CELLULOSE CHEMISTRY AND TECHNOLOGY

LIGNIN BY-PRODUCTS OF SOVIET HYDROLYSIS INDUSTRY: RESOURCES, CHARACTERISTICS, AND UTILIZATION AS A FUEL

MIKHAIL L. RABINOVICH

A. N. Bach Institute of Biochemistry, Russian Academy of Sciences, 119071 Moscow, Russia
✉ *Corresponding author: mirabi@mail.ru*

Received October 28, 2013

The development of new biorefineries and large scale second generation biofuel production from lignocellulosic feedstock will result in the formation of millions of tons of lignin by-products annually. Although many applications are now being developed for the utilization of the produced lignin in the manufacturing of new materials, it is not yet clear whether they would be able to consume the increasing amounts of lignin without spoiling the environment. This review presents the production of lignin by the Soviet hydrolysis industry, which reached 1.5 million ton/yr in the 1980s. The characteristics of different types of hydrolysis lignin are considered and the lignin stocks accumulated in the dumps and landfills of the former Soviet Union are evaluated. The utilization of hydrolysis lignin as an industrial and household fuel, as well as the consequences of lignin accumulation for the environment are also analyzed.

Keywords: wood saccharification, biorefinery, lignin, combustion, second generation ethanol, composting, environmental effects

INTRODUCTION

The increasing interest in various lignin by-products is explained by their increasing availability based on the modern biorefinery concepts and an increasing demand in the 2nd generation biofuels (ethanol, butanol) from lignocellulosic biomass. Most of the developing lignin utilizations are focused on the production of new materials for durable use, such as carbon fibers, polyurethanes, isocyanate-cured ligno-phenol-formaldehyde resins of novolac type, and various lignin blends with synthetic polymers.[1] It is, however, not obvious that the production of lignin-based materials can utilize increasing lignin supply by an appropriate scale-up of 2nd generation biofuel production. Just by the production of ethanol from pine or eucalyptus, the best calculations[2] lead to amounts of lignin substantially exceeding those of ethanol. The potential supply of hydrolysis lignin would in this case exceed 66 million tons/yr, which is more than all lignin wastes produced by the pulp and paper industry.[2] Therefore, a substantial (if not major) fraction of hydrolysis lignin should be either used as a fuel with a competitive price and quality, or obtained in an environmentally friendly form, to be consumed or deposited without substantial additional expenses. The former Soviet hydrolysis industry experienced such a problem of excessive lignin since its establishment in the 1930s and till the collapse in the 2000s. This review presents aspects concerning the production and accumulation of hydrolysis lignin residues in the former USSR, as well as their characteristics and utilization as a fuel, and the environmental impact of the dumps.

TYPES OF LIGNIN RESIDUES FORMED BY SOVIET HYDROLYSIS INDUSTRY

Soviet hydrolysis plants produced technical grade ethanol, fodder yeast, furfural, and xylitol, depending on the type of renewable feedstock. Ethanol was manufactured mostly from the softwood residues by the oldest hydrolysis plants. So-called hydrolysis yeast plants utilized predominantly hardwood residues for production of non-sporulating pentose-utilizing fodder yeast. Furfural and xylitol were in turn mostly produced from agricultural residues, such as cottonseed hulls in the former Soviet Central Asian republics, sunflower seed hulls, rice husk, or corncobs in Russian Stavropol and Krasnodar krai, Ukraine, and Moldova. Besides that, some amount of furfural was produced from hardwood and tannin waste by means of an acid-free procedure.[3-5] The obtained post-hydrolysis residues of ethanol plants constituted mostly softwood lignin, the solid residues of fodder yeast plants contained mostly hardwood lignin, and those of furfural and xylitol plants contained lignin of agricultural feedstock. Some furfural plants also produced the so-called cellolignin consisting of hardwood lignocellulose after conversion of hemicelluloses fraction into furfural. An average ratio of different types of lignin produced by the Soviet hydrolysis industry in the 1970s-1980s roughly equaled to 3:2:1 for softwood, hardwood lignin and lignin of agricultural feedstock, respectively.[5,6] It should however be noted that neither ethanol nor yeast plants produced exclusively softwood or hardwood lignin, respectively. In fact, both types of plants produced both types of hydrolysis lignin, although one of them usually dominated (softwood lignin for ethanol plants and hardwood lignin for yeast ones). Excluding cellolignin, almost all the other types of Soviet hydrolysis lignin were obtained by one- or two-stage percolation hydrolysis of corresponding renewable feedstock with diluted (0.5-2%) sulfuric acid at 150-200 °C for several hours.[5-7] The only exception was the so-called HCl lignin manufactured by a semi-industrial facility of Kansk hydrolysis plant in limited amounts since 1958 till 1974 as a by-product by crystalline glucose production.[3,4] However, the cumulative amount of the production of this type of lignin, which was close to the spruce Willstätter lignin, did not exceed 15-20 thousand tons. In contrast with that, the total hydrolysis lignin and cellolignin production by the Soviet hydrolysis industry grew from 0.5 in the mid-1960s[8] to 1.5 million ton/yr in the mid-1980s.[5]

Cellolignin principally differs from hydrolysis lignin by the content of polysaccharides (>50% or <30%, respectively), the absence of sulfuric acid (up to 2% in hydrolysis lignins), particle size distribution, degree of lignin condensation, heat capacity, and carbonization behavior. The content of lignin in industrial cellolignin and hydrolysis lignin dumps may therefore vary from 40 to >80%.

CHARACTERISTICS OF INDUSTRIAL HYDROLYSIS LIGNIN

Soviet hydrolysis lignin experienced two peaks of scientific and industrial interest: in the 1960s-1970s, as a result of the rapid development of Soviet hydrolysis industry,[8-13] and in the first decade of the 2000s following the rapid growth of oil prices, as an accumulated secondary resource.[14-19] In this review, an attempt has been made to compare and combine the data obtained in the 1960s-1970s by the laboratories of lignin chemistry and delignification of the All-Union Research Institute VNIIGidroliz with those reported in the last 10-15 years.[19,20] It should, however, be noted that the data published 40-50 years ago characterized the freshly prepared hydrolysis lignin, whereas most of the data reported in the last period refer to the lignins from the dumps and, for this reason, might differ from those obtained earlier. The only recent systematic study of the composition of technical hydrolysis lignins (the content of Klason lignin, extractives, polysaccharides, ash) from seven bioethanol plants directly after production and from the dumps has been performed by the group of Prof. S. M. Krutov from the St. Petersburg Forest Technical Institute.[14-19]

The granulometric composition of hydrolysis lignin is far from uniform because of simultaneous utilization of different ratios of wood chips and sawdust in the hydrolysis reactors. The size distribution of hydrolysis lignin particles may vary in a wide range from hundreds nm to >1 cm. 17-46% of lignin particles are <0.25 mm and 0.1-4.3% particles are <1 mm in the largest dimension.[10-12] The lignin resulted at the Arkhangelsk hydrolysis plant contains 85% of particles <0.25 mm, 14% of particles between 0.25 and 0.5 mm and only 1% of particles >1 mm.[21] All hydrolysis lignins and cellolignins contain as a rule a fraction of partially non-processed wood, which can be separated by sieving. Freshly prepared commercial hydrolysis lignin for further industrial utilization should in principle contain moisture <65%, ash <4.5%, H_2SO_4 <1.5%. The bulk density of freshly produced lignin with the moisture content <40% varies in the range 200-460 kg/m^3, whereas that of lignin containing 65% of moisture is about 700 kg/m^3. Lignin from the dumps might have higher bulk density (600-700 kg/m^3) and lower humidity (38-43%) depending on conditions. The slope angle of the moist lignin falls within 40-43°. All this makes the transportation of hydrolysis lignin expensive. A commercial cellolignin should in principle contain moisture <52%, ash <2.5%, organic acids (accounted as acetic acid) <3.5%. However, these standards were usually controlled by further production of granulated lignin (particle size 20 mm for >90% granules, moisture <20%, ash <7%, bulk density >550 kg/m^3), which was used for crystalline Si and Al-Si alloys production, or lignin flour (moisture 10-20%, specific surface area 200-300 m^2/g), which was consumed as a filler in glues, plastics, or linoleum. The parameters of the major part of lignin or cellolignin kept in local dumps within 10-20 km around the production facility, were usually not controlled.

COMPOSITION OF HYDROLYSIS LIGNIN BY-PRODUCTS

The hydrolysis lignin of the Soviet industry "as received" contained in fact only 1/3 of solids, whereas the acidic moisture containing residual amounts of water-soluble components of hydrolyzate constituted up to 70%. Being dried in corresponding dryers or under natural conditions, industrial hydrolysis lignin still retained nonvolatile or tightly absorbed volatile components of sugar hydrolyzate together with the feedstock fractions of non-polar nature or sugar decomposition products, which are not soluble or become insoluble in the process of high-temperature acid hydrolysis.

For this reason, dry hydrolysis lignin represented a multicomponent composition of lignin itself (usually 60-70%, but in fact from 40 to 88%) together with:

- a wide variety of extractives soluble in water and/or in organic solvents of different polarity (monosaccharides and their decomposition products, such as furfural, 5-hydroxymethyl furfural and their short-chain oligomers, usually assayed as reducing substances, volatile organic acids, mainly acetic and formic, diverse terpenoids and their oxygen derivatives, low molecular weight aromatic compounds of phenyl propane origin, aliphatic hydrocarbons originated from waxes, long-chain fatty acids, original and modified resin acids etc.) in the amounts always greater that their content in the original renewable feedstock (up to 22%);
- sometimes a small fraction (2-5%) of easy-to-hydrolyze residual polysaccharides of xylan or glucomannan origin depending on feedstock,
- typically a (substantial) fraction of residual cellulose, from 3-5 to 30%;
- so-called lignohumic substances built of furfural and 5-hydroxymethyl furfural condensation products;
- a fraction of inorganic constituents of quite different composition, depending on the origin, nature, and age of the feedstock, hydrolysis and storage conditions, but usually different from the ash composition of the original feedstock, together with residual sulfuric acid.

