

Lignin Utilization Options and Methods

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Abstract—Trends in use were explored for lignins which rank among the most abundant renewable organic resources and attract much interest due to their complex structure and suitability for diversified applications as determined by natural origin. A lignin production and processing technology was described.

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Timber enterprises generate considerable quantities of waste products whose insignificant proportion is used by various industries, and the rest is dumped or discharged to water bodies. At the same time, wood waste is a valuable secondary raw material whose rational use is becoming a matter of increasing concern [1, 2].

A considerable part of wood pulp production waste is represented by lignin, a complex polymeric compound aromatic in nature. Among the currently available options for lignin utilization, the most important are those based on exploitation of its sorption properties (31%), incorporation into coatings, composites, and polymers (28%), introduction into agrochemical and biological products (9%), application in building industry (5%), use as fuel (5%), reducing agent (4%), and agent for various syntheses (4%), other (14%).

The lignin application possibilities have been most extensively explored for various types of technical lignins, in particular, alkaline lignins formed from wood cooking in alkali solutions, lignosulfonates yielded by sulfite cooking of wood, and hydrolytic lignins which result from acid hydrolysis of wood.

Here, we discuss both the already implemented solutions and those recommended for application in the lignin utilization options listed above.

Sorbents

Hydrolytic lignins and lignosulfonates constitute a cheap feedstock for production of sorbents, in particular, of active carbons. This utilization option for hydrolytic lignin was for the first time proposed by

Ollila and Harva (1948) who suggested lignin impregnation with zinc chloride or phosphoric acid and carbonization at 700°C into active carbon. The latter proved to be capable of adsorbing ~700 mg of Methylene Blue per gram of sorbent.

Today, the implementation of sorption properties of lignins is the focus of extensive exploration activities whose outcomes will be overviewed below.

Simitris and Sturakis [3] suggested a route for preparation of active carbon adsorbents by pyrolysis of novolac lignin mass. The focus of study by Alvarez-Tallacla et al. [4] was on preparation of active carbon via gasification of kraft lignin carbonizate (alkaline sulfate lignin resulted from pulp production by the Kraft process) with carbon dioxide in a fluidized-bed reactor at 800°C and chemical activation of kraft lignin by impregnation with zinc chloride.

A procedure was proposed for active carbon preparation by kraft lignin carbonization at 352°C in an H₂ medium for 2 h, followed by graphitization at 1100°C in an argon atmosphere at a heating rate of 50°C min⁻¹ and keeping at 1100°C for 1 h. The structure of the resulting carbon and its activity towards oxygen and carbon dioxide gas were determined [5].

The physicochemical properties of the carbonizate and of the end product, active carbon, were examined in relation to lignin carbonization conditions [6]. Study of the abrasion kinetics for carbons derived from raw material pastes with and without furfural and lignin additions, as well as of the strongest domestic carbon adsorbent FAS-3, demonstrated how the pore

structure of the carbonizates and active carbon are affected by the H_2SO_4 /polymer ratio (w/w) and heat treatment mode [7].

A spectroscopic examination by Ivanova et al. [8] showed that lignin carbonization already at 350°C gives liquid oxygen-containing aromatic products dominated by benzene and furan series compounds. The basic process of lignin transformation at this temperature is the polymer chain fragmentation. At higher lignin carbonization temperatures ($400\text{--}600^\circ\text{C}$) the resulting liquid product contains up to 75% oxygen-containing nonaromatics. Under the conditions indicated the major processes include compression of the aromatic structures and hydrogenation of low-molecular-weight moieties resulted from fragmentation of the polymer chains of lignin.

Also, sorbents were prepared by high-voltage discharge exposure of aqueous-alkaline suspensions of hydrolytic lignin [8].

Polarographic techniques were applied to study the adsorption of some nitro group-containing pesticides by lignin [9]. Also, the compressibility and filtration properties of lignins were examined. Nevzorov et al. [10] reported the results from cyclic-loading experiments on hydrolytic lignin compression, in which the filtration coefficient was measured at various degrees of compaction of the product.

