ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 13, pp. 2632–2642. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © S.M. Krutov, A. P. Voznyakovskii, I.V. Gribkov, I.V. Shugalei, 2014, published in Ekologicheskaya Khimiya, 2014, Vol. 23, No. 3, pp. 145–158.

# Lignin Wastes: Past, Present, and Future

**S. M. Krutov[a], A. P. Voznyakovskii[b], I. V. Gribkov[c], and I. V. Shugalei[d]**

[a] St. Petersburg State Forest Technical University, Institutskii per. 5, St. Petersburg, 194021 Russia
[b] Lebedev Research Institute of Synthetic Rubber, ul. Gapsal'skaya 1, St. Petersburg, 198035 Russia
[c] GCE Group, ul. Bukharestskaya 6, St. Petersburg, 192102 Russia
[d] St. Petersburg State Institute of Technology, Moskovskii pr. 26, St. Petersburg, 190013 Russia
e-mail: shugalei@mail.ru

Received June 9, 2014

**Abstract**—The review considers problems related to processing of lignin-containing wastes.

**Keywords:** lignin, lignin uses, bioenergetic complex

**DOI:** 10.1134/S1070363214130222

Depletion of fossil organic raw materials has aroused the problem of switching to renewable resources. The key point in the development of technologies based on renewable sources is comprehensive utilization of renewable materials. Especially challenging is efficient involvement of wastes from processing of wood or other plant raw materials in production cycle. The main substrates in wood biomass are cellulose and partly lignin.

Comprehensive utilization of plant raw materials, extension of product assortment, and minimization of wastes constitute the key problems in the development of wood processing enterprises and environmental safety. These problems may be solved via implementation of up-to-date chemical technologies and combination of works to achieve comprehensive utilization of wood.

At first glance, wood resources on the Earth are huge. Forests occupy about 3.5 billion ha on the Earth surface, and wood resources amount to more than 350 billion m$^3$. The annual wood increment is estimated at 5.5 billion m$^3$, and the annual timber harvesting is more than 3 billion m$^3$. However, taking into account high urbanization rates, reduction of forest fund, and insignificant net annual wood increment, extensive way of development of wood chemical industry seems inadmissible at present.

The key product of the processing of carbohydrate-containing plant biomass is ethanol which is obtained by acid hydrolysis and is now actively offered as a promising substitute for traditional fuel. Wood conversion into ethanol, fodder yeast, and furfural in the presence of mineral acids (acid hydrolysis) is accompanied by formation of so-called “technical lignins” whose amount reaches many millions of tons per annum. Technical lignin is a large-scale waste product of microbiological industry and is a burdensome and environmentally harmful substance.

The problem of utilization of huge lignin wastes is not only the problem of rational utilization of plant resources and increase of wood processing depth but also a very important environmental problem which dates back to.

The lignin waste problem dates back long ago [1–19]. During the industrialization period after industrial drop caused by the First World War and subsequent revolution Russia encountered the necessity of manufacturing rubber to substitute for natural rubber which was deficient at that time. In 1928 S.V. Lebedev obtained synthetic rubber by polymerization of butadiene by the action of metallic sodium. The new production required manufacture of ethanol. The ethanol production technology by wood hydrolysis with dilute sulfuric acid has been developed in a short time. In January 1934 Cherepovets pilot plant equipped with six 1-m$^3$ hydrolysis apparatuses was put into operation. At the same time it was decided to construct first hydrolysis plants in Leningrad, Bobruisk, Khorsk, Arkhangel'sk, Saratov, and Volgograd. Leningrad hydrolysis plant was put into operation in December 1935, and Bobruisk and Khorsk hydrolysis plants began to operate in 1936 and 1939, respectively. In 1939, the Main Directorate of Hydrolysis and Sulfite–Alcohol Industry at the Council of People's Commissars of the USSR was established. During the Great Patriotic War the needs of technical ethanol sharply increased, for it was used for defense purposes. Since 1941 till 1945 alcohol production in the Arkhangel'sk, Saratov, Kansk, Krasnoyarsk, Tavdinsk, and Volgograd plants was launched. In 1943, the first fodder yeast workshop was put into operation in the Saratov plant, and in 1944, in the Khorsk plant. Thus, manufacture of synthetic ethanol vigorously developed until 1950s. Correspondingly, lignin accumulated as the main waste material in the alcohol production industry.

Manufacture of cellulosic alcohol in the USSR was a large-scale and highly profitable branch of industry. As the Soviet Union had collapsed, the Ministry of Microbiological Industry that determined the branch development strategy and represented the interests of hydrolysis plants at the Union level ceased to exist. By that time, synthetic ethanol had become almost unnecessary for the manufacture of synthetic rubber due to implementation of Ziegler–Natta catalysts. As a result, the alcohol production dropped, and only eight hydrolysis plants (among 38 ones operating in the USSR) operated in Russia by early 2000; they were capable of producing about 5 million daL of ethanol [20–36].

However, the present production volume in wood chemical industry is very huge, and the waste problem therein is extremely important and urgent [37–79].

Therefore, much attention is now given to the development of technologies utilizing renewable raw materials. The main products of wood processing are cellulose, ethanol, fodder yeast, xylitol, and (partly) lignin. Prospects are related to synthesis of ethanol, butanol, and other compounds via hydrolysis of plant biomass according to different procedures.

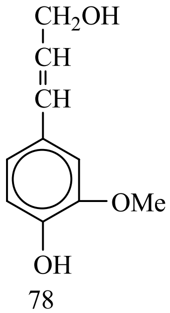
Comprehensive utilization of wood as renewable raw material is the main way of improving the efficiency of wood chemical industry.

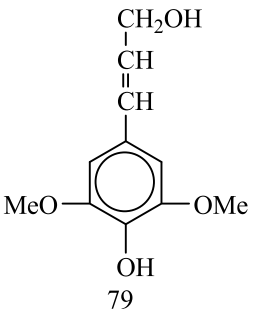
At present, Kirov biochemical plant may be regarded as one of the most successfully operating plants in Russia. It was founded in 1973 as the largest microbiological plant purposed to produce fodder yeast from sawmilling and wood processing wastes. Its successful operation is largely determined by comprehensive utilization of raw materials, combination of works, and extension of product assortment. The plant produces technical rectified alcohol, fodder yeast, technical furfural, acid hydrolysis lignin, and new production facilities have been implemented. The plant also produces wood pellets, a new environmentally safe fuel, fuel ethanol (additive to gasoline), *Bioperit-detoks* (disinfecting agent), liquid carbon dioxide, and liquified hydrogen.