The lignin accumulated in the former Central Asian Soviet republics was mostly of cotton plant origin (cottonseed hulls, stalks). The hydrolysis lignin of South Russian and Ukrainian yeast and furfural plants was both of agricultural and woody origin, whereas that produced by White Russian, North-European Russian, Ural, Siberian and Far Eastern plants originated from soft- and hardwood. Table 1 summarizes the yields of industrial hydrolysis lignins from different types of feedstock (dry basis) and the variation in the contents of its major constituents, which were determined in the period of active development of the Soviet hydrolysis industry (1960s-1980s).

About one half (ca. 10%) of 20% tightly bound polysaccharides could be released as glucose by a treatment of freshly obtained hydrolysis lignin (68% of moisture, 1.3% of H_2SO_4) at 300 °C in an autoclave.[9] Predominantly softwood lignin from ethanol plants differed from predominantly hardwood lignin of yeast plants by higher content of Klason lignin and residual polysaccharides.[24]

Table 1
Yields and composition of different hydrolysis lignins[8-13,22,23]

Feedstock	Yield (% db)	Components	% db
		Klason lignin	48-72
Softwood	38	Polysaccharides	13-32
		Resins	7-19
Hardwood	32	Reducing substances	2-10
Cottonseed hulls	37	Lignohumates (alkali-soluble)	5-15
Corncobs	24	Sulfuric acid	0.5-2
Sunflower seed hulls	32	Ash	0.7-12

Table 2
Average composition of softwood hydrolysis lignin[11]

Components	% db
Sulfuric acid	0.6-1.5
Reducing substances	1.5-3.0
Non-hydrolysed polysaccharides	15-20
Ash	<3
-OCH_3-groups	10-11
Phenolic OH-groups	<3
Resins (dichloroethane-soluble)	7-12

Table 3
Percentage composition of hydrolysis lignin from different plants[24,27,31-33]

Plant location	Ash, %	Extractives	Klason lignin	Residual polysaccharide	Reducing substances	H_2SO_4
Kirov	3.5 (2.3)	14.3 (9.8)	67.0	18.7		1.68
Tavda	3.5	15.4 (22.0)	59.8 (70.7)	24.8 (4.9)		
Lobva	0.6(1.0)	18.0	52.3(61)	29.7		
Segezha	2.0	20.8	66.1	2.8	28.3	3.6
Bobruisk	10.0 (8.2)	22.0	60.1 (64.1)	2.9		
Syktyvkar	4.7	7.1 (7.3)	60.1	7.8		
Arkhangelsk	0.48	12.0 (9.3)	65.8	21.7	2.34	1.53
Zima	5.4 (12.6)		62.1	10.1		1.0
Zaporozhye	6.5 (7.5)	8.7	67.0	31.6	3.6	0.24 (1.24)
Tulun	1.3 (17.6)	10.0				
Krasnoyarsk	3.3	15.0	61.3	13.3		

Data in parentheses are the results determined by other authors

Relatively new data, which were obtained in the period of collapse of the Russian hydrolysis industry, demonstrate that the fractions of certain components may be also beyond the limits shown in Table 2. Some authors[20,25] evaluate the ash composition of Russian hydrolysis lignins in the range of 1.7-5.1%, H_2SO_4 content as 0.5-1.1%, water-soluble components as 2.7-6.5%, extractives (ethanol+benzene) as 3.16-17.9%, easy-to-hydrolyze polysaccharides as 0.5-1.5%, recalcitrant polysaccharides as 4.9-31.7% and Klason lignin as 48.3-87.5%. Siberian plants also utilized, together with other coniferous, larch wood containing up to 20% of arabinogalactan. The latter decomposed under harsh hydrolysis conditions forming lignohumic substances condensed with lignin. According to these authors, the content of extractives in the lignins from the hydrolysis plants of European Russia and Ural does not exceed 11.4%. The hydrolysis lignin of mostly hardwood origin and relatively low moisture content (25%), which is still produced in a limited amount by the Kirov biochemical plant (European Russia), has relatively low content of water-soluble (5.9%), and resinous substances (3.9%),[26] and lignohumates (3%).[27] The average composition of the lignins from the Leningrad, Kirishi, and Syktyvkar plants was characterized by moisture content of 58-67%, pH 2.3-2.7, ash content of 0.5-4% (db), Klason lignin content of 70-84%, easy to hydrolyse polysaccharides of 2.5-5-8%, recalcitrant cellulose of 9-28% (daf).[28,29] The cellolignin of the Manturovo plant had moisture content of 66%, pH 4.1-4.5 and ash content of 8.9% (db).[30]

Examples of composition of various hydrolysis lignins are given in Table 3. Differences in the content of extractives and reducing sugars may be attributed to the applied pretreatment procedure, whether resinous and water-soluble substances were removed or not.

However, it cannot be excluded that some data might refer to lignins from the dumps.

Structure of lignin constituents of the industrial hydrolysis lignins

Although hydrolysis lignin always represented a minor fraction of the total Soviet lignin production, which grew from 4 to ca. 10 million t/yr from the 1960s till the 1970s, its lignin component was considered the most condensed by-product, which could not be readily utilized.[8-13] It contained substantially less functional groups (excluding -OCH_3) than lignins of the pulp and paper industry and could not be easily dissolved in alkali or polar solvents. According to M. I. Chudakov,[8-11] the thermal and hydrolytic effect of hot diluted sulfuric acid on wood resulted in the condensation and formation of new intramolecular bonds including conjugated ones. It was proposed that such a prolonged treatment (several hours) would lead to the formation of secondary cross-links and more rigid network of secondary (polynuclear) aromatic structures, whereas the number of ether bonds would decrease drastically.[11] This secondary cross-linking involves both free functional groups of aromatic and aliphatic fragments of phenylpropane moieties and the secondary functional groups formed under acidic treatment. In this condensation process, C-C-bonds of the α-6 type dominate, although α-5 and α-1 bonds also form. In contrast with "native" lignins, secondary polynuclear aromatics in hydrolysis lignin form benzene-polycarboxylic acids upon alkaline MnO_4^- oxidation. Conjugated secondary aromatic structures, among which biphenyls, aromatized lignan structures, hexa-, penta- and tetra-substituted benzene rings, condensed guaiacyl propane moieties may be named, reveal semiconductor and paramagnetic features.[8-11]

Recent studies by solid state ^{13}C MAS NMR spectroscopy have confirmed the formation of the new C-C-bonds in the condensation processes in hydrolysis lignins upon prolonged treatment with hot diluted sulfuric acid.[24,27] Compared with Björkman spruce lignin (96% of G-units), which contained on average 2.3 Ar-O, 1.2 Ar-C, and 2.5 Ar-H bonds per one C9 unit, the hydrolysis lignin of the Kirov yeast plant (predominantly from hardwood, 74% of G-units) and that of the Lobva ethanol plant (predominantly from softwood, 80% of G-units) contained reduced or equal average numbers of Ar-O (2.2 and 2.3, respectively) and reduced numbers of Ar-H bonds (2.4 and 2.3, respectively), whereas the average number of Ar-C bonds definitely increased in both hydrolysis lignins to 1.4, thus revealing the formation of new C-C-bonds, which substituted C-H and/or C-O bonds in the aromatic nucleus. Nevertheless, the new studies have provided an evidence of the presence of a substantial number of ether bonds in hydrolysis lignins. In the Kirov hydrolysis lignin, relatively small fragments corresponding to di- and trimers of C9-units (Mw 480-540), which constitute ca. 16% of its structure, are linked to the major lignin network just by ether bonds.[24,27] Further SS NMR studies have revealed the presence of a significant number of the most stable β-O-4 bonds in hydrolysis lignin. Furthermore, a decrease in the structures containing the *erythro*-form of β-O-4 bond and the corresponding enrichment with the more stable structures having this ether bond in *threo*-form were detected under the conditions of hydrolysis lignin formation.[24,27] The studied samples have been confirmed to contain aromatic methoxyls, OH-groups at Cα-atoms in the C9 moieties linked via β-bonds, OH-groups at Cγ-atoms, carbonyl groups, G- and S-nuclei with substantial domination of G-nuclei in the hydrolysis lignins of ethanol plants. The latter were found to retain more reactive centers in their aromatic nuclei compared to the predominantly hardwood hydrolysis lignins of yeast plants.[24,27]

However, the most reactive and close to the native state lignin that has not been subjected to intramolecular cross-linking was found in cellolignin, which is obtained in furfural industry under less severe conditions than hydrolysis lignin.

Table 4 summarizes the elemental and functional composition of lignin fractions from hydrolysis lignins resulted at different plants.

Lignohumates and extractives of hydrolysis lignins

The formation of the humin-like substances has been modeled under conditions of hydrolysis lignin industrial production.[27] Monosaccharides (both pentoses and hexoses) and disaccharide (cellobiose) products of wood hydrolysis with dilute sulfuric acid were shown to undergo a series of dehydration and condensation stages resulting in the formation of cross-linked polymers of furan nature with the yields of approximately 20 and 30% from hexoses and pentoses, respectively. The obtained humin-like substances consist of up to 60% of furan rings and up to 20% of aliphatic fragments. In the case of hexoses, the formation of humin-like substances proceeds via 5-hydroxymethyl furfural, which enters further polycondensation by electrophilic substitution with the formation of ether or acetal bonds between the rings. In the case of pentoses, the forming furfural also enters further polycondensation reactions, though by aromatic electrophilic substitution, with the formation of C-C bonds between the rings. Further spectroscopic studies have confirmed the similar nature of lignohumates in the hydrolysis lignin produced by the Kirov yeast plant.[27]

A comprehensive study of the extractives from technical hydrolysis lignins was undertaken by the specialists of St. Petersburg State Forest Technical Institute (earlier Academy).[27,39-41] More than 150 components were identified by GC-MS in aqueous and various organic extracts of hydrolysis lignins. The major fraction of the extractives was represented by monosaccharides (xylose, arabinose, glucose, galactose, mannose) in different conformations. Glucose definitely dominated and constituted ca. 75% of the monosaccharides content. The content of extractives in hydrolysis lignin exceeded 4-7-fold that of original wood. This was attributed to the ability of lignin to efficiently adsorb and concentrate several hydrophobic components from the hydrolyzate, as well as to the co-precipitation with lignin of resin acids and other wood components, which are insoluble in diluted sulfuric acid. The structures of several extractives, which were isolated from hydrolysis lignin, also differed from the structures of their precursors in the original wood. It was concluded that hydrolysis lignin was enriched with those wood extractives or their derivatives, which demonstrated thermal and acid stability under hydrolysis conditions.

