
MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Lignin: Applications and Ways of Utilization (Review)

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Abstract—The main applications and ways of utilization of industrial lignins, which are a large-tonnage waste from pulp and hydrolysis plants, are considered. The first group of methods includes nonthermal methods of lignin processing with preservation of the natural polymeric structure of lignin. The second group of methods includes thermal methods for lignin processing with the formation of low- and high-molecular-mass compounds and combustible gas. The largest-tonnage application fields of lignins are building, mining, metallurgical, oil-extracting, and agro industries, and also water treatment.

Keywords: lignin, lignin utilization, chemical modification, thermal processing

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INTRODUCTION

One of topical problems in efficient nature management is utilization of large-tonnage industrial wastes. The volume of some kinds of carbon-containing wastes is so large that they can be considered as secondary technogenic resources.

Large-tonnage lignin waste from wood-chemical enterprises, formed in the course of wood processing, is among industrial wastes whose management involves major problems.

In 2015, Zion Research published data on the lignin turnover in the world. It amounted to \$775 mln in 2014 and is expected to approach \$900 mln by the year 2020 (see figure).

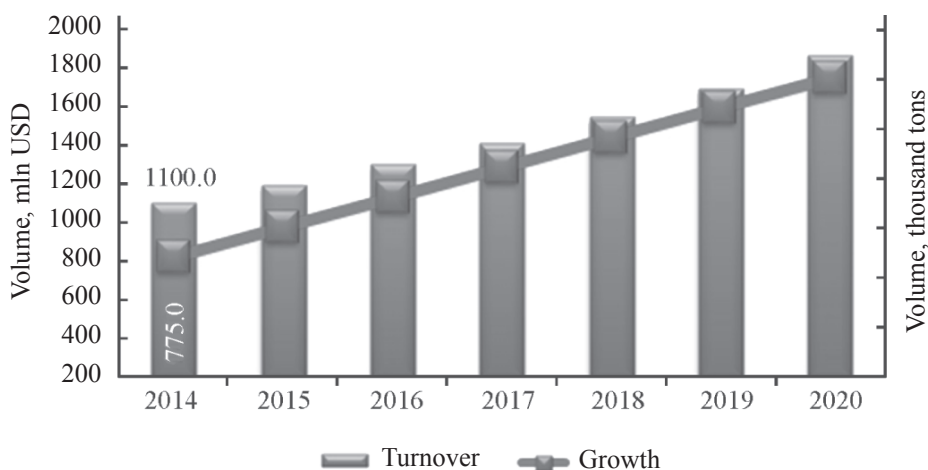
KINDS OF LIGNINS

From the viewpoint of modern chemistry, lignin is an irregular polymer with branched macromolecules built mainly of residues of variously substituted phenolic alcohols. The structure and properties of lignin differ essentially from those of other wood components, cellulose and hemicelluloses. Lignin is an aromatic

component of wood. It is not an individual substance with strictly definite properties, composition, and structure, but a mixture of aromatic polymers of related structures. The major factor complicating study of lignins is its complex structure; as a consequence, it cannot be isolated pure. Therefore, there are numerous different forms of lignins isolated from wood, having different structures and properties. It should also be noted that lignins isolated from coniferous and deciduous wood differ essentially in the composition and structure [1].

In industry, lignin is formed from wood and other plants in the course of sulfate and sulfite pulp cooking. The lignins obtained differ in the structure and properties from each other and from native lignin. Hydrolysis of lignin leads to irreversible changes in its structure with a drastic decrease in the amount of aliphatic, carbonyl, carboxy, and hydroxy groups; as a result, its reactivity decreases.