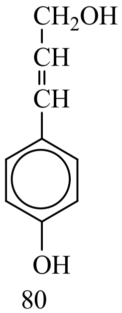
Kirov biochemical plant has now become a central unit of the bioenergetic complex rapidly developing in Russia under the direction of Federal Center for the Development of Bioenergetics. The key condition for successful development of the complex is continuous implementation of innovation technologies. The complex comprises interrelated research centers, companies, and institutions which successfully launch biotechnology projects. The innovation constituent is a key factor ensuring competitive performance of the complex.

A promising line in biochemical wood processing implies the use of technical lignin in the production cycle on the basis of innovation technologies for manufacture of new materials. Formerly, the major part of lignin was wasted in dumps where tens million tons have been accumulated. Advanced lignin processing and extension of the assortment of products obtained from lignin should be accompanied by studying the composition and structure of technical lignins and specific features of its production.

Lignin biosynthesis involves dehydration polymerization of three main precursors that are derivatives of cinnamyl alcohol: coniferyl (4-hydroxy-3-methoxycinnamyl), sinapyl (4-hydroxy-3,5-dimethoxycinnamyl), and *p*-coumaryl (4-hydroxycinnamyl) alcohols. The corresponding phenylpropane units of lignin are guaiacyl, syringyl, and *p*-hydroxyphenyl.


78


79


80

Me–$CH_3$ group

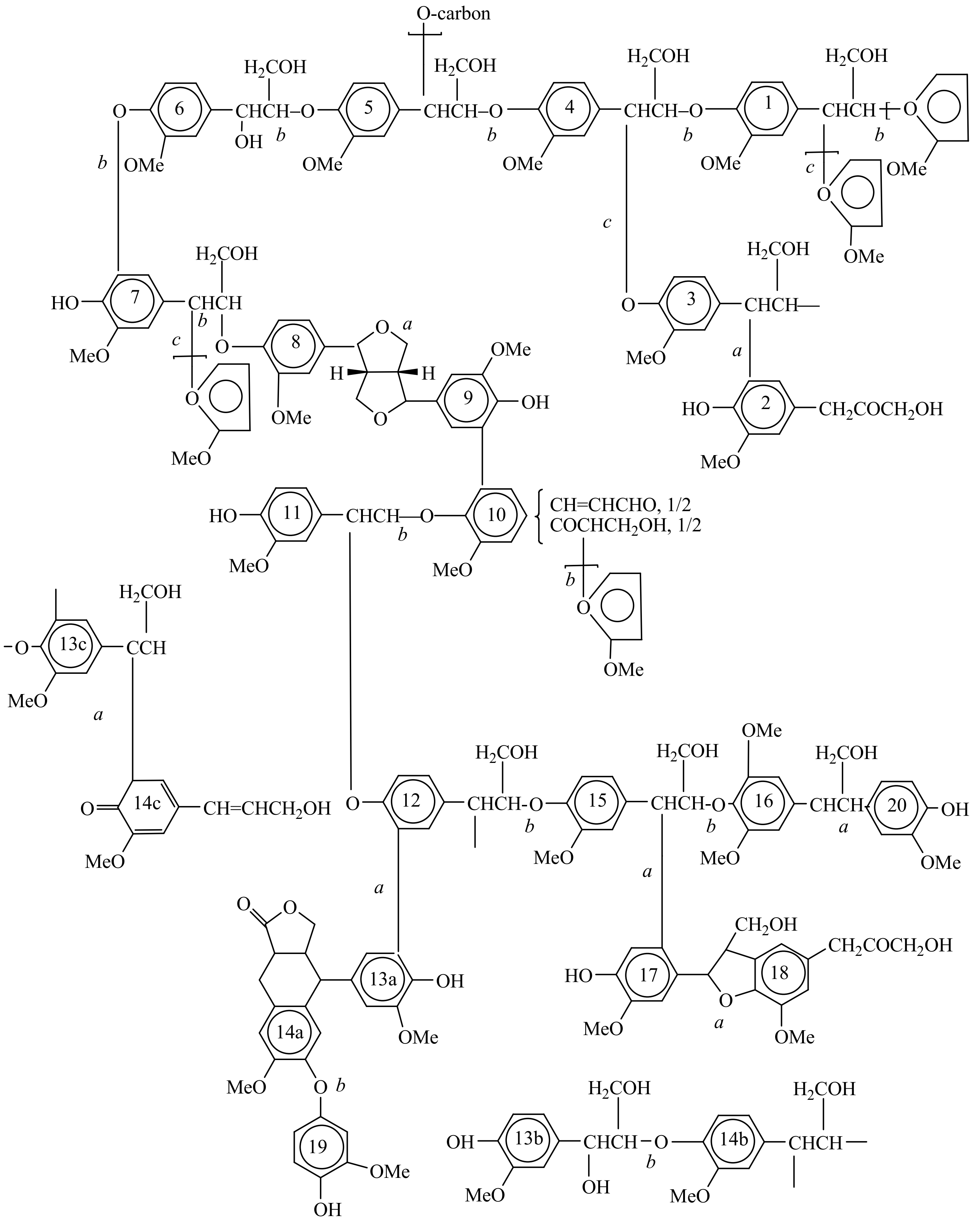


**Fig. 1.** A fragment of spruce lignin molecule.

Characteristics of technical lignin produced by different plants

| Hydrolysis plant | Ash content | Extractable substances (alcohol–toluene, 1 : 2) | Klason lignin | Residual polysaccharides |
|---|---|---|---|---|
| Segezh | 2.0 | 20.8 | 66.1 | 2.8 |
| Bobruisk | 8.2 | 22.0 | 64.1 | 2.9 |
| Tavda | 3.5 | 15.4 | 70.7 | 4.9 |
| Syktyvkar | 4.7 | 7.3 | 60.1 | 7.8 |
| Tavda | 3.5 | 15.4 | 70.7 | 9.4 |
| Kirov | 7.9 | 8.9 | 77.3 | 13.8 |
| Arkhangel’sk | 4.2 | 4.2 | 72.4 | 12.1 |
| Lobva | 0.6 | 18.0 | 68.3 | 28.3 |

Figure 1 shows a fragment of spruce lignin molecules according to Freudenberg (Harkin’s modification). Lignin is capable of forming covalent bonds (unit 5) with hemicellulose polysaccharides in plant tissues. These covalent bonds in combination with hydrogen bonds give rise to an integral supernetwork structure. Natural lignin is a cross-linked polymer, and its isolated samples are not individual polymers but mixtures of chemically heterogeneous irregular branched heteropolymers.