Among the components identified by GC-MS, terpenoids (monocyclic monoterpens, oxygen-containing bicyclic monoterpens of pinane structural type, tricyclic resin acids, sterols) together with aliphatic C9-C18 hydrocarbons and saturated C16-, C18-, C20-, C22-, C24-, C26, mono- di-, and tri-unsaturated C18-fatty acids constituted the major fraction extracted with organic solvents.[27] Hydrolysis lignin of the Lobva ethanol plant contained saturated C16-C24-fatty acids, unsaturated linoleic and oleic acids, pimaric, isopimaric and dehydroabietic resin acids as major components, and stigmasterol as a minor component. Dehydroabietic acid, β-sitosterol, betulinol, and the saturated C22-C24 fatty acids dominated in the extractives of hydrolysis lignin of the Arkhangelsk ethanol plant. [39-41]

Inorganic constituents of industrial hydrolysis lignins

Specialists of the leading Russian group in the hydrolysis lignin research from the St. Petersburg Forest Technical University report a very high content of SiO_2 (4.5-20%), SO_3, (3.7-18.4%), CaO (5.6-8.5%) and Fe_2O_3 (2.6-3.4%) in different layers of the lignin dump of the Arkhangelsk hydrolysis plant, from its surface and up to the depth of 1.5 m (XRF).[42] Although the use of energy dispersive XRF (Na-Sc) leaves a space for speculations in the determination of Si and S, such a high content (>30%) of inorganic contaminants may be attributed to the ashes of smoldering fires, as well as slags or other wastes of inorganic nature that were used to extinguish these fires, or deposited together with lignin in the same dump. Other sources[38,43] report lower content of inorganic components in the hydrolysis lignins from other dumps (Table 5).

Alterations of lignin composition in the dumps

Different moisture and solid contents were reported in central and surface zones of the Razlog stockpile,[44] while the sulphur content remained near 0.7%. A decrease in cellulose content in the landfill was reported for both Razlog[44] and Arkhangelsk lignin dumps (Table 6).

A systematic study of the evolution of hydrolysis lignin composition in the dump was performed by the specialists of the chair of organic chemistry from the St. Petersburg State Forest Technical University.[21,27,39-41,43,45] ^{13}C MAS NMR studies have shown that, with the increase in the depth of lignin sampling from the surface to the depth of 1.5 m, a 10% increment of CAr-O and CAr-C bonds is observed along with the concomitant 30% decrease in the content of the more reactive Cα–ethers and 20% decrease in the content of Cβ–ethers and Cγ–hydroxyls, whereas the methoxylation degree of lignin remains unchanged.

Table 4
Elemental and functional group composition of various lignin fractions from Soviet hydrolysis lignins [24,27,28,31-38]

Lignin (daf)	C	H	O	OCH_3	COOH	OH	S	N	Brutto-formula
Average Leningrad, Kirishi	63-66	3.7-4.5	30.0-32.3	7.3-9.7		4.55 (0.63**)		0.03-0.35	
Leningrad	58.9	6.18		7.36(7.83)	1.32	8.73(9)			$C_9H_{10.06}O_{3.35}$
Kansk HCl lignin	62.0	5.93		15.22	0.40	11.83			$C_9H_{8.51}O_{2.88}$ $(OCH_3)_{0.94}$; $(O_{co})_{0.02}$
Arkhangelsk	61.8	5.39		9.71(9)	1.49				
Krasnoyarsk	60.0(62.7) (60.2)	6.2(5.8) (6.0)	33.4(30.9) (33.0)		3.2*	9.8	0.4(0.6)	<0.8	
Zaporozhye	57.0	6.0	35.0				1.0	1.0	
Kirov	62.7	5.9	31.2	12.16	1.63+1.25*	8.57(1.96**)	0.05	0.21	
Bobruisk	54.0	6.2	37.2				2.4	0.1	
Tulun	60.2(54.1)	6.2(4.7)					0.4(0.9)		$C_9H_{11.07}O_{3.6}$
Zima	52.05	5.09					0.66	3.03	
Yangiyul cottonseed husk hydrolysis lignin	54.5 (57.3)	5.3 (6.14)		5.4 (4.83)	1.8+7.1* (7.85*)	7.1(4.7**) (5.41)			$C_9H_{11.38}O_{3.88}$ $(OCH_3)_{0.37}OH_{0.59}$ $(O_{co})_{0.55}$ $(OOH_{COOH})_{0.12}$
-"- rice husk hydr. lignin	61.85	6.28		4.48	4.62*	5.28			
-"- wood hydr. lignin	55.7	7.0		6.72	3.85	7.21			
Kedainiai	59.6	5.6					0.04 (1.8)	0.18 (0.63)	

* carbonyls, ** phenolic OH-groups

Table 5
Elemental composition of some hydrolysis lignin (recalculated per dry basis)[38,43]

Lignin source	P_2O_5, ‰	K_2O, ‰	Pb, ppm	As, ppm	Ni, ‰	V, ‰	Fe, %	Cu, ‰	Mn, ‰	Zn, ‰	Ca, ‰	Mg, ‰
Kedainiai	0.81	1.66	28.4	-	0.19	0.16	6.24	0.19	0.37	-	-	-
Kirov	0.4	0.6	-	0.25	-	-	0.4	0.0015	0.09	0.01	1.3	1.0

n.d.: not determined

Table 6
Composition of Arkhangelsk hydrolysis lignin dump[45]

Sample depth	Ash, %	Extractives, %	Lignin, %	Residual polysaccharides, %
Surface	0.48	12.03	65.81	21.68
0.5 m	1.91	11.74	73.44	12.92
1.5 m	10.19	9.43	78.0	1.59

The distribution of the major extractive components in the hydrolysis lignin of the Arkhangelsk plant also strongly varies with the depth of sampling. A remarkable increase in the content of saturated fatty acids C22 and C24 with the concomitant drop of unsaturated fatty acids and dehydroabietic acid content was also observed.[21] For example, the contents of fatty acid 22:0, fatty acid 24:0 and that of sitosterol increase, respectively, from 3 to 12, from 3 to 14% and from 8 to 10% of the total extractives for the sampling depth of 1.5-2 m, compared to the surface of the dump, whereas the contents of fatty acid 18:1, of 8,15-isopimaradien-18-oic acid and that of dehydroabietinic acid decrease from 5 to 1.5%, from 8 to 3.5% and from 13 to 10%, respectively, with the corresponding increase in the sampling depth.[21] Therefore, the content of more stable components in the hydrolysis lignin, namely its polyphenyl propanoid structure, and long-chain saturated fatty acids have increased with time, whereas the content of polysaccharides, unsaturated fatty and resin acids decreased. The lignin network also apparently becomes more rigid and condensed, while the relative number of ether bonds and aliphatic hydroxyls decreases. It is however not clear whether such alterations occur as a result of the presence of residual sulfuric acid or if this is a natural process.

ESTIMATION OF HYDROLYSIS LIGNIN BY-PRODUCTS IN THE DUMPS AND LANDFILLS OF THE FORMER USSR

Estimations of hydrolysis lignin amounts in the dumps of the former Soviet Union are controversial. The values from 1995, [33,34,46] of several hundred million tons,[43,47-49] are reported for Russian lignin stocks. Ukrainian lignin dumps can contain from 2 to 15 million tons[47-50] of lignin of unknown moisture content. The annual production of hydrolysis lignin was estimated as 1.5 million tons (1985, db) in Soviet Union,[5] or 3.5 million tons only in Russia.[51]

Table 7 summarizes the publicly available data on the lignin stocks in the dumps of different plants. The two bottom rows refer to the hydrolysis lignin dumps at present within the borders of European Union.[38,44] The other data were published by local mass media of Russia, Ukraine, and White Russia. Some data (e.g. those of Kirov, Gubakha, or Segezha) are certainly overestimated. The reported areas of the dumps and the maximal depth of the lignin layer do not exceed 66 ha and 30 m, respectively. The total volumes of the lignin dump should therefore be <20 million m^3 or <15 million tons at the bulk density <0.7 g/cm^3. Finally, the same dump might be used not only for lignin but also for other industrial or municipal solid wastes, particularly after the hydrolysis plants were closed in the 2000s. The average data reported for most lignin dumps fall within 2-3.5 million tons accumulated on an average 25-35-ha area. Some enterprises, e.g. the Rechitsa plant in White Russia, used several dumps to dispose of the produced lignin residues.

Although lignin by-products were not precisely counted in the hydrolysis industry, the available data on feedstock consumption, manufacturing of major products, their yields, as well as the yield of lignin allow the estimation of the amounts of lignin (db) produced by separate plants, regionally, or by the whole hydrolysis industry. From the available public domain data, it can be calculated for example that the Tavda plant could not produce substantially more than 1.5 million ton of lignin since its establishment in 1943 and till bankruptcy in 2004. Similarly, at the maximum annual consumption of 1 million m^3 of solid wood, three plants of Irkutsk oblast (Biriusinsk, Tulun, and Zima), which were built in the 1950s and closed between 2002 and 2006, could not produce together substantially more than 8 million tons of lignin (db). Maximal annual lignin production would not exceed 35 thousand t for Tavda and 160 thousand t for all three oldest Irkutsk plants. In this respect, the annual values reported by the internet resources, of 60 thousand tons in 1997 for the Tavda plant, or 70 thousand tons in 2003 for each of the three ethanol plants in Irkutsk oblast,[47,52,53] or 400 thousand tons for all the plants of Irkutsk oblast,[54] or 14 million tons cumulative lignin stocks in Zima, Biriusinsk and Tulun, seem to account for hydrolysis lignin of different moisture contents rather than dry basis. The value reported for the oldest Bobruisk plant (150-230 tons of lignin daily, or 50-80 thousand tons annually seems to be also an over- rather than an underestimation, whereas the cumulative lignin production of 9 million tons by Komi republik (Syktyvkar plant), Perm (Gubakha plant), and Sverdlovsk oblast (Tavda, Lobva, and Ivdel plants)[55] seems to be closer to reality.