Sulfate (kraft) cooking is the prevalent method of pulp production, but kraft lignin has yet limited applications. Only less than 100 thousand tons of lignin is isolated annually from black liquors to obtain target products. Alkali kraft lignin is formed in amounts of 30–35 wt % relative to the feed. In kraft pulping, lignin is recovered



World's lignin market in 2014–2020 (www.marketresearchstore.com).

from black sulfate liquor by precipitation with sulfuric acid or carbon dioxide. Dry kraft lignin is a brown powder. It is soluble in alkaline aqueous solutions and in some organic solvents (acetone, dioxane, dimethyl sulfoxide, pyridine, ethylene glycol, etc.). The kraft lignin composition (wt %) is as follows: ash 1.0–2.5, acids (in terms of sulfuric acid) 0.1–0.3, water-soluble compounds 9–11, resinous substances 0.3–0.4, and Klason lignin 85. Tall kraft lignin is obtained in a small amount (3–5 wt % relative to the feed) in the course of decomposition of sulfate oil with sulfuric acid and consists of kraft lignin, tall oil, water, and inorganic sulfates. A fraction of kraft lignin is used in power facilities at pulp plants.

The main useful products prepared from lignin are sulfite lignins (lignosulfonates). Westvaco and LignoTechSweden companies produce lignosulfonates from kraft lignin by its sulfonation. Except the countries of the former Soviet Union, the world's annual capacity for producing lignosulfonates is estimated at 1175 thousand tons in terms of the dry substance [2]. In the former Soviet Union, the fraction of sulfite cellulose in the total volume of production of fibrous intermediates was relatively high (>30%); therefore, the volumes of lignosulfonates were large (>1 mln tons). By now, the production of fibrous intermediates in Russia has appreciably decreased, especially that of intermediates obtained by sulfite methods; they are produced today in 8 times smaller amount compared to the production in the former Soviet Union [3]. Therefore, today lignosulfonates are produced in Russia in an amount not exceeding 150 thousand tons annually. The amount of the

sulfite liquor (lignosulfonates) formed is approximately 30 wt % relative to the feed. The sulfite liquor contains also hemicellulose sugars (hexoses and pentoses) and some organic and mineral impurities (furfural, organic acids, sulfur dioxide, etc.). The composition of lignosulfonates is strongly influenced by the sulfite cooking procedure. Sulfonated lignin complex contains toxic products (phenol derivatives); therefore, their discharge into water bodies is prohibited. Lignosulfonic acids formed as sodium, ammonium, or calcium salts in production of sulfite cellulose have variable composition depending on the extent of sulfonation and recovery methods. The approximate general composition of the acids is $C_{26}H_{30}O_{12}S$, and the mean elemental composition (wt %) is as follows: C 53, H 5, OCH_3 12, S 5, and O the remainder.

Along with pulp plants, large amounts of lignins (about 1 mln tons annually) were formed in the former Soviet Union at hydrolysis enterprises producing as target products ethanol and forage yeast. Hydrolysis lignin is formed in amounts of 30–40 wt % relative to the wood raw material; at some hydrolysis plants, its production reached 70 thousand tons annually. Technical lignin has high moisture content (50–70 wt %) and contains unhydrolyzed polysaccharides (15–30 wt %), unwashed monosaccharides (2–10 wt %), and substances of the lignohumic complex (5–15 wt %); the ash residue is 2–10 wt %. Hydrolysis lignin differs essentially from natural and technical lignins produced at pulp plants. It is characterized by considerably lower content of the main functional groups, except methoxy groups resistant to hydrolysis. Hydrolysis lignin is insoluble in alka-

lis and polar solvents. A distinctive feature of hydrolysis lignin is its polynuclear structure.

The amount of lignin waste in Russia (waste from yeast, forage, and pulp-and-paper industries), according to different estimates, varies from 100 to 200 mln tons. Only slightly more than 1 mln tons (about 2%) of more than 50 mln tons of lignin isolated annually from vegetable raw materials is used for various practical purposes [4].

Vegetable lignins are practically harmless for living bodies [2]. Their structural changes in the course of cooking do not make the products noticeably more toxic, which allows their use in almost all the fields of the human activity.

USE OF LIGNINS IN INDUSTRY

The major problem in using lignins is strong heterogeneity of the substances with respect to the structure and properties, associated both with the raw material origin and with the processing conditions. Hence, special pretreatment of industrial lignins is required for obtaining materials with standard properties, which increases the product cost.

Various substances are produced from lignins using two approaches. The first approach involves preservation of the macromolecular nature of lignins, and the second approach involves preparation of low-molecular-mass substances from lignin macromolecules.