Lignin molecules contain ether (C–O) and carbon–carbon bonds of several types, namely Alk–O-Ar (alkyl aryl ether bond), Ar–O–Ar (diaryl ether bond), Alk–O–Alk (dialkyl ether bond) and Ar–Alk (2–3, 15–17, 16–20), Ar–Ar (9–10, 12–13a), Alk–Alk. Carbon–carbon bonds are stable to hydrolysis; therefore, lignin solvolysis (acidolysis, ethanolysis, etc.) could not ensure 100 yield of monomeric products. On the other hand, C–C bonds can be broken by oxidation or via physical (thermal or mechanical) decomposition.

The lignin structure is characterized by considerable heterogeneity in both phenylpropane units and bonds between them. In addition, lignin contains low molecular weight fractions soluble in various solvents. The structure of lignin may be regarded as three-dimensional network.

Lignin is obtained as insoluble nonhydrolyzable residue after removal of extractable substances and complete hydrolysis of polysaccharides. However, lignin in fact is not a nonhydrolyzable polymer since carbon–oxygen bonds therein can be hydrolyzed by the action of acids with retention of carbon–carbon bonds, and new bonds can be formed.

Hydrolysis lignin is a residue obtained from hydrolysis of wood of different origins. In the manufacture of ethanol the starting material should consist of no less of 80% of softwood, and the other 20% may be hardwood. In addition, lignins produced by different plants differ in particle size and chemical composition. Characteristics of some lignin samples are given in table.

Decomposition of lignin and its condensation are concurrent processes. Condensation processes become predominating in strongly acidic media and lead to the formation of insoluble cross-linked polymer. The rate of condensation processes increases as the temperature rises; however, the contribution of hydrolysis also increases. Under large-scale acid hydrolysis conditions, up to 10% of softwood lignin, 10–20% of hardwood lignin, or 40% of corncob lignin is transferred to solution. Lignin and its decomposition products in the hydrolyzate occur as true or colloidal solution or as dispersed particles with different sizes.

The main factor responsible for weak reactivity of lignin, its low solubility, and high molecular weight is the formation of cross-linked structure as a result of condensation processes. Acid-catalyzed heterogeneous hydrolysis of plant raw materials involves the following consecutive transformations of lignin: (1) formation of a three-dimensional network with sparse cross links between macromolecules; (2) formation of a rigid three-dimensional network; (3) synthesis of polycyclic benzoid structures.

Sparse cross linking of lignin macromolecules in acid medium occurs even at room temperature, and its rate sharply increases as the temperature rises. Three-

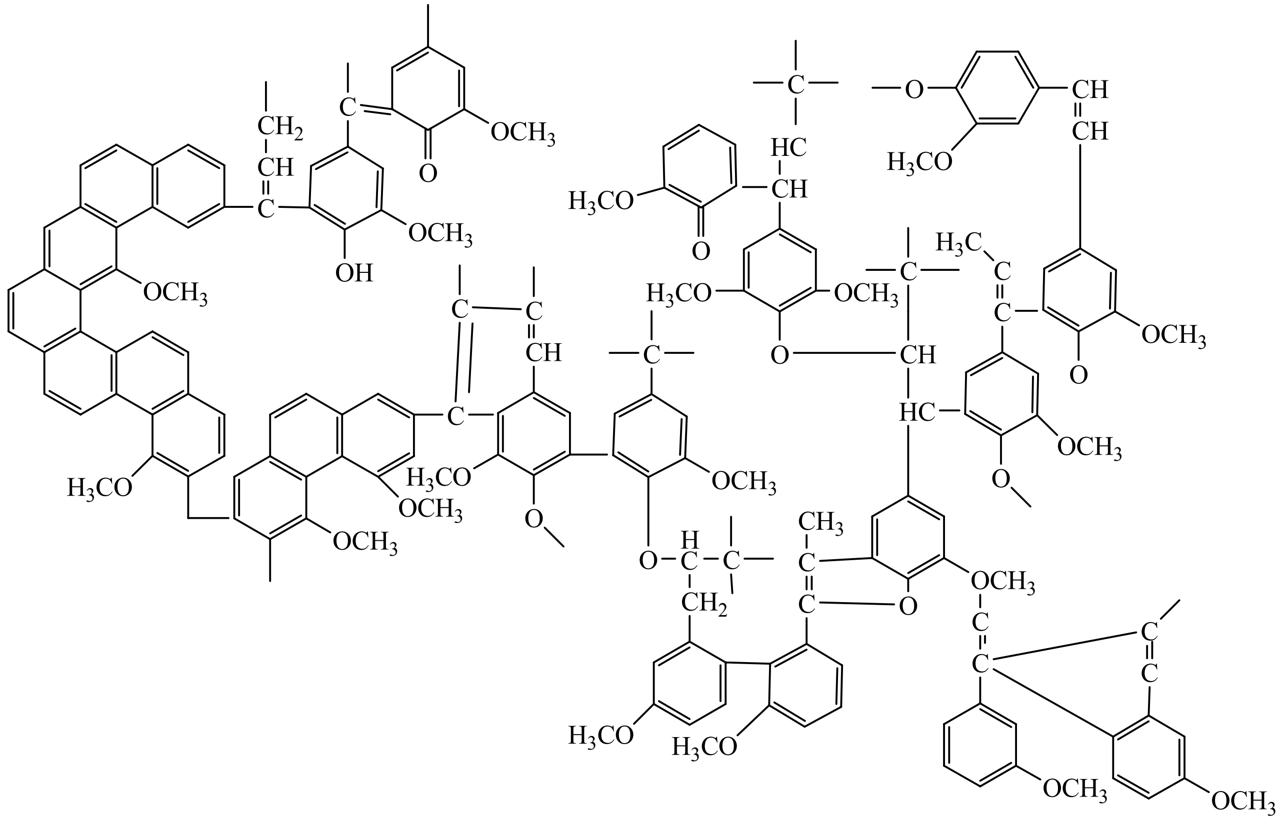


**Fig. 2.** A fragment of hydrolysis lignin molecule [6].

dimensional network is formed above 100°C (second step). This process includes formation of new bonds between phenylpropane units with participation of aliphatic chains and aromatic rings. Condensed lignin is a polymer containing conjugated bonds and possessing paramagnetic properties. Despite development of new technologies for the hydrolysis of biomass, e.g., enzymatic biodegradation, modified technical lignin is obtained as waste product.