Chemical activation of technical lignins gave supermicroporous carbon sorbents [11] whose characteristics for pilot batches can be summarized as follows: specific micropore volume $1.1\text{ cm}^3\text{ g}^{-1}$, micropore width $0.7\text{--}1.1\text{ nm}$ at the particle size distribution range of $0.01\text{--}0.2\text{ nm}$, specific surface area $100\text{--}250\text{ m}^2\text{ g}^{-1}$, adsorption energy $11\text{--}14\text{ kJ mol}^{-1}$, Methylene Blue decoloration ability $600\text{--}780\text{ mg g}^{-1}$, iodine sorption activity $155\text{--}190\%$, and heptane sorption capacity $550\text{--}1130\text{ mg g}^{-1}$.

Earlier [12] we examined the sorption activity of hydrolytic lignin in treatment of oil-containing wastewater of railway enterprises.

Also, it was found that sorption materials based on lignin and lignin-containing products display antibacterial and antiviral activities [13, 14].

Along with hydrolytic lignins, a promising raw material for production of special-purpose sorbents can be found in waste from processing of plant-based products, e.g., cedar nut shell [15].

In Russia, hydrolytic lignin is used for preparation of medicinal enterosorbents, in particular, Polifepan. Also, a procedure was proposed for preparation of an enterosorbent based on hydrolytic lignin and its associated iodine by alkaline treatment of lignin, rinsing with water, neutralization, concentration of the suspension to the desired content of solid phase, and treatment with an aqueous or alcoholic iodine solution [15, 16].

Veprikova et al. [17] prepared enterosorbents from birch wood debarking waste containing $\sim 84\%$ inner bark and 16% birch bark. Treatment of this raw material with an alkali solution under standard conditions gives a product whose properties are close to those of commercial enterosorbent Polifepan.

Owing to its metal ion-complexing ability, lignin can be used as metal sorbent. Degradation of protolignin yields oligomers which undergo demethoxylation, and this leads to accumulation of *o*-diphenolic and *o*-oxyquinoid groups that specifically coordinate to metals [18]. Experiments by Popova et al. [19] validated the presumed chelation of phosphorus-containing lignins with metal cations via *p*-OH groups, whereby these lignins exhibit high exchange capacity and selective sorption action. Rachkova [20] reported on sufficiently high sorption power displayed by modified lignins with respect to ^{60}Co , ^{137}Cs , ^{90}Sr , and some other radionuclides. In particular, they are able of efficiently sorbing uranium, radium, and thorium from solutions of complex salt composition.

Of much interest is the capability of lignin-based sorbents to recover Au(III) [21]. Strakhov and Okladnikov [22] proposed a technology in which hydrolytic lignins are used for preparation of a sorbent intended for recovery of noble metals from process solutions. The main procedures involved in this technology include drying, briquetting, carbonization, and grinding. The process parameters were optimized for preparation of lignin coke characterized by the maximum sorption capacity with respect to Au and Ag. Pilot industrial testing of the sorbent properties of the resulting lignin coke showed that it recovers $>93\%$ gold from cyanide process solutions.

Drozdov et al. [15] prepared hydroxypropylcellulose-based thermosensitive hydrogels by hydroxypropylation of lignin-containing unbleached pulp in the presence of ethylene glycol diglycidyl ether as cross-linking agent. Comparison of the adsorption capacities of lignin-containing hydroxypropylcellulose and commercial hydroxypropylcellulose showed that lignin

affects the adsorption properties both toward Methylene Blue and ionic surfactants. Several types of adsorption gels were prepared by chemical modification of lignin wood. The gels compare favorably with carbon activation products due to selective sorption ability and high adsorption capacity towards Au^{3+} and other metal ions [23]. Using a lignocatechol gel prepared by immobilization of catechol on lignin and cross-linking of the immobilized product [24], a small quantity of Pb^{2+} was separated from a significant quantity of Zn(II) by column elution.