Polymeric products prepared from lignin have found the widest use. Although spent sulfite liquors are used for some purposes without any pretreatment, in most cases impurities negatively affect the required properties; therefore, purification and/or modification of lignosulfonates is required. Purification methods involve removal of carbohydrates by fermentation or chemical degradation [2]. Ultrafiltration and chemical precipitation are also used in industry for producing high-purity lignosulfonates [5].

Kraft lignin is recovered from liquors in the form of a finely dispersed precipitate formed after solution acidification either with sulfuric acid or with carbon dioxide (treatment with flue gases) [6].

To improve the dispersing, complexing, adhesion, and other properties, lignins can be subjected to chemical modification involving sulfonation, sulfoalkylation, desulfonation, oxidation, carboxylation, alkylation, ac-

ylation, amination, condensation, depolymerization, copolymerization, and combined methods.

The largest-tonnage application fields of lignins are building, mining, metallurgical, and oil-extracting industries, water treatment [7], agro industry [8], etc.

Approximately half of lignosulfonates produced in the world are used in production of cement and concrete [2]. In addition, lignosulfonates are used as additives (0.5–2.0%) in production of bricks and ceramics, as components of plasterboard (0.1–0.3%) [9], and for dust suppression in road building. Procedures are being developed for binding chlorinated organic waste from chemical plants with hydrolysis lignin to obtain modifying additives for bitumen in road building [10].

The use of lignosulfonates as binders for granulating finely divided raw materials is well known [9, 11]. Another important application of lignin polymers is ore dressing by flotation [12]. Sulfite liquors play the role of a binder in casting production. A relatively new application of lignin substances in metallurgical industry is increasing the yield of valuable metals from sulfide and carboniferous ores.

In oil-extracting industry, lignins are used in drilling oil wells as components of drilling fluids (0.2–0.5%) [13, 14] and for decelerating the cementation and enhancing the output of oil wells [12, 15].

Lignosulfonates are resistant to salt contaminations and to mechanical and thermal actions. Therefore, they are used as stabilizers of water–oil emulsions in various fields, from paper gluing to asphalt stabilization [16].

Modified lignosulfonates are an important component of lead batteries [2]. It is assumed that the macromolecules inhibit the crystal growth, allow preservation of the porosity of the negatively charged plate, and thus ensure its longer operation life.

Owing to the phenolic structure, lignins, like phenol–formaldehyde resins, can be used as adhesives [17–20]. To this end, technical lignins should be cross-linked to obtain a network structure. Up to 10% lignin is introduced into the urea–formaldehyde resin formulation in production of particle boards in West European countries [17]. This additive exerts a positive technological effect and reduces the amount of phenol and formaldehyde, which are toxic components of phenol–formaldehyde resins.

A procedure was developed for preparing Arboform thermoplastic composite material from vegetable fibers

and lignin [21]. Arboform items resemble plastic items in external appearance, but are similar to wood items in properties. One of the advantages of the biopolymer is the possibility of its repeated reprocessing without changes in the characteristics. A plant for producing plastics from wood in amounts of up to 5 t per month was put into operation in 2000 in Germany. This material is suitable for producing internal panels for cars, shotgun butts, furniture parts, ballpoint pens, casings for TV, receivers, computers, and mobile phones, etc. However, there is a small drawback: The production involves release and accumulation of sulfur-containing gases requiring utilization.

Photocatalytic studies of transformation of lignin into valuable products were considered in detail in [22]. Titanium dioxide applied onto a nanocomposite containing iron oxide or onto a zeolite with the addition of iron was used as a catalyst [23]. Under UV irradiation, a half of benzyl alcohol present in the lignin structure transformed into benzaldehyde in 4 h. The advantages of this procedure are the use of new photocatalysts free of expensive metals and mild process conditions (room temperature and atmospheric pressure).

Sulfur-free lignins are a new class of lignin products [24]. Their properties differ from those of kraft and sulfite lignins and open prospects for new applications of lignin products [25, 26].

Despite numerous studies, production of low-molecular-mass products from lignins is yet limited. Only vanillin (3-methoxy-4-hydroxybenzaldehyde) is commercially produced from lignin. Today 70% of the total vanillin amount produced annually (about 12 thousand tons) is produced from lignosulfonates [27]. The vanillin yield is in the range 6–12% depending on the kind of lignosulfonates and oxidation conditions and is appreciably lower than the theoretically possible yield (25–30%) [28].