Thus, the available and potential lignin processing methods do not ensure utilization of lignin wastes to a sufficient extent, and new advanced technologies are necessary, especially with account taken of growing needs of ethanol.

Figure 2 shows a fragment of a hydrolysis lignin molecule.

Extension of lignin utilization includes manufacture of products without profound chemical modification of the substrate and technologies implying radical change of its chemical structure. The least expensive way is that avoiding profound chemical modification. The corresponding products are sorbents, construction materials, materials for agriculture, and fuels.

**Sorbents.** A traditional way of lignin utilization is manufacture of sorbents for various purposes. The synthesis of carbon sorbents is the largest-scale production line. Apart from the manufacture of activated charcoal analogs, new methods for the preparation from lignin of porous carbon materials with controlled pore size (including carbon molecular sieves), specified surface functional groups, and enhanced mechanical strength are being developed. The scope of application of lignin-based sorbents is fairly broad; they are used in the treatment of industrial wastewaters, decontamination of oil spills, and removal of heavy metal ions, as well as in medicine and veterinary. One of the most promising lignin utilization lines is manufacture of enterosorbents like *Polifepan*. This sorbent is produced by Saintek ltd., as well as by Kirov Biochemical Plant.

**Heat power engineering.** Hydrolysis lignin is used to produce fuel pellets, including those with mixtures with sawdust and peat and carbon dust. Lignin-based low-smoke fireplace pellets are quite needed. Addition of lignin to furnace fuel oil is also promising. It was proposed to use lignin in the manufacture of pelletized reducing agents as substitutes for coke, semicoke, and charcoal in metallurgy.

**Building construction.** Lignins are used in the construction industry, in particular in the manufacture of bricks and porcelain (as cellulating agents instead of sawdust and woodflour). Lignins turned out to be good fillers for plastics and components of composite materials. A dry mixture of sulfonated lignin and alkali lignin slows down hardening in the manufacture of foamed portland cements and slag, puzzolan, gypsum, high-aluminate, and high-alkali cements. Relatively recently lignin additives were successfully used in the manufacture of foamed polyurethane.

A plant for the manufacture of bioplastics was put into operation in 2000 near Karlsruhe. It utilizes lignin, flax or hemp fibers, or other materials of vegetable origin.

**Road construction.** Lignin is added to asphalt concrete (preparation of lignin bitumen mixtures) to improve its performance. In particular, the strength increases by 25%, water resistance, by 12%, and crack resistance (brittleness), from –14 to –25°C.

**Tribotechnology.** In interesting way of lignin utilization is manufacture of such highly rare materials as efficient tribo additives based on chlorinated lignins. The main components of the composition are chlorinated lignin, low-molecular-weight polyethylene, and waste diesel engine oil.

**Agroindustry.** Agroindustrial complex can also actively consume lignin wastes. Effective lignin consumption by agroindustry is primarily determined by its low toxicity (4th class of hazard) and good compatibility with both mineral and organic products. Lignin, both pure and as organic–mineral mixtures, can be used as fertilizer in agriculture. It approaches high moor peat in agrochemical properties, but contains growth substances favoring increased yield of crops, potato, etc. Lignin improves the structure of soils, increases its sorption capacity, and restores original productivity. Lignin is used to produce structuring agents for natural and artificial soils. Experiments were performed to compost lignin with activated sludge, bird droppings, and manure at a ratio of 1 : 1. Such composts mature in 3–6 months. This procedure for the manufacture of composted fertilizers requires no energy-consuming technologies and ensures environmental safety and economic efficiency.

The use of lignin and its modification products in agriculture is largely determined by their sorption properties which provide conditions for retention of nutrients and their gradual emission rather than rapid washout with precipitations and groundwater. In many cases lignin may be regarded as not only porous sorbent but also a substance capable of forming complexes with a number of fertilizers. This is the basis for the manufacture of organic–mineral fertilizers from partly decomposed hydrolysis lignin by composting it with mineral soils, manure, and azotobacters. The effective period of such fertilizers is considerably longer. An efficient composite organic–mineral fertilizer, Lifogum, has been developed on the basis of lignin and double superphosphate.

However, the most promising line in the extension of lignin uses is its profound chemical modification. Lignin can be converted into a number of products highly efficient for agroindustry. Oxidation of lignin with nitric acid gives quinone nitropolycarboxylic acids whose ability to stimulate plant growth is comparable to that of gibberellic acid. Ammonium salts of these acids also stimulate plant growth, and they can be used in the manufacture of malt and in enzymatic hydrolysis for accumulation of amylolytic and proteolytic enzymes.

In recent years, attempts were made to use modified hydrolysis lignin in animal production as biologically active additives to food of ruminant animals. Preliminary results showed positive effect of these additives.

**Other uses of lignin.** It should be noted that further effective extension of the scope of lignin uses is based on its profound chemical modification and decomposition. Hydrolysis lignin obtained from renewable raw materials attracts particular interest from the viewpoint of preparation of aromatic compounds and their subsequent use in organic synthesis.

In this connection, various methods were tried to decompose lignin into low-molecular-weight compounds, in particular pyrolysis, enzymatic decomposition, radiolysis, alkaline and acid hydrolysis, etc. Hydrolysis lignin is used as starting material for the preparation of phenol and acetic and oxalic acids. Lignin is a promising raw material for the manufacture of products substituting traditional commercial fuels, biodiesel and biogasoline. The presence of a large number of aromatic rings in lignin molecules suggests the possibility for obtaining toluene and benzene. Apart from chlorinated lignin (see above), an important line of chemical modification directed toward manufacture of commercial products is nitration of lignins.