Table 7
Some reported lignin and cellolignin dumps in the former USSR and the Eastern Block*

State	Location	Plant	Amount, million t	Remarks	Fires
Russia	Khabarovsk krai	Lesozavodsk yeast, furfural	5.5-8		Yes
		Khor ethanol, yeast	2-5	S 66 ha	
	Irkutsk oblast	Zima ethanol	2.3-11	S 25 ha, h 30 m	Yes
		Tulun ethanol	1.5-2	S 18 ha	Yes
		Zima, Biryusinsk, Tulun, Baykalsk	S15-20	mostly softwood	
	Krasnoyarsk krai	Kansk ethanol	2.5-3	S 20 ha	Yes
	Sverdlovsk oblast	Ivdel ethanol	>2.5	S 58 ha	Yes
	Kirov oblast	Kirov yeast	50	S 59 ha	Yes
	Perm oblast	Gubakha ethanol, yeast	30 million m^3		
	Arkhangelsk oblast	Onega ethanol	3		Yes
	Karelia republic	Segezha yeast	30		
	Khakasia republic	Ust-Abakan yeast	4	S 40 ha	Yes
	Kostroma oblast	Manturovo yeast, furfural	3	S 14 ha,+cellolignin	
White Russia	Mogilev oblast	Bobruisk ethanol, yeast	2.5-3	S 34 ha	Yes
	Gomel oblast	Rechitsa yeast, furfural	1.7-5	+cellolignin, 2 dumps	
Ukraine	Zaporozhska oblast	Zaporozhye yeast	2.5-3	S13 ha, from agr. waste	
Lithuania		Kedainiai yeast	1-1.5	S 6 ha	
Bulgaria		Razlog yeast	0.35-0.4		

*data of mass media, not official statistics

The largest Kirov biochemical plant was built to convert 700-720 thousand m^3 of solid wood annually.[5] Since its establishment in 1973, its hydrolysis facility could consume <29 million m^3 of solid wood and produce no more than 4.5-5 million t of hydrolysis lignin (db). If the plant has actually utilized 96 million tons of woody wastes, as it is stated in the corresponding presentation on the website of the plant, most of the wood must be consumed beyond its hydrolysis facility.

Here an evaluation of the upper limits of lignin by-products (db) was made based on the available data[5,24,56-58] of annual ethanol, fodder yeast, furfural, and xylitol production by the USSR/CIS hydrolysis industry (Figure 1). The yields from 1 t (db) of corresponding feedstock were taken as:

- 150 L for ethanol from predominantly softwood;
- 180 kg for yeast from predominantly hardwood;
- 60 kg for furfural from agricultural wastes;
- 60 kg for furfural from tannin waste or birch by acid-free hydrolysis;
- 80 kg for xylitol from agricultural wastes;
- 400 kg for lignin from softwood feedstock;
- 360 kg for lignin from agricultural feedstock;
- 370 kg for lignin from predominantly hardwood;
- 750 kg for cellolignin from the tannin waste or other hardwood by acid-free furfural production.

The yields of useful products are close to the minimal reported ones,[4,5] whereas the maximal yields were taken for lignin by-products (cf. Table 12.1 from the work by Yuri Ivanovich Kholkin[5]). The production of furfural by 14 specialized furfural plants and of fodder yeast by 16 hydrolysis yeast plants was taken to be 70% and

80% of the overall annual furfural and yeast production, respectively, while the rest was produced by the hydrolysis plants of another specialization, without concomitant lignin production.[5,57]

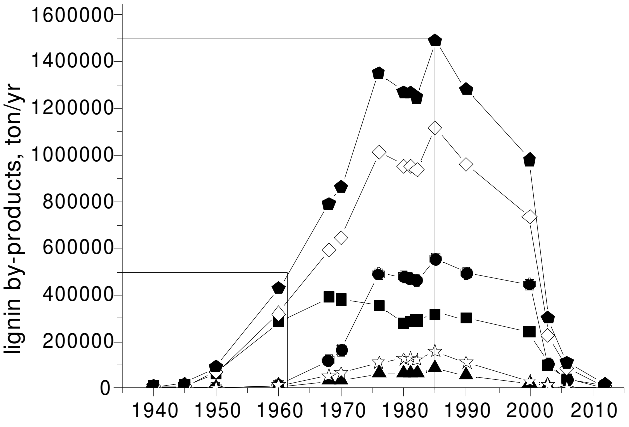

Figure 1: Dynamics of annual hydrolysis lignin production (pentagons) and accumulation (diamonds) by Soviet and Russian hydrolysis industry on the assumption of 25% consumption. Squares: predominantly softwood lignin, circles: predominantly hardwood lignin; asterisks: lignin of agricultural residues; triangles: cellolignin from tannin waste. Areas under the curves demonstrate the relative accumulated amounts of different lignin by-products and their total amount (for details of calculations, see text)

Two reference points, 0.5 and 1.5 million tons (db) of annual hydrolysis lignin production in the middle of the 1960s[8] and 1980s,[5] respectively, were used to verify the ascending route of the graph (Figure 1).

The following assumptions were made:

1. From the available data,[5,56-58] the highest annual productions of ethanol, yeast, furfural, xylitol were chosen, if they did not contradict strongly with the data reported by others.

2. The descending route of the graph since 1990 is based on the reported production of 360 thousand ton of fodder yeast and 120 million L of ethanol by the hydrolysis industry at the end of the 1990s[24] and the other semi-quantitative evaluations.[58] In fact, since 1990 most of the hydrolysis plants completely or partially substituted the lignin-containing feedstock for the food or forage ones (grain, potato, molasse, bran).[6,7] For example, the Tavda plant utilized in 1997 about 30% of food or forage feedstock together with wood. After introducing the excise tax for hydrolysis ethanol in the 2000s and a penalty of $24/t for solid wastes transported to the dumps, these plants went bankrupt between 2002 and 2006.[6,7] White Russian plants in Bobruisk and Rechitsa utilized woody feedstock (at least partially) till 2007. At present, only the Kirov biochemical plant produces lignin in limited amounts. Therefore, the descending route of this graph might also be an over- rather than an underestimation.

3. The overall production capacity of the cellolignin-depositing plants in Manturovo (5000 t/yr of furfural), Shumerlya and Rechitsa was estimated as 20% of the overall furfural production (expert evaluation).

4. The structure of feedstock consumption was taken roughly the same as reported in the 1980s (8 million m^3 of solid wood at the softwood:hardwood ratio of 3:2, 700 thousand tons of agricultural wastes (including 250 thousand tons of cottonseed hulls and 450 thousand tons of other agricultural wastes converted to furfural or xylitol as the major product and yeast as a co-product).[5]

5. The consumption of hydrolysis lignin was assumed to be 25%. Actually, in the 1960s the ethanol hydrolysis plants did not utilize lignin in significant quantities.[8] Building of the new hydrolysis yeast plants in the 1970s and the development of more sophisticated equipment utilizing moist lignin as a fuel for yeast dryers has promoted lignin combustion, which did not however exceed 50% in the 1980s.[5] Since the collapse of the hydrolysis industry, lignin has also been utilized by domestic companies to produce briquets or pellets. Finally, the amount of stored lignin decreases due to natural reasons: smoldering fires and decomposition of residual

polysaccharides and extractives. Therefore, the value of 25% is a reasonable approximation of lignin consumption, closer to the lower rather than the upper limit.

By these assumptions, the total amount of lignin by-products manufactured since the 1940s by the Soviet hydrolysis industry (area under the curve 1, Figure 1) does not exceed 49-50 million tons (db) and the amount of currently accumulated lignin residues (at 25% consumption) would be close to 37 million tons (db). The dumps in White Russia (Bobruisk) and in Russian Karelia, Arkhangelsk, Perm oblast, Ural, Irkutsk oblast, Krasnoyarsk and Khabarovsk krai would contain overall 15 million tons (db) of predominantly softwood lignin deposited in 1950-2000 (area under curve 4). Near 2 million tons of cellolignin deposited in the 1970s-1990s, would be distributed between White Russian Rechitsa and Russian Manturovo and Shumerlya (area under curve 5). From 3.7 million tons of lignin of agricultural origin accumulated by furfural and xylitol plants,

- 1.0 million tons of cottonseed husk lignin might be accumulated by 4 hydrolysis plants of the former Central Asian Soviet Republics,
- 2.7 million tons of lignin from the other agricultural wastes distributed between 4 Russian furfural and xylitol-producing plants in Krasnodar and Stavropol krai, 2 Moldavian, and 5-6 smaller Ukrainian plants;
- 16 million tons of predominantly hardwood lignin accumulated by two yeast plants in White Russia, Kedainiai plant in Lithuania, Zaporozhye plant in Ukraine, and large Russian yeast plants in Kirov, Manturovo, Volzhsk, Ust-Abakan, Lesozavodsk, Baykalsk.