THERMAL METHODS FOR LIGNIN PROCESSING

Depending on the conditions of thermal processing of lignins, valuable products can be obtained: solid carbonized residue, combustible gas, and liquid resins. Direct combustion of lignins is used seldom because of high moisture content, heterogeneous composition, and formation of toxic combustion products.

Various thermal methods are used for preparing liquid fuels from lignins and their mixtures with

polymers [29]. One of promising thermal methods of lignin processing is rapid contact pyrolysis of the lignin biomass upon energy transfer from the working metal surface onto sample containing the lignin biomass at their direct contact. In this case, the pyrolysis temperature is determined by the metal temperature. The efficiency of the rapid contact pyrolysis is mainly determined by the metal surface temperature and contact time. The yield of liquid products in lignin pyrolysis is directly proportional to the rate of chemical transformations and inversely proportional to the residence time of products in the reaction zone [30].

Methods of thermal dissolution of lignin in organic solvents lead to the formation of mainly high-boiling products with high oxygen content [31]. After that, the products can be subjected to catalytic decomposition and hydrotreating to obtain motor fuels [32].

In hydrogenation of lignins under pressure, the yield of low-boiling products increases and their oxygen content decreases [33]. The drawbacks of the hydrogenation methods are high hydrogen consumption, with the major fraction of hydrogen transforming into water. Catalytic hydrotreating of lignin at 350–400°C (in the presence of cobalt, nickel, ruthenium, iron, palladium, and chromium catalysts) under a hydrogen pressure of 130–200 atm leads to the formation of alkylcyclohexanes, alkylbenzenes, cycloalkanes, C₇–C₁₀ alkanes, and other compounds.

Celeghini et al. [34] studied the liquefaction of lignin prepared from sugarcane bagasse. Monoethanolamine was used as a hydrogen source. Conditions for producing liquid biofuels were found, and the process was optimized to increase the yield of light oils by varying the temperature, time, and solvent to solute ratio.

Joint thermal degradation of lignin and synthetic polymer waste is a promising method for producing liquid hydrocarbons. Synthetic polymers based on polyolefins contain up to 14 wt % hydrogen. It is believed that hydrogen-enriched products of thermal degradation of polymers can participate in saturation of radical fragments formed by thermal degradation of lignin, increasing the degree of lignin conversion [35].

The composition of liquid products of thermal degradation under argon was studied for the following lignin samples: hydrolysis lignin from Krasnoyarsk Biochemical Plant, organosolvent lignin, “sulfuric acid lignin” (residue from aspen wood hydrolysis in sulfuric acid), and “alkali lignin” recovered from

aspen wood by extraction with aqueous alkali. Liquid products of thermal transformation of lignins isolated from wood by acid hydrolysis under severe conditions are characterized by increased content of aromatic and polyaromatic substances. Liquid products from alkali and organosolvent lignin are characterized by high content of phenols and enhanced heat resistance.

Products of joint conversion of hydrolysis lignin with polyethylene or polypropylene are enriched in aliphatic compounds and have decreased content of polyaromatic compounds in high-boiling fractions [36]. Their composition is determined by the preparation conditions. The fractions boiling out in the interval 180–350°C, prepared by hydrogenation of a hydrolysis lignin/synthetic polymer blend, are characterized by decreased content of cycloalkanes and of polyaromatic and heterocyclic compounds.

Oxidation of lignins yields aromatic aldehydes, which are a valuable raw material for food, pharmaceutical, and perfume industries. Various catalytic systems are suggested for increasing the yield of aromatic aldehydes in lignin oxidation, e.g., nitrobenzene–phenanthroline and copper phenanthroline–polyethylene glycol; atmospheric oxygen in the presence of a copper catalyst is suggested as an oxidant [37, 38].

Oxidative degradation of lignin in alkaline solution allows under definite conditions conversion of 75–80% of the lignin organic matter into organic acids, volatile and nonvolatile. The new substances (oxidates) can be used for biochemical processing.