A procedure for nitration and oxidation of hydrolysis lignin with a mixture of nitric and sulfuric acids is known. Nitrolignin production has been implemented at the Andizhan Hydrolysis Plant. Nitrolignin is used mainly in oil-and gas industry as efficient additive improving structural and mechanical properties of drilling muds. Nitrolignin effectively reduces the funnel and plastic viscosities, gel strength, and Bingham yield point of drilling fluids and thins weighted fresh and mineralized drilling muds. Nitrolignin is compatible with all known chemical agents used for the treatment of drilling muds, and it inhibits corrosion. The preparation of anti-corrosion agents on the basis of lignin has been developed further.

Profound chemical modification of lignins afforded polyfunctionalized silylated and phosphorylated derivatives as sorbents of new generation. Electrochemical modification of lignin with phthalic anhydride gave ion exchangers possessing high exchange capacity and enhanced physicomechanical characteristics.

Silylated lignins turned out to be useful in the manufacture of adhesive compositions and epoxide compounds. Addition of silylated lignins to the commercial polyurethane adhesive *Vitur* increases the bonding strength by a factor of 1.8, which exceeds the effect of addition of toxic toluylene diisocyanate.

Phosphorylated lignins containing more than 10% of phosphorus cure EDP epoxy resin at 15–20°C, simultaneously acting as filler and reducing combustibility of the compound. Fluorinated lignin in an amount of 2–10% is an efficient additive to iron powder furnace charge for powder metallurgy; it favors formation of sintered steel with enhanced strength, hardness, and wear resistance without loss of plasticity.

Hydrolysis lignins can be endowed with new unique chemical properties via electrochemical silylation, phosphorylation, fluorination, and thiocyanation.

Various methods for utilization of hydrolysis lignin are known: gasification, carbonization, preparation of fuel pellets, biofuels, composts, sorbents, clarifying charcoals, nitrolignin and chlorolignin, foamed lignopolyurethanes, polymeric cathode materials, substitutes for natural leather tanning agents, phenol–formaldehyde resins, etc. Lignin activation with alkali was the subject of many publications. The resulting products turned out to be satisfactory reinforcing agents in the manufacture of rubber. Alkali-activated lignin is converted into lignophenol–formaldehyde resins and benzenepolycarboxylic acids, and the latter are used in the preparation of lacquers, plasticizers, adhesives, etc.

Chlorolignin effectively reduces the viscosity of drilling muds used to flush wells to remove broken rocks and improve well walls. Chlorolignin added to drilling mud to an appropriate concentration can protect it from coagulation by the action of mineral salts. This makes chlorolignin a valuable reagent for drilling geologic profiles with highly mineralized stratal water. Chlorolignin endows industrial textile with biostability and outdoor resistance; it can also be used as flotation agent in reverse flotation of heavy metal ores. An interesting chlorolignin application is its use as artificial leather tanning agent. It was also proposed to use chlorolignin for extraction of rare earth elements from dilute solutions of their salts.

Crown Zellerbach Corp. utilizes sulfate lignin as the major component of black lye for the manufacture of dimethyl sulfoxide. A new procedure has been proposed for the preparation of aqueous paints from disperse dyes containing sulfonated and/or sulfomethylated lignin with an average molecular weight of 25 000 as dispersing agent.

Rust solvent PRL-2 is produced by Zaporozh'e and Nikolaev Hydrolysis Yeast Plants from lignin-containing wastes. Lignin can be used to obtain anticorrosion agents to protect metal surface without preliminary treatment. For this purpose, hydrolysis lignin is treated with 10–20% aqueous salt [$SnCl_4$, $CoSO_4 \cdot 7H_2O$, $LaCl_3$, $ZrCl_3$, $ZnCl_2$, $Ru(OH)Cl_3$, $TiCl_4$, $BiCl_3$, $Pb(NO_3)_2$] under pressure at 160–200°C (hydromodulus 1 : 10; 0.5–2 h).

High surfactant and dispersing properties of lignosulfonates are useful in the manufacture of cement, concrete constructions, and gypsum wallboards, drilling of gas and oil wells, flotation of ores, and textile industry. Adhesive and binding properties of lignosulfonates underlie their applications in foundry for the preparation of various core and molding sand mixtures, wafering, coal and ore chip briquetting, and iron swarf clogging, in the manufacture of cardboard, fiberboards, heat-insulating materials, linoleum, ceramics, whiteware, abrasives, as well as in road construction and other industries.

Vanillin and its derivatives can be obtained by chemical modification of lignin.

A promising line in the utilization of lignins is synthesis of azolignins which were tested as dyes. Azolignins were used for the manufacture of thin packing and writing paper which was colored pink red or beige brown with simultaneous improvement of its mechanical strength and sizing ability. The light fastness of paper colored by lignin derivatives turned out to be no less than that of the dye. Red paper colored by the lignin coupling product with diazo-2-amino-5-hydroxynaphthalene-7-sulfonic acid was characterized by the highest light fastness. An accessible and commercially viable dye obtained on the basis of lignin effectively dyed leather in brown.

Involvement of lignin in combined waste processing technologies deserves attention. Useful products were obtained by processing hydrolysis lignin jointly with liquid propellant wastes (*Melanzh*) or slime from electrochemical aluminum production. Fluorinated nitro derivatives of lignin thus obtained exhibited biocidal properties. The spectrum of efficient biocides was extended by inclusion into the technological process of waste powder coating from used luminescent lamps; the biocidal efficiency increased due to the presence of mercury in the product.

Lignin-based biocides were also modified by addition to the initial mixture of copper-containing wastes from non-ferrous metallurgy, so that the products were enriched in copper ions. The resulting biocide surpassed traditionally used copper salts in biocidal effect.

The proposed technologies for combined waste processing are quite urgent for improvement of the environment in Siberia and Russian Far East where tremendous volumes of wastes from metallurgy and missile industry have been accumulated. An antifouling paint for coating ship's bottoms and submerged constructions has been prepared at the Institute of Chemistry (Far Eastern Branch, Russian Academy of Sciences) on the basis of combined processing of wastes from aluminum and missile-and space industries.

The scope of application of lignin-based materials continuously extends. A radically new line in the utilization of lignin is manufacture of carbon materials. Artificial graphite comparable to natural graphite has been obtained for the first time by thermal modification of hydrolysis lignin. Its properties were confirmed by X-ray analysis and by using it in electrochemical preparation of insertion compounds of graphite and thermally expanded graphite. Artificial graphite can also be used to prepare high-capacity electrodes (720 W h kg$^{-1}$) for lithium ion rechargeable batteries.