A heavy metal ion-complexing ability of lignin offers prospects for development of lignin-based sorbents intended for water treatment purposes. Liu and Huang [25] described a spherical adsorbent for cationic dyes, prepared from lignosulfonate. It was shown [26] that lignin efficiently recovers traces of nickel ions, and sawdust-derived modified lignin, Cr^{3+} and Cr^{6+} ions [27]. Also, the kinetic features of Fe^{2+} sorption from wastewater, as well as of cobalt and mercury sorption by modified lignin were examined [6, 28]. Chopobaeva et al. [29] examined sorption of rhenium ions by high-permeability lignin ion exchangers.

Wang et al. [30] explored the possibility of removal of pyrene, phenanthrene, naphthalene, and 1-naphthol by sorption on biopolymers comprised of lignin or its complexes with cellulose. A comparative study of the sorbent formation from Kansk-Achinsk brown coal and lignin was carried out, and the texture characteristics of the resulting sorbents and their sorption power with respect to iodine and phenol were determined [31, 32]. It was found that lignin sorbents and sorbents based on lignin and coal are characterized by medium steam activation and sorption powers.

Nikolaichuk et al. [33] analyzed combined methods of chemical and thermal modification of solid cellulose- and lignin-containing plant-based waste from food and process industries and examined how they affect the chemical composition and sorption properties of the resulting materials.

Coatings, Composites, and Polymers

Lignins can be used for preparation of electrically conductive polymer films comprised of coalescent liquid dispersion of fluoropolymers, conductive systems with linearly conjugated π -electron systems, and residues of sulfonated lignin or a sulfonated polyflavonoid [34]. The liquid dispersion in thin layer is cast onto a support at 225°C to form a conductive polymer film; this is followed by drying, coalescing,

and possibly orientation of the resulting film. Dispersions may contain aluminum particles.

Bittencourt et al. [35] prepared films from sulfonated lignins mixed with polyvinyl alcohol, and Jin et al. [36], films from alkaline lignin and poly(ethylene glycol) and poly(phenyl methyl diisocyanate) with dimethylformamide as solvent.

Mishra et al. [37] examined the performance of lignin-based polyblends with polyvinyl chloride, which can be used for preparation of scratch-, bending-, and shock-resistant films whose strength is due to the interaction between the phenolic components.

Lignins can be used for synthesis of flocculants for water decoloration [38] by the Mannich reaction between calcium lignosulfonate with grafted acrylamide copolymers and a 1:1 formaldehyde–dimethylamine mixture at 50°C for 3 h. The aggregation of dyes and other water pollutants was examined as influenced by the flocculant content and pH. Also, lignins displayed flocculation efficiency in removing oil products [39].

Hydrolytic lignin is easily blended with resins into adhesives of homogeneous consistency; it only insignificantly swells in resins [40]. A low-thermal-conductivity polysilicate adhesive was prepared from hydrolytic lignin, which also comprised sodium silicate, sodium silicofluoride (hardener), and styrene-butadiene latex. The adhesive preparation procedure consists in mixing lignin and sodium silicofluoride powders with liquid latex and aqueous solution of sodium silicate. The characteristics of the adhesive containing 3–7% lignin are as follows: adhesion strength with respect to concrete 0.33–0.36 MPa, water resistance after 30-day soaking 0.80–0.98, thermal conductivity of adhesive joint $0.621\text{--}0.511\text{ W m}^{-1}\text{ deg}^{-1}$, and weather resistance after 50 cycles in an artificial weathering apparatus 0.88–0.98%. The adhesive is characterized by sufficient adhesion, good rheological properties, and high heat resistance [41].

Lignins and phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde, and polyurethane resins can be used for preparing adhesives intended for gluing wood materials and woodwork [42, 43]. For example, environmentally friendly adhesive formulations were developed with the use of chloroprene rubber-based adhesives with lignin as additive [6]. Kamel [44] determined the properties of adhesives based on lignin, furan resins, and furfuryl alcohol as influenced by Mn, Cu, and Fe ions. Graupner [45]

examined how the type of lignin and the transition metal salt concentration affect the gluing of paper by such systems and found that lignin additive makes the adhesive joint more resistant to rupture [45].

