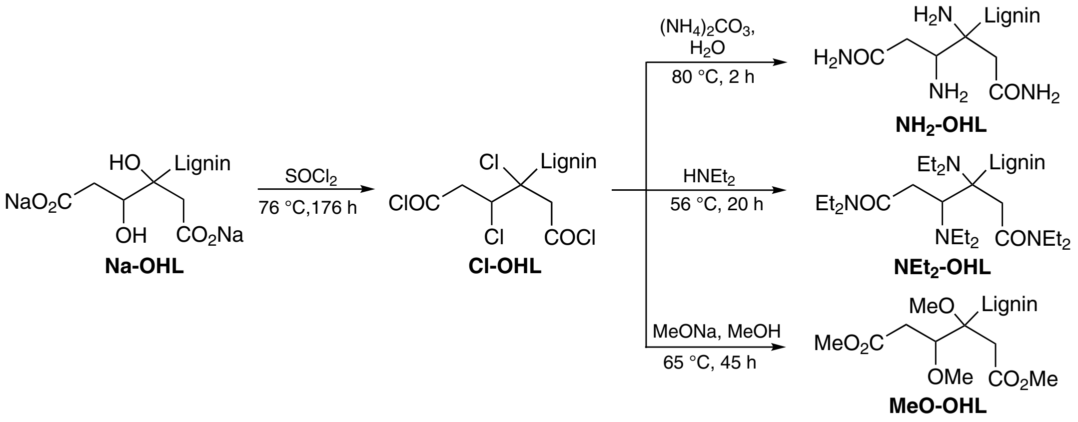
Lignin hydrogels allow the binding of significant amounts of heavy metals such as lead, iron and copper. Depending on the content of acidic groups in lignin and the molar mass of sorbate, the sorption capacity is *ca*. 25–50% of the lignin weight, which makes them promising reagents for wastewater treatment.[106]

Recently, the mechanism of reactions occurring during the oxidation of HL to give OHL and, subsequently, the sodium salt of OHL has been established.[115] Oxidation of hydrolyzed lignin

Scheme 7



Scheme 8



in the $H_2O_2-H_2SO_4-H_2O$ system involves the oxidation of methoxyhydroxy-substituted aromatic rings of lignin to derivatives of 3,4-dihydroxyadipic acid, which spontaneously cyclize into the corresponding dilactones under acidic conditions (Scheme 7). This explains the presence of such dilactone motifs in the structure of OHL. When treating OHL with alkali, the dilactones open to form fragments of disodium 3,4-dihydroxyadipate (Na-OHL). This transformation is reversible, and upon acidification of the aqueous solution of Na-OHL, the dilactone rings in OHL are formed again (see Scheme 7).

The reaction of Na-OHL with thionyl chloride can produce a highly reactive polychlorinated OHL derivative (Cl-OHL), which, when reacting with amines and alkoxides, gives the corresponding nucleophilic substitution products: amino–amide- (NH_2OHL, NEt_2-OHL) and methoxy derivatives of OHL (MeO-OHL) (Scheme 8).[115] Synthesis of such polyfunctional oligomeric materials opens up new opportunities for practical application of hydrolysis lignin.

9. Other directions of using of lignin

Recent studies suggest new prospects for lignin valorization. For example, lignin extracted from poplar wood with mixtures of deep eutectic solvents based on choline chloride and lactic acid contains a large amount of phenolic groups, which is responsible for its high antioxidant acility.[116]

A copolymer of kraft lignin with polyethyleneimine cross-linked using chloromethyloxirane showed good sorption capacity towards Cd^{2+} and Ni^{2+} cations, as well as chromate CrO_4^{2-} and arsenate AsO_4^{3-} ions and the drug diclofenac.[117]

Corn lignin was employed to produce a good adhesive material for wood bonding.[118] Its synthesis involved the initial demethylation of the methoxyaryl groups of lignin by treatment in an alkaline aqueous solution of sodium sulfite. Then the demethylated lignin was oxidized with sodium periodate. The authors believe that aliphatic primary alcohol groups are oxidized and converted into aldehyde groups. Apparently, at the final stage, such lignin is additionally cross-linked due to the formation of acetal bonds between aldehyde and phenolic hydroxyl groups, which provides high adhesion properties to wood.

Lignin can give rise to flame retardant materials. For example, treatment of alkaline lignin with ammonium polyphosphate and additional cross-linking of lignin with phenol and melamine render it highly flame resistant.[119] It was shown that impregnation of bamboo with ammonium hydrophosphate $(NH_4)_2HPO_4$ and urea leads to phosphorylation of hydroxyl groups of cellulose.[120] The authors explain good flame retardant properties of such material by additional interaction of phosphorus-containing groups of cellulose with lignin.