Assuming Russian dumps roughly contain 2/3 of cellolignin, 1/3 of the lignin from agricultural wastes (excluding lignin from cottonseed hulls), 95% of softwood and 80% of hardwood lignin, current lignin stocks in Russian Federation equal to ~30 million tons (db). Lignin dumps in Krasnodar and Stavropol krai (Kropotkin and 3 other plants) can contain <1 million tons of lignin from agricultural residues. Cellolignin dumps in Shumerlya and Manturovo accumulate overall <1.5 million tons of cellolignin from tannin waste and birch. The stocks of predominantly hardwood lignin (total <13 million tons) are distributed mostly among Kirov (<4 million tons), Ust-Abakan, Manturovo, Volzhsk, and Lesozavodsk. Predominantly softwood lignin (~14.5 million tons) is distributed among European Russia (Segezha, Onega, Arkhangelsk, Gubakha), Ural (Tavda, Ivdel, Lobva), Siberia (Biriusinsk, Tulun, Zima, Krasnoyarsk, Kansk), and Far East (Khor). It can be therefore concluded that, on the assumption of 25% lignin utilization, an average dump of Russian ethanol hydrolysis plant contains 1-1.5 million tons of predominantly softwood lignin (db) with the largest ones <2 million tons.

Ukrainian lignin dumps should accumulate ca. 1 million t of lignin from agricultural wastes and <1 million tons of hardwood lignin (mostly in Zaporozhye), whereas White Russian dumps most likely accumulate overall ~3 million tons of lignin by-products: ca. 1.5 million tons of softwood and hardwood lignin in Bobruisk and <1.5 million tons of hardwood lignin and cellolignin in Rechitsa.

HYDROLYSIS LIGNIN AS A FUEL

Although a variety of promising applications of hydrolysis lignin have been developed in Russia and the former USSR,[5-13,47,59,60] its utilization as a fuel still remains the major alternative to the lignin dumps and landfills. However, hydrolysis lignin as an industrial or domestic fuel has some drawbacks and limitations.[61]

The combustion of the produced lignin could in principle cover >25% of the overall energy consumption by a hydrolysis plant. Though, the use of unprocessed lignin as a fuel in the standard boilers was limited because of high (50-70%) moisture content and the presence of residual H_2SO_4. On the one hand, the average heat capacity of hydrolysis lignin strongly depends on its moisture content, decreasing from 23-27 MJ for 1 kg of db lignin to 20; 7.8; 6.2-6.9; or 5.7 MJ/kg of lignin containing 18-25; 60; 65; or 68% of moisture, respectively. On the other, at the moisture content of 20% or below, hydrolysis lignin is flammable and the dust of lignin is highly explosive. Ignition, self-ignition and smoldering fire temperatures of hydrolysis lignin were estimated as 195, 425 and 185 °C, whereas the lower explosive limit for lignin dust in the air equals 57.5 g/m^3. Self-ignition temperature of lignin dust on a hot surface equals 300 °C and for lignin aerosol it is 450 °C; minimum concentration of flame spread equals 40 g/m^3, maximum explosion pressure is 710 kPa, maximum rate of pressure rise is 35 MPa/s, minimum ignition energy is 20 MJ. Limiting oxygen concentration strongly depends on the moisture content in lignin, decreasing from 19.8% (v/v) at 50% of moisture to 14.5% at 20% and 11.0% for fully dried lignin. To avoid the danger of explosion, minimum excess of air is recommended by lignin combustion, which can be achieved by drying of the moist lignin with the flue gases rather than with the hot air.

Industrial hydrolysis lignin as a waste is always contaminated with inorganic impurities (see above). Because of that and also because of different feedstock sources, the content of ash may vary by a decimal order of magnitude reaching sometimes almost one quarter of the overall lignin dry mass. Depending on the prehistory of the dump, the ash composition may also significantly vary and differ strongly from the ash composition of the original renewable feedstock, although silicates always dominate (Table 8). The reported softening point of lignin ash is near 1200 °C.[3,4] Hence, temperatures below 1100 °C are recommended to be kept in the lignin furnaces for clogging prevention. Residual sulfuric acid may also corrode furnaces resulting in their rapid failure.

Table 8
Ash composition of some hydrolysis lignins

Component, %	CaO	MgO	Fe_2O_3	Al_2O_3	SiO_2	P_2O_5	TiO_2	Na_2O	K_2O	SO_2
Arkhangelsk	32.8	0.6	16.5		49.5	1.5				
Zaporozhye	1.5	0.3		1.0	93.4	1.5	0.1	0.3	0.3	
Bobruisk	7.86	0.65	2.56	1.11	77.8		0.04	0.09	0.24	7.95
Kirov	5.38	0.94	7.23	4.35	75.13	0.30	1.19	0.85	1.40	3.17

For environmental reasons, it was originally projected that the new hydrolysis yeast plants would burn >50% of lignin in their boilers and yeast dryers. However, only the demo Leningrad plant at "VNII gidroliz" burned ~70% of lignin in its boilers.[8] The other plants burned much less lignin, because its moisture content should be initially reduced to <45% for a stable burning without black oil or natural gas co-firing. This increased the expenses, making lignin fuel non-competitive with the cheap black coal from Kuznetsk basin, particularly in the East of Russia. The Tavda hydrolysis plant was one of the typical examples in this respect. Till the 1980s, freshly unloaded lignin was dried to ~40% of moisture content and pumped through a 800-m pipeline directly to the boilers. However, later the plant management found such a solution unprofitable, and the lignin was discharged to the nearest dump 10 km from the plant. In the 2000s, a penalty of $24/t for solid wastes deposition in the dumps was introduced. This finally led to the bankruptcy of the plant.

In the last 10-20 years, a number of studies were undertaken to overcome the multiple problems caused by the incineration of such a moist and non-uniform fuel as hydrolysis lignin. One of the proposed technical solutions included filtration combustion of moist lignin under super-adiabatic heating conditions.[62-65] Superadiabatic regimes of combustion were obtained for moist lignin mixed with an inert solid with filtration of the steam-air mixture. The accumulation of heat released in the combustion wave resulted in the development of temperatures highly exceeding those of adiabatic fuel combustion. This in turn gave rise to the utilization of highly moist fuels with high ash content and inorganic inclusions. A two-stage scheme of gasification followed by combustion of the formed fuel gaseous products was developed based on the obtained results.[63-65] Other authors[66] proposed a stabilized suspension of coal dust and moist hydrolysis lignin (1:1) as a liquid fuel, whereas the invention of the specialists from the former Tulun plant proposed co-firing of the moist lignin together with hydrogen gas obtained as a by-product by acetone-buthanol-ethanol fermentation of saccharified wood.[67]

Semi-dry forming of lignin as a fuel was initially introduced on the Bobruisk plant. The technique included two-stage drying of lignin to the moisture content of 12-18%. Later, improved schemes of drying and transportation of fresh lignin to the boilers were used by the Kirov, Volzhsky, and Khakasky (Ust-Abakan) plants. Onezhsky, Kirishsky, Kedainiaisky, Bratsky and some other hydrolysis plants used non-milled lignin of 60-65% moisture in the low-temperature vortex combustion boilers E-50-24K NTV or E-75-40K NTV equipped with black-oil torches. The boilers were designed by the chair of steam generators at the St. Petersburg Polytechnic University.[68] The largest one consumed 32 t/h of moist lignin and produced 65-75 t/h of steam at 440 °C and the pressure of 4 MPa with the energy conversion efficiency of 85-88%. The major principle was based on arranging a strong hot air flow, which simultaneously dried the moist non-milled lignin and separated it from heavier inorganic inclusions and large wood pieces in a pre-chamber, and provided swirling in the furnace chamber. Once the ignition temperature of lignin was reached and the air flow was sufficiently heated, the black oil torches could be switched off or consumption of black oil strongly reduced. However, after the hydrolysis plants were closed, these boilers did not incinerate lignin anymore. Attempts to use three large NTV furnaces at the Bratsky plant for combustion of non-milled bark and sawdust without co-firing of black oil failed and the wood residues are now incinerated in the fluidized-bed furnaces, whereas the old lignin boilers are not in use.

Swirling-type low-temperature furnaces for stable lignin burning without substantial feeding with black oil were designed by "Biyskenergomash" for relatively small-scale boilers. The larger boilers with the capacity from 30 to 100 MWt for lignin, peat, or sawdust incineration, e.g. boiler E-75-3,9-440DFT, are produced by the Belgorodsky plant for boilers manufacturing (OAO ZKO) and utilize the fluidized-bed combustion principle. However, whether hydrolysis lignin is actually used within the country for incineration at the current internal prices for fossil fuel in Russia is not clear.

In contrast with Russian Federation, White Russia strongly depends on imported fuel. This motivates local authorities for lignin utilization. Current annual production of hydrolysis lignin in White Russia is equivalent to ca. 25000 TOE or about 4.4% of the total secondary energy resources produced in the country. Commercial hydrolysis lignin for energy production in White Russia should contain moisture <60%, ash <23% db, ^{137}Cs <18 Bq/kg. Heat capacity should be within 8.51-11.76 MJ/kg at the lowest value >6.2 MJ/kg.

Established in 1936, the Bobruisky hydrolysis plant (White Russia) has placed significant amounts of hydrolysis lignin in the dumps. According to the local mass media, since 2004 the Bobruisky plant has produced fuel briquets from lignin. The plant acquired the abandoned turf briquet manufacturer “Redkij Rog” in the suburb Tugolitsa together with 8 ha land for lignin deposition. In the summer time, the specialists of the plant prepare lignin of 40% moisture content by a standard turf drying and storage technology for the whole-year briquet production. To avoid the undesirable effects of H_2SO_4, freshly obtained lignin is neutralized directly in the hydrolysis apparatus before unloading. In 2005-2006, the state power generation company "Mogilevenergo" ordered a project of a special boiler for lignin incineration in the Bobruysk heat power station TEC-1. According to the project prepared by BelNIItopproject, 17 ha of the local 34-ha lignin dump were adapted for lignin processing. The plant, together with the national Ministry of Natural Resources, has invested $3.2 million in the necessary machines used in peatery and garbage separation. Other $15 million were invested by the local power station and the ministry in the equipment, including boiler E-30-3,9-440DF of the Beloozersky energomechanical plant for lignin incineration. The boiler produces 30-35 t/h of steam at a pressure of 3.9 MPa, consuming 14 t/h of lignin (moisture 55-60%) with the energy conversion efficiency of 87-88%. In 2009, 68000 t of lignin were consumed by this boiler of TEC-1, whereas the other 40000 t were used in the briquets production for household. The heat and electricity produced by this boiler were twice as cheap as those from Russian natural gas. However, the existing lignin dump in Titovka (7 km from Bobruisk) can continuously supply cheap fuel (<20 $/t) for the exploitation period (30 years) of only one lignin-fueled boiler, therefore no more such boilers will be installed.