New electrochemically modified (fluorinated, silylated, phosphorylated, etc.) lignins were prepared [46], and technological recommendations on their application (as hardeners and fillers for epoxide compounds and additives to adhesives, feed stocks for powder metallurgy, and polymer matrix composite) were provided. Owing to its specific structure, hydrolytic lignin is suitable as filler that can replace conventional fillers (woodflour, technical carbons) in plastics or enhance the physicomechanical properties of chipboards. It is recommended that lignin be introduced into compositions intended for manufacture of molded products [47]. Semifinished products to be used for internal linings in cars can be prepared by suspending natural thermoplastic resins (lignin and its derivatives, rosin, etc.) in water and spraying onto woodflour, natural-fiber canvases, followed by drying in an air stream (to water content of 2–15%) and pressing into articles [48].

A composition intended to reduce the wheel–rails friction pair wear was prepared from spent diesel oil (10–25%), hydrolytic lignin (15–25%), and low-molecular-weight polyethylene as balance [49].

Siegle [50] showed that lignin is a renewable raw material that constitutes an alternative to polymers produced from petrochemical feedstock.

Useful properties are exhibited by hydrolytic lignins activated by alkalis, as well as by methyl-carboxylated lignins (materials possessing high sorption properties) and phosphityled and amidated lignins (strong inhibitors of oxidative processes, which effectively perform in polymer compositions) derived thereof [51, 52]. When introduced into unsaturated rubber-based elastomer compositions, phosphorylated lignins surpass commercial amine and phenolic stabilizing agents in the stabilizing effect they exert without significantly affecting the properties of elastomers. Aged rubbers are characterized by better preserved strength and elongation, as well as by improved dynamic endurance and tear resistance. Upon phosphitylation, and particularly phosphitylation and amidation, lignins exceed spatially hindered phenols and arylamines in the effect exerted on the oxidation stability of isoprene rubber.

Alkaline lignins can be used as fillers and modifiers in plastic, rubber, vulcanized rubber, and ceramics

production [53]. In synthesis of phenol-formaldehyde resins, 20, 30, 40, and 50% phenol can be replaced by lignins; the latter were used for phenol replacement in novolac-type phenolic formulations [54, 55].

Lignin acts as nucleating agent able for accelerating nonisothermal crystallization of poly(ethylene glycol terephthalate): The higher the lignin content, the lower the glass transition temperature and the melting temperature of the polymer; thereby, the processing of composite materials is facilitated [56].

Hatakeyama et al. [57] studied the thermal and mechanical properties of composites comprising lignin- and molasses-based polyurethane foams. The role of lignin in rubber stabilization was elucidated [58–63]. It was found [58, 63] that the stabilizing effect produced by lignin is comparable to that of conventional synthetic antioxidant, and its phosphorylation [61] and subsequent amidation with arylamines give products with even better characteristics [62].

A series of hydrolytically stable phosphoryled and amidated hydrolytic lignins were synthesized [64, 65] which act as efficient stabilizers of polymeric compositions.

Biological Products and Agrochemicals

Lignins find medicinal applications, e.g., as components of antineoplastic agents [53, 66, 67], antioxidants [66, 68, 69], natural geroprotectors [70], and prebiotics in laxatives [71]. Also, lignins serve for reduction of allergenicity of natural latex rubber [72] and for antibacterial skin treatment (particle size <40 nm) [73]. Lignins are suitable as constituents of blends intended for treatment and prevention of skin damages caused by UV radiation and ozone exposures and for treatment of inflamed and degenerative skin conditions [74].

One successful example of pharmaceutical application of lignin is Olipifat which lignin-based drug displays antineoplastic, antiviral, and antioxidative activities. Intramuscular injection of Olipifat leads to formation in the thigh muscle of structures that are morphologically identical to lymph nodes, for which purpose a single injection is sufficient [66]. Olipifat also exerts hepatoprotective and wound healing actions [67].

Lignins show much promise for agricultural applications. It is recommended that lignin be applied as a constituent of agrochemicals, particularly fertilizers.