Artificial graphite obtained from lignin was shown to be efficient as lubricant additive which reduces the coefficient of sliding friction and wear of friction surface and prevents scoring under high load. Lignin-based artificial graphite may be used as starting material for the preparation of nanotubes.

A new impetus was also given to the development of traditional ways of processing of plant raw materials and lignin wastes.

The current world energy crisis forces a new look at the problem of fuel production from renewable raw materials. Some countries have positive experience of using cellulosic ethanol as fuel substitute. European Union countries are working hard to replace a part of automotive fuel by ethanol. China has a state program for considerable increase of consumption of ethanol as fuel. Analogous program for the use of ethanol has been developed in Brazil.

The Ministry of Industry and Trade of the Russian Federation has issued an order to restructure hydrolysis plants toward the production of motor fuel additives. Addition of 8–10% of ethanol to gasoline should make the latter more environmentally safe. According to the current state standard for *benzanol* (GOST R 52-201-2004), gasoline should contain up to 10% of alcohol. This creates a vast market for bioethanol producers.

A green gasoline containing 10% of alcohol (gasohol, E-10) is now produced in the US, and boom in the construction of fuel alcohol plants is observed worldwide. Russian hydrolysis plants are capable of actively joining development of the fuel alcohol market, and they attract serious interest as investment objects for both domestic and foreign businesses.

For example, Arkenol Inc. (US) is a pioneer in the conversion of cellulose biomass into ethanol; agricultural wastes, straw, leaves, mowings, sawdust, and old newspapers can be used as feedstock. The company utilizes its own technology of concentrated acid hydrolysis and is now completing the construction of a plant in Sacramento (CA) for the processing of rice straw with a capacity of 48 million liters per year.

Iogen Corporation (Canada) also occupies a leading position in the development and production of ethanol from cellulose. The production technology involves preliminary steam explosion of lignocellulosic material and preparatory lignocellulosic material and enzymatic hydrolysis [19].

In 2007 the United States Department of Energy (DOE) has funded three projects in an amount of $160 million, but the funding was increased after the State of the Union Speech. In his address to Congress in January 2007, G. Bush called to reduce gasoline consumption by 20% in 10 years. The total investment for six bioenergy projects was $1.2 billion. These plants will produce annually 130 million gallons (490 million liters) of ethanol. The funds were distributed as follows:

Abengoa Bioenergy Biomass (Kansas): grant $76 million; 44 million liters of ethanol annually; 700 t of cornstalks, wheat straw, and other agricultural wastes processed daily.

– ALICO, Inc. (Florida): grant $33 million; 54 million liters of ethanol annually and also electric power, 8.8 t of hydrogen, and 50 t of ammonia daily; 770 t of wood and sugar cane wastes processed daily.

– Blue Fire Ethanol (California): grant $40 million; 74 million liters of ethanol annually; 700 t of wood and plant wastes processed daily.

Broin Companies (South Dakota): grant $80 million; 484 million liters of ethanol annually, including 25% of cellulosic ethanol; 842 t of straw and corn wastes processed daily.

Iogen Biorefinery Partners (Virginia): grant $80 million; 70 million liters of ethanol annually; 700 t of wheat, barley, and rice straw and corn wastes processed daily.

Range Fuels (Colorado): grant $76 million; 160 million liters of ethanol and 36 million liters of methanol annually; 1200 t of wood wastes processed daily.

Foreign experience may be quite useful in the upgrade of Russian facilities for biochemical wood processing.

## CONCLUSIONS

Huge amounts of lignin have been accumulated throughout the world, including Russia. The course of development of modern civilization clearly indicates that its amount will permanently increase. Despite continuous extension of the lignin application scope, it is now obvious that the lignin production–utilization balance is displaced toward the former. This creates a serious environmental problem whose solution requires keen attention. For instance, the amount of technical lignin proposed for utilization only at hydrolysis plants of Irkutsk oblast of Russia is more than 600000 t annually.

It should also be recognized that current trends in the solution of world energy crisis problems cannot be regarded as environmentally safe and completely admissible until the problem of utilization of lignin wastes via their conversion into commercial products remains unsolved.

## ACKNOWLEDGMENTS

This review was performed under financial support by the Russian Scientific Foundation (project no. 14-13-00448).

## REFERENCES

1. Khol’kin, Yu.I., *Tekhnologiya gidroliznykh proizvodstv* (Technology of Hydrolysis Processes), Moscow: Lesnaya Promyshl., 1989.
2. *Lignins: Occurrence, Formation, Structure, and Reactions*, Sarkanen, K.V. and Ludwig, C.H., Eds., New York: Wiley, 1971.
3. Sharkov, V.I., *Tekhnologiya* (Technology), Moscow: Lesnaya Promyshl., 1973.
4. Sharkov, V.I., *Gidroliznoe proizvodstvo* (Hydrolysis Production), Moscow: Goslestekhizdat, 1945.
5. Krutov, S.M., Zarubin, M.Ya., and Sazanov, Yu.N., *Ligniny* (Lignins), Politekh. Univ., 2011.
6. Chudakov, M.I., *Promyshlennoe ispol’zovanie lignina* (Industrial Utilization of Lignin), Moscow: Lesnaya Promyshl., 1983.
7. Zakis, G.F., *Funktsional’nyi analiz ligninov i ikh proizvodnykh* (Functional Group Analysis of Lignins and Their Derivatives), Riga: Zinatne, 1987.
8. Lin, S.Y., *Methods in Lignin Chemistry*, Berlin: Springer, 1992.
9. Zarubin, M.Ya. and Krutov, S.M., *Osnovy organicheskoi khimii ligninov* (Fundamentals of Organic Chemistry of Lignins), St. Petersburg: Sankt-Peterb. Gos. Lesotekh. Akad., 2010.
10. Bogolitsyn, K.G., *Fizicheskaya khimiya lignina* (Physical Chemistry of Lignin), Moscow, Akademkniga, 2010.
11. Karmanov, A.P., *Khim. Rastit. Syr’ya*, 1999, no. 1, p. 2098.