Sazonov and Gribanov in their review [39] considered in detail and classified in detail the thermochemical reactions determining various steps of conversion of native lignin in the course of its thermal processing in a wide temperature range, and also discussed applied aspects of directional thermochemical synthesis of new low- and high-molecular-mass compounds from lignin.

Evstigneev [40] reported a procedure for oxidation of hydrolysis lignin with hydrogen peroxide to obtain a product soluble in dilute alkali [40]. The relationship between the functionalization and solubility of hydrolysis lignin and its oxidation products was found.

By now, rich experience has been accumulated in the use of hydrolysis lignin waste for preparing cheap adsorbents for various purposes such as treatment of wastewater and removal of dust and harmful components gases from off-gases [41–45]. Polifepan medical enterosorbent prepared from lignin and its derivatives

is well known. It is effective in treatment of poisonings and in prevention of gastrointestinal diseases.

The problems of lignin processing are still unsolved, and they become more and more acute as the amount of production waste from wood hydrolysis increases. Eighteen hydrolysis plants operated in Russia, and approximately 95 mln tons of hydrolysis lignin has been accumulated [46]; this is a source of serious environmental hazard.

Polydispersity of hydrolysis lignin in combination with high moisture content determines problems with its utilization, including thermal processes. For incineration in steam boiler furnaces, moist lignin is preliminarily mixed with coal. The resulting mixture is fed to a mill, slightly dried with flue gases, and milled. After that, the fuel dust is fed with an air stream to a steam boiler furnace. Because of high moisture content, the calorific value of such lignin is low. Therefore, at some hydrolysis plants moist lignin is preliminarily dried with flue gases from a boiler plant. The dried lignin with 20–40% moisture content can be incinerated in steam boiler furnaces separately or in a mixture with other kinds of fuel.

The use of drying complexes and installations for fuel milling requires additional expenditures for the special equipment and increased operation expenditures, making the lignin utilization less profitable. The drying facility is characterized by high explosion hazard. Furthermore, the known technologies are insufficiently efficient.

Analysis of the more than 15-year experience of incineration of wood and its waste in Estonia and of several successful projects in Latvia, Lithuania, and northwestern Russia shows that installations of Wartsila BioGrate type [47] and fluidized-bed installations [48] are quite suitable for incineration of hydrolysis lignin of the quality varying in a wide range. The fluidized-bed incineration process is implemented in two versions: incineration in a bubble layer and in a circulating fluidized bed. The process is versatile and suitable for incineration of virtually any kinds of fuel or combustible waste with up to 60% moisture content of up to 70% ash residue relative to the working mass. Furthermore, fluidized-bed incineration ensures significant environmental advantages: 2–5-fold decrease in the emission of nitrogen oxides and 90% decrease in the emission of sulfur oxides. Operation of furnaces of up to 20 MW power demonstrated their high

economic efficiency due to reduction of the loss caused by mechanical incomplete combustion compared to the existing fixed-bed furnaces.

Incineration of lignin is a radical way of its utilization, but in this case many valuable properties of lignin find no use. Rapid contact pyrolysis allows, if necessary, preparation of liquid products in high yield [30]. Significant conditions for this procedure are very high heat fluxes, thoroughly controlled temperature of the order of 500–550°C, and residence time of pyrolysis vapor in the reactor no longer than 1 s. The secondary products of rapid pyrolysis are coke residue and pyrolysis gas.

For efficient utilization of solid fuels and wastes (including lignins) in power engineering, a procedure for gasification in the superadiabatic combustion mode was developed at the Institute of Problems of Chemical Physics, Russian Academy of Sciences (Chernogolovka, Moscow oblast, Russia) [49, 50]. This method allows cheap and environmentally clean conversion of a solid fuel into a combustible gas, which can then be used in more efficient power facilities for producing thermal and electric energy [51, 52]. The use of a two-step processing procedure makes the requirements to the quality of the starting fuel considerably less stringent. A principally new method for gasification in superadiabatic combustion modes allows the gasification and pyrolysis to be performed in one reactor [53]. The method differs from the existing methods in the record high chemical efficiency (up to 90%) and in the possibility of using raw materials with any ash residue (up to 90%) [54] and high moisture content (up to 70%) [55]; it does not require sophisticated and expensive gas treatment systems (formation of toxic combustion products decreases by a factor of 10–100 compared to direct combustion). A significant advantage of such technologies is the possibility of using relatively cheap substandard fuels and some process wastes [56].