Methods of lignin *in situ* modification in wood have been developed. Oxidation of balsa wood with hydrogen peroxide under ultraviolet light irradiation promotes partial destruction of lignin by the mechanisms of free-radical transformations and secondary lignin transformations.[121] Wood obtained in this way has a number of practically relevant properties such as water resistance, mechanical strength, *etc*. Bogolitsyn *et al.*[122] explored the effect of thermochemical activation of wood (steam explosion and extraction with supercritical carbon dioxide) on the properties of extracted lignin. It was found that steam explosion provides lignin more rich in phenolic and carboxyl groups.

The application of lignin for the preparation of carbon quantum dots in semiconductor materials is of special interest. Fluorescent N,S-doped carbon quantum dots were obtained from alkaline lignin and aminobenzenesulfonic acids by a hydrothermal method; the resultant materials have colours from blue to yellowish green and high quantum yields (30.5%).[123] Quantum dots were similarly prepared and used as highly sensitive and selective nanoprobes for the detection of Fe^{3+} ions.[124] Chao *et al.*[125] prepared carbon quantum dots from balsa wood lignin and ethanediamine for their application in photothermal evaporation of water for desalination under sunlight.

In addition, lignin can be used to produce terephthalic acid[126] and also as a component of asphalts and cements.[127,128]

Apart from the search for new ways of valorization, instrumental methods of lignin research have been actively developed in recent years to obtain data on the structure and physico-chemical properties of this biopolymer that are inaccessible using traditional approaches. Such methods include the quantification of functional groups and individual structural motifs in lignin by ^{13}C NMR (in solution and solid phase),[112] as well as matrix-assisted laser desorption/ionization and electrospray ionization mass spectrometry.[129,130]

10. Conclusion

Over the last 5–10 years, there has been a marked evolution of views on lignin biosynthesis, especially with respect to the assembly of macromolecules of this biopolymer from precursor monomers. It turned out that not only canonical monolignols (coniferyl, synapyl, and *p*-coumaryl alcohols) but also other phenolic compounds can participate in this process. The process is essentially combinatorial, in which all available combinations are possible (see Fig. 1), but they are not equally likely. To date, there is no convincing experimental evidence that there is any control over the primary structure of lignin as a biopolymer by an organized assembly process.

The analytical data on macromolecular properties, functional composition, and types of bonding between PPUs of lignin allow us to refer it to polydisperse, polyfunctional, and irregular heteropolymers. The lack of control at the stage of macromolecule assembly explains why lignin is not an individual compound but a mixture of related compounds.

There are two main trends in practical application of lignin: valorization of technical lignins as such, devoid of prior depolymerization, and valorization *via* low-molecular-weight compounds, mainly monomers formed through lignin degradation by various methods. The first trend includes the application of lignin in medicine and pharmacology, as well as for the production of carbon fibres and biofuels, polyurethanes, adhesives and other marketable products.

The main route for obtaining high value-added products from lignin is considered to be the isolation and utilization of monomeric compounds. To selectively degrade lignin to monomers, catalytic methods are used to cleave α-O-4 and β-O-4 linkages. These include hydrogenolysis, oxidation, electrochemical reduction and oxidation, photochemical and enzymatic degradation, derivatization followed by reductive cleavage. It was found that selective, catalytic cleavage of these bonds provides the maximum yield of monomeric aromatic compounds, which is 23% for natural softwood lignin and 51% for deciduous lignin as starting materials.

In our opinion, further advances in this area of lignin chemistry is associated with practical implementation of numerous findings on the valorization of technical lignins, with the development of specific technologies and the production of innovative products. These include the production of carbon fibres for the automotive, aviation and space industries; hydrogels and aerogels for bioelectronics (biosensors, bioelectrodes), materials for solar energy storage and conversion, composite materials for 3D printing used for the manufacture of complex-shaped products, including biological implants; surface-active compounds, including reagents for the treatment of drilling muds, as well as the production of bio-oil and sorbents for wastewater treatment.

11. List of abbreviations

D — polydispersity index,
HL — hydrolysis lignin,
LNP — lignin nanoparticles,
$\bar{M}_n$ — number average molecular weight,
$\bar{M}_w$ — weight average molecular weight,
MWL — milled wood lignin,
OHL — oxidized hydrolysis lignin,
PPU — phenylpropane units.

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