12. Cateo, S.A., *Doctoral (Biol.) Dissertation*, Grenoble, 2008.
13. Krutov, S.M., Abstracts of Papers, *IV Vserossiiskaya nauchnaya konferentsiya "Khimiya i tekhnologiya rastitel'nykh veshchestv"* (IVth All-Russian Scientific Conf. "Chemistry and Technology of Plant Raw Materials"), Syktyvkar. 2006.
14. Krutov, S., Abstracts of Papers, *10th European Workshop on Lignocellulosics and Pulp*, Stockholm, 2008, p. 298.
15. *Proceedings of 12th ISWPC*, USA, 2003, vol. 1, p. 239.
16. Adler, E., *Wood Sci. Technol*., 1977, vol. 11, p. 169.
17. Brunow, G., Karlsson, O., Lundquist, K., and Sipila, J., *Wood Sci. Technol*., 1993, vol. 27, pp. 281.
18. Nimz, H.H., Tschirner, U., Stable, M., Lehmann, R., and Schlosser, M., *J. Wood Chem. Technol*., 1984, vol. 4, p. 265.
19. Brunow, G., Kilpeläinen, I., Sipilä, J., Syrjänen, K., Karhunen, P., Setälä, H., and Rummakko, P., *Lignin and Lignin Biosynthesis* (ACS Symposium Series, vol. 697), Lewis, N.G. and Sarkanen, S., Eds., Washington, DC: Am. Chem. Soc., 1998, chap. 10, p. 131.
20. Ralph, J., Peng, J., Lu, F., and Hatfield, R.D., *J. Agric. Food Chem*., 1999, vol. 47, p. 2991.
21. Matsumoto, Y., Akiyama, T., Ishizu, A., Meshitsuka, G., and Lundquist, K., Abstracts of Papers, *10th Int. Symp. on Wood and Pulping Chemistry*, Yokohama, Japan, 1999, vol. 1, p. 126.
22. Ralph, J., Marita, J.M., Ralph, S.A., Hatfield, R.D., Lu, F., Ede, R.M., Peng, J., Quideau, S., Helm, R.F., Grabber, J.H., Kim, H., MacKay, J.J., Sederoff, R.R., Chapple, C., and Boudet, A.M., *Advances in Lignocellulosics Characterization* Argyropoulos, D.S., Ed., Atlanta, GA: TAPPI, 1999, p. 55.
23. Ralph, J., Kim, H., Peng, J., and Lu, F., *Org. Lett*., 1999, vol. 1, p. 323.
24. Ralph, J., *Proc. 6th Brazilian Symp. on the Chemistry of Lignins and Other Wood Components*, 1999, p. 97.
25. Brovenko, G.N. and Gusel'nikova, T.V., *Gidrol. Lesokhim. Prom–st*., 1993, no. 2, p. 14.
26. Nemirovskii, V.D. and Kostenko, V.G., *Khim. Drev*., 1989, no. 6, p. 71.
27. Tsutsumi, Y., Kondo, R., and Imamura, H., *J. Wood Chem. Technol*., 1993, vol. 13, p. 25.
28. Li, S., Lundquista, K., and Westermark, U., Abstracts of Papers, *6th European Workshop on Lignocellulosics and Pulp*., 2002, p. 45.
29. Tanczos, I., Volk, G., and Balla, J., Abstracts of Papers, *8th European Workshop on Lignocellulosics and Pulp*, 2004, p. 173.
30. Alekseev, S.R., Krutov, S.M., and Zarubin, M.Ya., *Gidroliznyi lignin. Sostav i vozmozhnye puti utilizatsii* (Hydrolysis Lignin. Composition and Possible Ways of Utilization), St. Petersburg: Izv. Lesotekh. Akad., 1999, p. 65.
31. Argyropoulos, S.D. and Menachem, S.B., *Adv. Biochem. Eng./Biotechnol*., 1997, vol. 57, p. 128.
32. *Methods in Lignin Chemistry*, Lin, S.Y. and Dence, C.W., Eds., Berlin: Springer, 1992, p. 42.
33. Fukushima, R.S. and Hatfield, R.D., *J. Agric. Food Chem*., 2001, vol. 49, p. 3133.
34. Ralph, J. and Lu, F., *J. Agric. Food Chem*., 1998, vol. 46, p. 4616.
35. Gilarranz, M.A., Rodriguez, F., Oliet, M., Garcia, J., and Alonso, V., *J. Wood Chem. Technol*., 2001, vol. 21, no. 4, p. 387.
36. Xia, Z., Akim, L.G., and Argyropoulos, D.S., *J. Agric. Food Chem*., 2001, vol. 49, p. 3573.
37. Kanitskaya, L.V., Deineko, I.P., Kushnarev, D.F., Klemper, A.V., and Kalabin, G.A., *Khim. Drev*., 1989, no. 6, p. 17.
38. Capanema, E.A., Balakshin, M.Y., and Kadlaa, J.F., *J. Agric. Food Chem*., 2004, vol. 52, p. 1850.
39. Brezny, R. and Schraml, J., *Holzforschung*, 1987, vol. 41, no. 5, p. 293.
40. Nieminen, O.J., Pulkkinen, E., and Rahkamaa, E., *Holzforschung*, 1989, vol. 43, p. 303.
41. Ahvazi, B.C. and Argyropoulos, D.S., *J. Agric. Food Chem*., 1996, vol. 44, no. 8, p. 2167.
42. Granata, A. and Argryropoulos, D.S., *J. Agric. Food Chem*., 1995, vol. 43, p. 1538.
43. Tohmura, S. and Argyropoulos, D.S., *J. Agric. Food Chem*., 2001, vol. 49, p. 536.
44. Ikeda, T., Holtman, K., Kadla, J.F., Chang, H., and Jameel, H., *J. Agric. Food Chem*., 2002, vol. 50, p. 129.
45. Guerra, A., Filpponen, I., Lucia, L.A., Saquing, C., Baumberger, S., and Argyropoulos, D.S., *J. Agric. Food Chem*., 2006, vol. 54, p. 5939.
46. Leary, G.J. and Newman, R.H., *Methods in Lignin Chemistry*, Lin, S.Y. and Dence, C.W., Eds., Berlin: Springer, 1992, p. 146.
47. Liitia, T., Maunu, S.L., and Hortling, B., *J. Pulp Paper Sci*., 2000, vol. 26, no. 9, p. 323.
48. Krutov, S.M., Zykov, V.N., and Zarubin, M.Ya., *Izv. Sankt-Peterb. Gos. Lesotekh. Akad*., 2005, p. 141.
49. Mokeev, M.V., Popova, E.N., Krutov, S.M., Sumerskii, I.V., Sazanov, Yu.N., and Yudin, V.E., Abstracts of Papers, *Khimiya i polnaya pererabotka biomassy lesa* (Chemistry and Complete Processing of Forest Biomass), 2010, p. 215.
50. Roman-Leshkov, Y., Barrett, C.J., Liu, Z.Y., and Dumesic, J.A., *Nature*, 2007, vol. 447, p. 982.
51. Binder, J.B. and Raines, R.T., *J. Am. Chem. Soc*., 2009, vol. 131, p. 1979.