Lignosulfonates were used for formulating aqueous dispersion systems intended for coating urea granules [75] and soil nutrients [69] in order to make them significantly more resistant to rainwater leaching. A procedure was developed for preparation of an agrochemical composition with controlled release of urea, in which lignosulfonate is mixed with urea in a melt to produce granules which are further coated with 20% ethyl cellulose solution in ethanol. The degree of encapsulation of urea in the granules reaches 97%. It was found that 90% of urea is released from granules into water within 48 h [75].

Lignin can be used as a constituent of humic acid-based plant growth stimulant. To this end, lignin (lignohumate) is treated with a mixture of equal volumes of 0.13–0.3% aqueous solutions of iron sulfate and 3% solution of hydrogen peroxide at the mixture to lignohumate ratio of 0.3–1:3.2 (w/w), after which the product is dried [76]. Demina [70] described a procedure for preparation of chemically modified lignin to be applied as fertilizer which improves the soil structure and sorption properties and modifies the qualitative composition of humus. Tests demonstrated that this new lignin-based organic fertilizer is an eco-friendly product able to significantly increase the productivity of agricultural crops.

Based on results from comparative assessment of the biological activities of composts prepared from hydrolytic lignins with the use of some aerobic and anaerobic microorganisms (yeasts and photosynthetic, lactic-acid, and nitrogen-fixing bacteria), an efficient microbial compost for lignins was developed [71].

Technical and modified lignins perform efficiently when introduced not only into natural soil substrates but also into artificial soil substrates prepared from wastes. Waste-lignin mixtures are suitable as soil substrates intended for technical applications; they can also be used for creation of a fertile layer on lawns in industrial zones and serve as nutritive supplements to natural soils when planting ornamental trees for gardening of industrial zones and human settlements [73]. Lignin is suitable as soil addition able to improve the soil structure [74].

Alkaline lignins can be efficiently used in manufacture of controlled-release pesticides with intent to prevent the agrosphere pollution with excess pesticides [77]. Application of a formulation comprised of 50% kraft lignin and 50% cyromazine allows retention of pesticides in soils and reduction of pesticide leaching concentrations.

Construction Materials

Hydrolytic lignins are suitable for manufacture of lignofiber boards, cement, and bricks; they also may be used as intensifying agents to facilitate grinding in Portland cement production. Further, hydrolytic lignins may serve as modifying antioxidant additives to paving bitumen, which are equal in the antioxidative action to commercial antioxidants [70, 78]. Hydrolytic lignins impart biodegradation resistance to asphalt concrete and to major components of organomineral mixtures [79].

Alkaline lignins can be used in building industry as additives to lubricants for metal molds [80] or to feedstocks for production of granular thermal insulation material [81]. They are also suitable as binders for wood (bamboo, sawdust, straw, etc.) structural materials [82].

Mixing lignosulfonate with bitumen yields a lignobituminous compound suitable as binder in which lignin grains are surrounded by thin structured bitumen shells with enhanced density and viscosity; the shell cohesion is sharply increased due to orderly orientation of the structural elements of bitumen. The adhesion stability is improved not only in the bitumen–lignin contact area, but also in the lignobitumen–asphalt-bitumen filler grain contact area, which yields a conglomerate-type structure of road-building material.

Fuel

Hydrolytic and alkaline lignins can serve as fuels. In particular, the efficiency of a boiler fired with hydrolytic lignin briquettes exceeds by 38% that for boiler fired with black coal; carbon loss in combustion of briquettes is 1% (against 48.2% for black coal), and the environmental pollution level due to harmful gas emissions is by a factor of 4.5 lower [82].

An industrial procedure was developed for biomass waste processing in which ethanol is produced from cellulose, and lignin is used as biofuel for heat power generation [84, 85].

Lignin-containing materials are suitable as constituents of both fuel raw materials and binder plasticizers in compositions intended for production of fuel pellets and briquettes. By contrast to liquid binders, lignin-containing systems improve the performance characteristics of briquettes/pellets, specifically, provide for higher strength (and lower crumbliness), enhanced surface gloss, increased (to $\geq 1.2 \text{ g cm}^{-3}$) density, longer burning (even, without smoke), higher

calorific value, and lower energy consumption for compression [85].