Unfortunately, this successful project seems to be unique. Indeed, lignin and cellolignin from Rechitsky furfural semi-industrial plant, deposited in Deryazhna and Kazazaevka (Gomel oblast, White Russia), have been used no more as a local fuel source since the plant bankruptcy, although the plant was equipped with a special lignin combustion chamber DE 24/25 with a capacity of 10 MWt (Axis Industries, Lithuania). The modern fully automated mini-heat power station of Rechitsa is designed for combustion of peat and sawdust, but not lignin.

The viscoelastic behavior of hydrolysis lignin under a pressure above 100 MPa promoted its utilization in the production of fuel briquets.[69] In the 1980s, Soviet plants in Bendery, Volzhsk, Zima, Shumerlya, Astrakhan produced ~17,000 tons/yr of lignin briquets as a domestic fuel or reductant for ferroalloys, using press-machines

BPD-2 at a productivity of 0.5-2 ton/h.[5] At present >20 manufacturers, mostly from Ukrainian regions Zaporozhye (Teplosintez, PeKo, Briksell and 4 others), Kharkov (Alfa Tech, Svet Shakhtera), Lvov (Ecotec), Donetsk (Fart PR, Energeticheskiy briquet), Novaya Kakhovka, Lugansk (Grandlug), Vinnitsa (Kamiral); as well as at least 6 companies from Russian regions Sverdlovsk (Uak Chistaya energiya), Vladimir (Triks), Yaroslavl (Yarinterles), Kropotkin Krasnodar krai, Elabuga Perm oblast, Girey Krasnodar krai (Ecosphera K); Onega Arkhangelsk oblast, and Tulun Irkutsk oblast (the former Tulun hydrolysis plant, currently East-Siberian Combine of Biotechnologies) and at least one from White Russia (Bobruysk plant, Mogilev oblast) produce and sell lignin briquets or pellets (Table 9).

A comparison of the lignin briquets from the Onezhsky plant with the ordinary black coal from Kuznetsk basin in a fuel-bed firing in a Universal-6 cast iron boiler installed in the municipal boiler room in Pushchino (Moscow region) has revealed some advantages of briquets dried to a low moisture content (Table 10).

Table 9
Manufacturers of hydrolysis lignin pellets and briquettes

Manufacturer	ton/month	$/ton	MJ/kg	Ash, %	H_2O, %	S, %
Ecosphera K, Girey, Krasnodar krai	1000, briquets		18	19	6	0.4
Bobruysk plant, Mogilev oblast	1200, briquets >25 mm	50-60	>13 (13.6)	<20 (11.8)	<22 (15.7)	0.4
Teplosintez, Zaporozhye	>500, briquets		24.7	20	8.7	0.45
Briksell, Zaporozhye	2500, briquets 30 x 70 mm	120	22-23	10-15	10-12	
Zaporozhye	1000-5000 briquets TBR-1		19	<15	<10	<0.56
Zaporozhye	pellets		18.9-25.6	20	20	0.6
Zaporozhye	300-500, pellets 6-8 mm	75-80 FCA	24.2	6.1	4.9	0.69

Table 10
Comparison of the fuel-bed firing of lignin briquets and black coal in a household Universal-6 boiler[70]

Characteristics	Black coal (Kuznetsk basin)	Briquets (Onega hydr. lignin)
Total moisture, % (as received)	16.1	7.3
Ash content, % db	24.4	5.8
Yield of volatile matter, % (as received)	20.4	59.6
S, % db	0.25	0.05
C, % daf	81.8	59.5
H, % daf	4.42	5.71
Gross calorific value, MJ/kg (kcal/kg) daf	30.74 (7342)	23.38 (5584)
Net calorific value, MJ/kg (kcal/kg) as received	19.11 (4565)	19.16 (4575)
Flue gas temperature, °C	127	146
NO, % x 10^2	10	9
CO, % x 10^2	723	1501
Water pressure, kg/cm^2	1.2	1.2
Water heating in the boiler, Dt, °C	6.8	6.9

According to the author,[70] the (total) efficiency of the boiler with the firing of lignin briquets was 38% higher than that with the use of CC coal. Carbon loss in the combustion of briquets and CC coal was 1% and 48.2% on an initial mass basis, respectively. It was concluded that the emission of harmful gas pollutants into the environment in the combustion of briquets was lower than that in the combustion of coal by a factor of 4.5.

Some enterprises also offer unprocessed hydrolysis lignin/cellolignin as a fuel for local heat power stations and for export into Poland, Turkey, China, and South Korea. Ukrainian businessmen from Zaporozhye offer 1,500-20,000 t/month for 30 €/t FCA or 60 €/t DAF (Izov – Khrubeshov). Linas Agro Group (Lithuania) planned to supply ~50000 t of lignin (standard EN 14961-1:2010) from the former Kedainiai hydrolysis yeast plant for €2.1 million. in 2010. Several Far-Eastern enterprises (Vostochnyj Veter and some others) offer hydrolysis lignin by-products from the Khor and Lesozavodsk plants (minimally 10,000 tons, up to 1 million tons/yr) for South Korean and Chinese consumers by the FOB price within 10-100 $/ton depending on the port (Vladivostok, Khabarovsk, Birobijan). Local authorities (Rechitsky Raizhilkomkhoz) in Gomel oblast offer a tender for 50-225 thousand tons of a lignin-cellolignin mixture (moisture <70%, ash <10%, H_2SO_4<1.5%) from the abandoned Rechitsa furfural plant on the condition of an establishment of a lignin-processing enterprise, creation of at least 5 new jobs, investment of $200-500 thousand at place, and providing fire-protecting measures for the rest of the lignin dump. The starting price is defined as 3.4 €/t of moist lignin-cellolignin mixture. It should however be emphasized that, as described in the previous sections, unprocessed lignin is a bulky material and its transportation is always expensive.

ENVIRONMENTAL ISSUES AND CONSERVATION OF LIGNIN DUMPS

In the last column of Table 7, the lignin dumps subject to smoldering fires are marked. The abandoned Ziminsky hydrolysis plant (Irkutsk oblast) has placed significant amounts of hydrolysis lignin in a 25-ha dump currently under the management of local authorities. According to numerous reports of mass media, in 2003, the local division of the Russian Ministry of Emergency Situations extinguished with water the smoldering lignin till the depth of 2 m on 13.3 ha with 18 firefighting cars and 305 firefighters for 1.5 months. However, in a short time the extinguished fires appeared again, since the lignin layer depth reaches 30 m.

In 2005-2006, the Limnology Institute (Irkutsk) tested its conservation technology for the recultivation of the Ziminsky lignin dump.[71] Earlier, the technology was used successfully for the preservation of the lignin dumps at Selenginsky pulp and paper combine near Baykal. For this purpose, 10000 t of the fly ash from the abandoned coal heat power station TEC-3 in Zima were spread on 1 ha of the lignin dump to a depth from 30 cm to 1-1.5 m (on the smoldering areas). This protected the recultivated area from further smoldering fires. Local authorities together with the A/S Irkutskenergo (owner of the abandoned coal station) planned to cover all the dump area with 262000 t of the fly ash stored on the coal station and invest about $1 million in the gardening of the dump area. The local authorities believe that in time the upper 1.5-m layer of the dump could still be utilized for the production of porous bricks or cement, or for building of roads, whereas the major thick bottom layer would be used as a new source of peat.

Mass media further report that in June-October 2010, following the personal request of Vladimir Putin, a similar technology was also used to extinguish the smoldering lignin of the Kansk hydrolysis plant (Krasnoyarsk krai) near the Trans-Siberian Highway, route M-53: Krasnoyarsk-Irkutsk. The local dump containing ca. 2 million t of hydrolysis lignin on 23 ha was covered with a 30-cm layer of a 2:1 mixture of clay (200000 t) and the fly ash (100000 t) of the Kansk coal power station. To provide gardening, the dung from a local chicken farm was then additionally spread on the surface. The total investment exceeded $1.5 million.

An alternative solution of the lignin dump problem was proposed by the management of the Kirov biochemical plant located in the North-East of European Russia. This plant remains the only hydrolysis enterprise still producing on a relatively regular basis ethanol and dried fodder yeast (ca. 10000 tons in 2010) from wood residues in Russia. Its currently available capacities can consume up to 2 million m^3/yr of solid wood (sawdust and non-utilized wood). In recent years, the plant has also produced fuel pellets from sawdust using the equipment of the German company Münch-Edelstahl GmbH, whereas hydrolysis lignin is not utilized. The lignin dump near the plant occupies by various evaluations from 30 to 60 ha, where millions of tons of hydrolysis lignin are stored. Soon after its opening in 1973, the plant built a water pumping station with an 800-mm pipeline to pump 150-400 m^3/h of water from Vyatka river to the lignin dump. However, in the 2000s the pump failed, and the lignin smoldering became a nightmare for the population of the city. In 2010, the water supply was recovered and the smoldering lignin was converted in a marsh. The expenses exceeded $0.4 million in 2010, total water consumption in the recent few years reached 0.6 million tons. However, the utilization of the fly ash from the local heat power station was not planned by the governments of Kirov city and the region responsible for the lignin dump.