Recently there has been increased interest in the world in using supercritical water for processing low-grade fuel, including lignins. Osada et al. [57–59] consider gasification of organosoluble lignin, catalyzed by Ni, Ru, Pt, and Rh salts on supports (C, Al₂O₃, TiO₂). The process occurs at a pressure of 220–300 atm, produced by water heated to 350–400°C. The lignin gasification occurs via its decomposition into low-molecular-mass compounds, actively occurring in supercritical water. The syngas yield increases in the presence of hydrogen donors, e.g., cellulose, xylan, or hexadecane. The syngas

can be used in Fischer–Tropsch synthesis of higher hydrocarbons.

Another modern procedure for hydrolysis lignin processing is high-temperature radiolysis [60, 61] consisting in sample heating to 400–500°C in a flow of a methane or propane–butane mixture under irradiation with an accelerated electron beam. The lignin macromolecule decomposes under the action of radiation and heat. As compared to common thermolysis, in radiation heating the yield of organic products increases by a factor of 2 and reaches ~35%. The thermal radiolysis products contain phenols and alkoxyphenols (with guaiacol and cresol prevailing). In a hydrocarbon atmosphere, the products transform into cyclic and acyclic alkanes, tetrahydrofuran derivatives, and acyclic ethers. The drawback of the process is the need for using special equipment, high-voltage resonance electron accelerator requiring special biological (radiation) protection. In addition, the procedure involves one more power-consuming step, preliminary drying of hydrolysis lignin. Implementation of this procedure also requires using methane or propane–butane atmosphere allowing stabilization of radical species formed under the action of ionizing radiation.

CONCLUSIONS

The amount of lignin waste in Russia ranges from 100 to 200 mln tons according to different estimates. No more than 1 mln tons, i.e., about 2%, of more than 50 mln tons of lignin annually recovered from vegetable raw materials finds practically use. The largest-tonnage lignin application fields are building, mining, metallurgical, oil-extracting, and agro industries, water treatment, etc.

The lignin processing to obtain useful products is based on two approaches. In the first approach, the macromolecular nature of lignin is preserved. Polymeric products prepared from lignin have found the widest use, although spent sulfite liquors are used for some purposes without any treatment. However, in most cases impurities negatively affect the properties; therefore, purification and/or modification of lignosulfonates are required. To improve dispersing, complexing, adhesion, and other properties, lignins can be subjected to chemical modification such as sulfonation, sulfoalkylation, desulfonation, oxidation, carboxylation, alkylation, acylation, amination, condensation, depolymerization, copolymerization, and combined methods.

The second approach consists in preparation of low-molecular-mass substances from lignin macromolecules. However, despite numerous studies, preparation of low-molecular-mass products from lignins has not yet found wide practical use. Only vanillin is commercially produced from lignin.

The polydispersity of hydrolysis lignin in combination with its high moisture content complicates its utilization, in particular, by thermal methods. Lignin is not incinerated anywhere in the initial form but is preliminarily dried to acceptable moisture content and then incinerated by one or another procedure, or mixed with coal prior to incineration, or incinerated under the conditions of supporting the combustion with black oil or natural gas.

Fluidized-bed installations appeared to be suitable for incineration of hydrolysis lignin with widely varied quality characteristics. The fluidized-bed incineration technology was implemented in two versions: bubble layer and circulating fluidized bed incineration. The lignin incineration is the radical way of its utilization, but many valuable properties of lignin do not find use in the process.

Various thermal methods are used today for lignin processing to obtain liquid fuels. Such processes as rapid contact pyrolysis, high-temperature radiolysis, hydrogenation, and catalytic gasification can be used if it is necessary to obtain liquid products in high yields. These products should then be subjected to catalytic cracking and hydrotreating to obtain motor fuels. However, these methods have not been implemented in industry because of poor economic efficiency.

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