52. Obolenskaya, A.V., El'nitskaya, Z.P., and Leonovich, A.A., *Laboratornye raboty po khimii drevesiny i tsellyulozy* (Laboratory Works on the Chemistry of Wood and Cellulose), Moscow: Ekologiya, 1991.
53. Obolenskaya, A.V., Shchegolev, V.P., and Akim, G.L., *Prakticheskie raboty po khimii drevesiny i tsellyulozy* (Laboratory Works on the Chemistry of Wood and Cellulose), Moscow: Lesnaya Promyshl., 1965.
54. Yokoyama, T. and Matsumoto, Y., *Holzforschung*, 2008, vol. 62, p. 164.
55. Hawkes, G.E., Smith, C.Z., Utley, J.H.P., Vargas, R.R., and Viertler, H., *Holzforschung*, 1993, vol. 47, p. 302.
56. Ponomarev, D.A. and Shergina, S.V., *Khim. Drev*., 1990, no. 3, p. 3.
57. Yavmetdinov, I.S., Stepanova, E.V., Gavrilova, V.P., Lokshin, B.V., Perminova, I.V., and Koroleva, O.V., *Prikl. Biokhim. Mikrobiol*., 2003, vol. 39, no. 3, p. 293.
58. Krutov, S.M. and Zarubin, M.Ya., *Izv. Sankt-Peterb. Gos. Lesotekh. Akad*., 2008, no. 184, p. 206.
59. Krutov, S.M., Pranovich, A.V., and Zarubin, M.Ya., *Lesn. Zh*., 2010, no. 1, p. 122.
60. Krutov, S.M., Pranovich, A.V., and Zarubin, M.Ya., *Lesn. Zh*., 2010, no. 2, p. 141.
61. Sumerskii, I.V., Krutov, S.M. and Zarubin, M.Ya., *Russ. J. Appl. Chem*., 2010, vol. 83, no. 2, p. 320.
62. Sazanov, Yu.N., Kulikova, E.M., Fedorova, G.N., Popova, E.N., Litvinova, L.S., Kever, E.E., Mokeev, M.V., Novoselova, A.V., and Gribanov, A.V., *Russ. J. Appl. Chem*., 2009, vol. 82, no. 9, p. 1592.
63. Ipatova, E.V. and Krutov, S.M., *Izv. Sankt-Peterb. Gos. Lesotekh. Akad*., 2013, no. 3, p. 135.
64. Russian Patent no. 2116080, 1998.
65. Borges da Silva, E.A., Zabkova, M., Araújo, J.D., Cateto, C.A., Barreiro, M.F., Belgacem, M.N., and Rodrigues, A.E., *Chem. Eng. Res. Des*., 2009, vol. 87, no. 9, p. 1276.
66. Hatakeyama, H., Tsujimoto, Y., Zarubin, M.Ja., and Krutov, S.M., *J. Therm. Anal. Calorim*., 2010, vol. 101, p. 289.
67. Knežvić, A., Milovanović, I., Stajić, M., and Ločar, N., *Bioresour. Technol*., 2013, vol. 138, p. 117.
68. Mu, W., Ben, H., Ragauskas, A., and Deng, Y., *BioEnergy Res*., 2013, vol. 6, no. 4, p. 1183.
69. Sukhodolov, A.P. and Khamataev, V.A., *Izv. Irkut. Gos. Ekon. Akad*., 2009, no. 3 (65), p. 49.
70. Simonova, V.V., Shendrika, T.G., and Kuznetsov, B.N., *Zh. Sibir. Fed. Univ., Khim*., 2010, no. 3, p. 40.
71. Brebu, M., Ca Zacu, G., and Chirila, O., *Cellul. Chem. Technol*., 2011, vol. 45, nos. 1–2, p. 43.
72. Sharypov, V.I., Beregovtsova, N.G., Baryshnikov, S.V., Kuznetsov, B.N., et al., *Zh. Sibir. Fed. Univ., Khim*., 2013, no. 6, p. 3.
73. Beletskaya, M.G. and Bogdanolvich, N.I., *Materialy V mezhdunarodnoi konferentsii "Fizikokhimiya rastitel'nykh polimerov"* (Proc. Vth Int. Conf. "Physical Chemistry of Plant Polymers"), Arkhangel'sk: Inst. Ekol. Problem Severa Ural. Otd. Ross. Akad. Nauk, 2013, p. 36.
74. Gordeeva, T.Kh. and Novoselov, S.I., *Materialy III Vserossiiskoi konferentsii "Aktual'nye voprosy khimicheskoi tekhnologii i zashchity okruzhayushchei sredy"* (Proc. IIIrd All-Russian Conf. "Current Problems of Chemical Technology and Environmental Protection"), Cheboksary, 2013, p. 117.
75. Evstigneev, E.I., Maiorova, E.D., and Platonov, A.Yu., *Khim. Drev*., 1990, no. 6, p. 41.
76. Evstigneev, E.I., *Russ. J. Appl. Chem*., 2013, vol. 86, no. 2, p. 258.
77. Kulikov, K.V., Litvinov, V.V., Piyalkin,V.N., Zabelkin, S.A., and Bashkirov, V.N., *Vestn. Kazan. Tekhnol. Univ*., 2012, p. 197.
78. Ponomarev, A., Kholodkova, E.M., and Metreveli, A.K., *Radiat. Phys. Chem*., 2011, vol. 80, no. 11, p. 1186.
79. Gribkov, I.V. and Krutov, S.M., *Tekhnicheskii gidrolicheskii lignin. Khimicheskii sostav i stroenie* (Technical Hydrolysis Lignin. Chemical Composition and Structure), St. Petersburg, 2011, p. 156.