Organic Products

Alkaline and hydrolytic lignins can be used for production of phenol compounds and other chemicals. Nenkova et al. [86] used technical hydrolytic lignin to synthesize 2-methoxyphenol, 2,6-dimethoxyphenol, 4-hydroxy-3-methoxybenzaldehyde, 1-(4-hydroxy-3-methoxyphenyl)ethanol, 4-hydroxy-3,5-dimethoxybenzaldehyde, and other products. Lignin was subjected to aqueous-alkaline depolymerization by treating with 5% NaOH at 180°C for 6 h (biomass to depolymerizing agent ratio 1:8); the resulting compounds were extracted from the aqueous phase with toluene.

Myasoedova [85] prepared catechol (28.37%), phenol (7.53%), *p*-cresol (7.87%), *o*-cresol, and other products from alkaline lignin. Yang and Xie [88] suggested an optimal technology for vanillin and alcohol recovery from alkaline lignin. These products can also be obtained from kraft lignin by oxidation using an ion exchange process [89].

Reducing Agent

Thermolysis of hydrolytic lignin briquettes (lignin is used in pure form or with finely grained ore materials) gives lumpy high-quality carbon suitable as a reducing agent for metallurgical applications. Self-reducing iron-carbon briquettes with lignin were prepared for which the degree of metallization is 88.7–89.4% and which need the use of fluxes [90]. Alternative carbonaceous reducing agents were proposed for ferroalloy production [91, 92].

As part of vegetable oil production waste (husk of sunflower seeds), lignin is capable for reduction of chromium(VI) to chromium(III) [93].

Other Applications of Lignin

Sulfate lignins are able to stabilize tall oil–water emulsions [94]. Calcium lignosulfonate is a specific dispersing agent for preparation of Portland cement–water suspensions. Zhou et al. [95] described a dispersing agent based on alkali lignin, which supercedes lignosulfonate in efficiency.

Hydrolytic lignin can be used for preparation of a rust converter which transforms corrosion products to stable salts, as well as of antioxidants [68, 69, 75]. Relative chemical inertness of hydrolytic lignin makes it suitable as bridging addition to drilling fluids [96].

Ul'yanov et al. [97] suggested a flowsheet for utilization of lignin slurries into drilling reagents.

Dry distillation of hydrolytic lignin under accelerated electrons exposure gives tar composed primarily of methoxyphenols, with guaiacol and creosol as the prevalent components [98]. The tar efficiently inhibits thermal polymerization of styrene and exceeds in this action commercial phenol-type inhibitors.

Andreikov et al. [99] demonstrated that hydrolytic lignin additions significantly accelerate liquid-phase thermal cracking of oil residues and increase the yield of distillation products from heat cotreatment of lignin and heavy oil residues at 350–415°C under atmospheric pressure.

Lignin can be used as a conditioner in production of cast aluminosilicon alloys [100]. Mixing lignin with “tailings” from beneficiating factories and carbonates allows the no-dam option to be implemented for gold mining waste storage and disposal [101].

Application of lignin derivatives in photoelectric transducers and photoelectrochemical cells was suggested [102], and a lignin-based sensitizer for photoelectrochemical cells was described [103].

Li et al. [104] examined the stability of coal water slurry and the sedimentation behavior of coal particles as affected by modified lignin-series and naphthalene-series dispersants and revealed that, with the addition dosage of 1%, the sedimentation rate decreases by 68%, which allows more efficient separation of coal into factions.

Mohr et al. [105] found that lignins in wood fiber-cement composites restrict the dimensional changes of fibers under cyclic wet/dry exposures.

The discussed range of products, agents, and materials obtainable with the use of lignins suggests that lignin is a secondary raw material with broad potentialities. Implementation of the above-described lignin utilization options is a factor significantly contributing to solving the global environmental problem of rational use of natural resources.

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