CONCLUSION

In the long history of the Soviet hydrolysis industry, many different applications of hydrolysis lignin as a fuel and as a feedstock for production of value-added chemicals, new polymeric materials, and absorbents were proposed and tested on a large scale.[5-19,32,33,46,47,51,59,60] However, even the utilization of hydrolysis lignin as a fuel (not to speak about more sophisticated applications) required in every case a specially equipped facility and substantial capital investments in the production or storage. Unfortunately, in all applications, lignin is not a unique and currently not the cheapest feedstock, compared to biomass or fossil resources. In a foreseeable prospect, lignin as a fuel for sale will be more expensive than black coal, natural gas, or fuel wood. Although in the last decade industrial hydrolysis lignin has been considered by many Russian authors as a cheap renewable feedstock for the increasing demand of inexpensive carbon fibers,[72-74] polyurethanes,[75] novolac-type phenol-formaldehyde resins, and other polymeric materials,[60] as well as adsorbents,[47,48,51,76] it is not certain whether this market will be capable of digesting annually dozens of millions tons of residual lignin manufactured by producers of the 2nd generation ethanol. Until this can be achieved, the lignin excess can be composted, used for soil improvement, recovery of its fertility, as a substratum for light soil or sand dune strengthening and planting, soil protection from erosion, ground recultivation and pollution protection, since it biodegrades easily in the soil, producing humus and chelate compounds with polyvalent transition metals or radionuclides.[38,77] Numerous studies of the utilization of industrial hydrolysis lignin for these purposes were performed in Russia, White Russia and other former Soviet republics.[28,29,38,53,54,78,79]

Original acidic hydrolysis lignin in amounts of 30-60 t/ha can be utilized for potato cultivation on neutral podzolic soil. After composting with mineral or organic fertilizers, lignin can be utilized for cultivation of various crops or vegetables in amounts of up to 100 tons/ha.[28] In the first year, original hydrolysis lignin is mineralized in various soils with different intensity, lowest in arable land (15%) and highest in woodland (22%), with the meadow occupying an intermediate position (19%). Enrichment with nitrogen source increases lignin mineralization to 19-26% in arable land, 24-30% in woodland and most strongly in the meadow (27-33%).[28,29] Industrial hydrolysis lignin supplemented with 1% lime, 0.7% KCl, 3% ammonium phosphate and sulfate can be readily composted by a mixed fungal (*Phanerochaete* or other white rot fungi) and bacterial cultures within a few months. Lignin composts neutralized and supplemented with cattle manure or chicken dung are ready for use within 3-6 months.

The acidity of industrial hydrolysis lignin provides obvious advantages by its utilization as an underlayer in the preparation of turf for the development of lawns.[80] A layer of hydrolysis lignin with a minimum thickness of 6-8 cm and pH of 2.5-4.2 can be covered with a compost layer and then the grass will be sown. The grass roots do not penetrate deep into the lignin underlayer because of its acidity and this makes possible to improve the acclimation rate of the prepared turf for landscape gardening due to minimum damage of the root system during turf cutting.

Cellolignin obtained right after the hydrolysis process was used for mushroom cultivation and mushroom compost production.[80.81] The sterility and humidity of such a substrate provide substantial advantages for cultivation of mushrooms (champignons, oyster mushrooms). Growing of lignin-degrading mushrooms, such as oyster mushroom and many other lignin degraders popular in the Asian region, provides an opportunity of rapid lignin mineralization along with harvesting of valuable fruit bodies.[82]

In the aforementioned applications, hydrolysis lignin can be used "as received" without fractionation, drying, or neutralization. This drastically reduces capital investment costs and energy consumption in the lignin downstream processing. Last but not least, such applications of hydrolysis lignin would result in numerous positive environmental effects including CO_2

sink. Therefore, it makes sense by planning the future 2nd generation ethanol plants or biorefineries that the constant end users in the neighboring region would be defined for lignin surplus utilization as a fertilizer or structure-forming soil component.

ACKNOWLEDGMENTS: The author is indebted to Dr. Klaus Niemelä and the Organizing Committee of the 4th NWBC, who have inspired him to undertake this study. The support of Svenska Institute (Project no 001-3053, Biobased materials, chemicals and fuels from forest industry waste product, Project coordinator Dr. Olena Sevastyanova, KTH) is also gratefully acknowledged.

ABBREVIATIONS: db – dry basis; daf – dried ash-free; SS NMR – solid state NMR

REFERENCES

[1] G. Gellerstedt, P. Tomani, P. Axegard, and B. Backlund, in "Integrated Forest Biorefineries: Challenges and Opportunities", edited by L. P. Christopher, J. H. Clark, and G. A. Kraus, RCS Publishing, 2013, pp. 180-210.

[2] N. Berglin, A. von Schenck, and C. Hoffstedt, in *Procs. 4th NWBC*, Helsinki, October 23-25, 2012, pp. 221-226.

[3] A. K. Slavyansky, V. I. Sharkov, A. A. Liverovsky, A. V. Buevskoy, F. A. Mednikov *et al*., "Khimicheskaya Tekhnologiya Drevesiny" (Wood Chemistry Technology), Goslesbumizdat, 1962, 576 pp.

[4] V. I. Sharkov, S. A. Sapotnitsky, O. A. Dmitrieva, and I. F. Tumanov, "Tekhnologiya Gidroliznyh Proizvodstv" (Technology of the Hydrolysis Industry), Lesnaya Promyshlennost, 1973, 408 pp.

[5] Yu. T. Kholkin, "Tekhnologiya Gidroliznyh Proizvodstv" (Technology of the Hydrolysis Industry), Lesnaya Promyshlennost, 1989, 496 pp.

[6] M. L. Rabinovich, in *Procs. 2nd NWBC*, Helsinki, September 2-4, 2009, pp. 111-120.

[7] M. L. Rabinovich, *Cellulose Chem. Technol.*, **44**, 173 (2010).

[8] M. I. Chudakov, in *Materialy vsesojuznogo soveshchaniya "Khimiya Drevesiny: Lignin i ego ispolzovanie"* (*Procs. All-Union Conf. "Wood chemistry: Lignin and its utilization"*), Riga, October 1966, pp. 311-322.

[9] M. I. Chudakov, D. Sc. Thesis, Institute of Wood Chemistry, Latvian Acad. Sci., Riga, USSR, 1966, 410 pp.

[10] M. I. Chudakov, *Sb. Trudov VNIIGidroliz* (*Bull. All-Union Res. Inst. Hydrolysis Plant Raw Mater.*), **20**, 151 (1971).

[11] M. I. Chudakov, "Promyshlennoe Ispolzovanie Lignin" (Industrial Lignin Utilization), Lesnaya Promyshlennost, 1972, 216 pp.

[12] M. I. Chudakov, "Promyshlennoe Ispolzovanie Lignin" (Industrial Lignin Utilization), Lesnaya Promyshlennost, 1983, 200 pp.

[13] Gidroliz rastitelnogo syrya i utilizatsiya gidroliznogo lignina (Hydrolysis of plant raw materials and utilization of hydrolysis lignin), *Sb. Trudov VNIIgidroliz* (*Bull. All-Union Res. Inst. Hydrolysis Plant Raw Mater.*), **36**, (1987) 143 pp.

[14] S. R. Alekseev, S. M. Krutov, and M. Ya. Zarubin, *Izvestiya LTA* (*Bull. St. Petersburg Forest Tech. Acad.*) **165**, 65 (1999).

[15] M. Ya. Zarubin, S. R. Alekseev, and S. M Krutov, in "Recent Advances in Environmentally Compatible Polymers", edited by J. F. Kennedy, G. O. Phillips, P. A. Williams, and H. Hatakeyama, Woodhead, 2001, pp. 155-160.

[16] M. Ya. Zarubin, and S. M. Krutov, *Izvestiya LTA* (*Bull. St. Petersburg Forest Tech. Acad.*), **169**, 222 (2003).

[17] I. V. Gribkov, S. M. Krutov, and M. Ya. Zarubin, *Izvestiya LTA* (*Bull. St. Petersburg Forest Tech. Acad.*), **179**, 201 (2007).

[18] S. M. Krutov, I. V. Sumerskiy, V. S. Soultanov, I. V. Gribkov, and M. Y. Zarubin, in *Procs. 16th ISWFPC*, Tianjin, June 8-10, 2011, vol. 2, pp. 835-838.

[19] I. Gribkov, S. Krutov, "Tehnicheskiy Gidroliznyi Lignin. Khimicheskiy Sostav i Stroenie (Gidroliz, Bioetanol, Lignin, Gidroliznyi Lignin, Utilizatsya Tekhnogennykh Otkhodov)" (Industrial Hydrolysis Lignin. Chemical Composition and Structure (Hydrolysis, Bioethanol, Lignin, Hydrolysis Lignin, Utilization of Industrial Wastes)), LAP Lambert Academic Publishing, 2011, 156 pp.

[20] L. V. Pashchenko, V. I. Saranchuk, T. G. Shendrik, and L. Ya. Galushko, *Solid Fuel Chem.*, **32**, 28 (1998).

[21] E. V. Ipatova, S. M. Krutov, in *Procs. Symp. Int. Young Scientists & Specialists, Conf. "Modern Problems and Perspectives of the Rational Forest Use in Market Conditions"*, St. Petersburg, November 10-11, 2011, pp. 359-362.

[22] S. I. Sukhanovskii, E. I. Akhmina, Z. I. Lisina, *Gidroliznaya i Lesokhimicheskaya Promyshlennost* (*Hydrolysis Wood Chem. Ind.*), **8**, 7 (1966).

[23] S. I. Sukhanovskii, E. I. Akhmina, Z. I. Lisina, *Sb. Trudov VNIIGidroliz* (*Bull. All-Union Res. Inst. Hydrolysis Plant Raw Mater.*), **17**, 210 (1968).

[24] I. V. Gribkov, Ph.D. Thesis, St. Petersburg State Forest Techn. Acad., St. Petersburg, Russia, 2008.

[25] D. S. Meteleva, K. S. Khitrin, S. V. Khitrin, S. A. Kazienkov, and S. L. Fuchs, in *Procs. Symp. Int. Young Scientists & Specialists Conf. "Modern Problems and Perspectives of the Rational Forest Use in Market Conditions"*, St. Petersburg, November 10-11, 2010, pp. 192-195.

[26] A. A. Alalykin, R. L. Vesnin, and D. A. Kozulin, *Russ. J. Appl. Chem.*, **84**, 1616 (2011).

[27] I. V. Sumerskii, Ph.D. Thesis, St. Petersburg State Forest Techn. Acad., St. Petersburg, Russia, 2010.

[28] A. A. Komarov, D.Sc. Thesis, Agrophys. Sci. Res. Inst., Russ. Agr. Acad., St. Petersburg, Russia, 2004.

[29] I. N. Khmelinin, V. M. Shvetsova, "Ekologo-biologicheskie Osnovy Vklyucheniya Gidroliznogo Lignina v Pochvoobrazovanie" (Environmental and Biological Backgrounds of Hydrolysis Lignin Involvement in (Fertile) Soil Formation), Nauka, 2000, 143 pp.

[30] V. S. Vinogradova, Ph.D. Thesis, All-Russian Sci. Res. Inst. Agric. Biotechnol., Moscow, Russia, 1993.

[31] N. N. Shorygina and L. I. Kolotova, *Bull. Acad. Sci. USSR*, *Chem. Ser.*, **2**, 505 (1953).

[32] N. N. Shorygina, O. P. Grushnikov, and V. D. Tychina, *Bull. Acad. Sci. USSR*, *Chem. Ser.*, **16**, 304 (1967).

[33] B. A. Trofimov, L. A. Oparina, O. V. Vysockaja, and N. K. Gusarova, in *Sbornik Statey po Materialam Vserossiyskoy Nauchno-Prakticheskoy Konferentsii "Lesnoj i Himicheskiy Kompleksy – Problemy i Resheniya"* (*Procs. All-Russian R&D Conference "Forest and Chemical Industries: Problems and Solutions"*) Krasnoyarsk, 2010, vol. 1, pp. 216-223.

[34] V. V. Budaeva, R. Ju. Mitrofanov, V. N. Zolotukhin, M. V. Obrezkova, E. A. Skiba *et al.*, *Polzunovskii Vestnik* (*Polzunov Bull.*) **4**, 158 (2010).

[35] G. N. Dalimova and E. L. Kristallovich, *Chem. Nat. Compd.*, **35**, 353 (1999).

[36] M. R. Yakubova, V. P. Ryabchenko, A. A. Stancheva, B. Kh. Pulatov, Kh. A. Abduazimov*et al.*, *Chem. Nat. Compd.*, **31**, 534 (1995).

[37] G. G. Podgornova, Z. K. Saipov, L. S. Smirnova, and Kh. A. Abduazimov, *Chem. Nat. Compd.*, **12**, 364 (1976).

[38] O. Belous, D. Ambrazaitienė, A. Žukauskaitė, and G. Shulga, *Environ. Res. Eng. Manage.*, **1**, 43 (2006).

[39] S. M. Krutov, I. V. Gribkov, V. N. Zykov, and M. Ya. Zarubin, in *Procs. 7th EWLP*, Turku, August 26-29, 2002, pp. 483-485.

[40] I. V. Gribkov, S. M. Krutov, A. V. Pranovich, and M. Ya. Zarubin, *Khimiya Rastitelnogo Syrya* (*Chemistry of Plant Raw Materials*), **2**, 15 (2008).

[41] I. V. Sumerskii, S. M. Krutov, A. V. Pranovich, M. Reunanen, and M. Ya. Zarubin, in *Procs. 4th All-Russian Conf. "Novye dostizheniya v khimii i khimicheskoy tekhnologii rastitelnogo syrya"* (*Advances in Chemistry and Chemical Technology of Plant Raw Materials*), Barnaul, April 21-23, 2009, vol. 1, pp. 90-91.

[42] I. V. Sumersky, A. S. Zemlianikina, I. V. Gribkov, M. M. Ravizkiy, Ju. N. Sazanov *et al.*, in *Procs. Int. Conf. "Renewable Wood and Plant Resources: Chemistry, Technology, Pharmacology, Medicine"* St. Petersburg, June 21-24, 2011, p. 222.

[43] M. I. Alibekova and S. M. Krutov, in *Materialy V Mezhdunarodnoj Nauchno-prakticheskoj Konferentsii "Lesa Rossii v XXI Veke"* (*Procs. 5th Int. R&D Conf. "Russian Forests in the XXI Century"*), St. Petersburg, 2010, pp. 174-179.

[44] S. Petrin, I. Valchev, S. Nenkova, and T. Radoykova, in *Abstr. MC Meeting and Workshop "Challenges in Lignin Analytics: Thermal Properties and Quantitation"*, Espoo, August 30-31, 2012, p. 36.

[45] S. M. Krutov, I. V. Sumerskii, A. V. Pranovich, Ju. N. Sazanov, and M. Ya. Zarubin, in *Materialy IV Mezhdunarodnoy Konferentsii "Fizikokhimiya Rastitelnykh Polimerov"* (*Procs. 4th Int. Conf. "Phys. Chemistry of Plant Polymers"*), Arkhangelsk, June 14-17, 2011, pp. 181-185.

[46] Russian Patent RU2409539, 2011.

[47] V. V. Simonova, T. G. Shendrik, and B. N. Kuznetsov, *J. Siberian Fed. Univ.*, *Chem. Ser.*, **4**, 340 (2010).

[48] T. G. Shendrik, V. V. Simonova, V. A. Kucherenko, L. V. Pashchenko, and T. V. Khabarova, *Solid Fuel Chem.*, **41**, 39 (2007).

[49] Yu. M. Velichko, I. N. Zhitar, and A. A. Protsko, in *Materialy Nauchno-prakticheskoi Konferentsii "Vidkhody Ta Vidkhidny Gazy Promyslovykh Pidpryemstv - Znachnii Potentsial Energoresursiv U Narodnomu Gospodarstvi* (*Procs. Sci.-Pract. Conf. Ind. Effluents & Emission Gases as Important Energy Res. for Nat. Economy*), Partenit (Crimea), October 1-5, 2001, pp. 14-15.

[50] N. T. Kartel and A. T. Nikolaichuk, *Ekotekhnol. Resursosberezh.* (*Ecotechnology and Resource Saving*), **4**, 38 (1999).

[51] B. N. Kuznetsov and M. L. Shchipko, *Bioresource Technol.*, **52**, 13 (1995).

[52] Report "O sostoyanii i okhrane okruzhayushchey sredy Irkutskoy oblasti v 2003 godu" ("On the state and protection of the Irkutsk region environment in 2003") Irkutsk, 2004.

[53] S. A. Medvedeva, I. V. Volchatova, G. P. Aleksandrova, I. A. Antipova, L. I. Antonova *et al.*, *Chem. Sustainable Dev.*, **14**, 163 (2006).

[54] I. V. Volchatova, S. A. Medvedeva, L. F. Korzhova, and N. V. Rudykh, *Appl. Biochem. Microbiol.*, **36**, 250 (2000).

[55] V. M. Popov, Ph.D. Thesis, St. Petersburg State Forest Techn. Acad., St. Petersburg, Russia, 1994.

[56] "Lesnaya Entsyklopediya", vols. 1, 2 ("Forest Encyclopedia") (Senior editor G. I. Vorobyev), Sov. Entsiklopediya, 1985, 563 pp.

[57] I. N. Gurkaeva, Ph.D. Thesis, Leningrad Forest Techn. Acad., Leningrad, USSR, 1984.

[58] A. P. Sukhodolov, and V. A. Khamataev, *Izvestiya Irkutskoy Gosudarstvennoy Ekonomicheskoy Akademii* (*Bull. Irkutsk State Econ. Acad.*) **3**, 49 (2009).

[59] M. L. Rabinovich, in *Procs. 4th NWBC*, Helsinki, October 23-25, 2012, pp. 159-168.

[60] K. S. Khitrin, S. L. Fuks, S. V. Khitrin, S. A. Kazienkov, and D. S. Meteleva, *Russ. J. Gen. Chem.*, **82**, 977 (2012).

[61] I. L. Marone, V. E. Maslov, M. A. Slavin, and N. S. Klepikov (Eds.), Ispolzovanie lignina v kachestve energeticheskogo topliva: Obzor (Utilization of lignin as an energy fuel: a review), *Obshchie voprosy mikrobiologicheskoy promyshlennosti: Obzornaya*

informatsiya (*General problems of microbiological industry: review information*) ONSh/TEI Mikrobioprom, 1979, **4,** 44 pp.

[62] N. A. Dudkina, Ph.D. Thesis, Inst. Probl. Chem. Phys., Chernogolovka, USSR, 1991.

[63] M. V. Salganskaya, S. V. Glazov, E. A. Salganskii, V. M. Kislov, A. F. Zholudev *et al*., *Russ. J. Phys. Chem. B*, **2**, 71 (2008).

[64] V. M. Kislov, S. V. Glazov, N. A. Chervonnaya, L. I. Patronova, M. V. Salganskaya *et al*., *Solid Fuel Chem*., **42**, 135 (2008).

[65] G. B. Manelis and E. V. Polianczyk, *Int. Sci. J. Altern. Energy Ecol*., **2**, 123 (2008).

[66] Russian Patent RU2183658, 2002.

[67] Russian Patent RU2460762, 2012.

[68] Russian Patent RU2109216, 1998.

[69] Russian Patent RU2132361, 1999.

[70] V. G. Lurii, *Solid Fuel Chem*., **42**, 342 (2008).

[71] Russian Patent RU2350369, 2009.

[72] T. N. Spirina, N. N. Saprykina, O. A. Andreeva, E. M. Kulikova, Yu. N. Sazanov *et al*., *Russ. J. Appl. Chem*., **85**, 794 (2012).

[73] Y. N. Sazanov, S. M. Krutov, A. V. Gribanov, T. N. Spirina, E. M. Kulikova *et al*., *Russ. J. Appl. Chem*., **84**, 1238 (2011).

[74] Y. N. Sazanov, E. N. Popova, I. V. Sumerskii, M. V. Mokeev, E. M. Kulikova *et al*., *Russ. J. Appl. Chem*., **83**, 1607 (2010).

[75] H. Hatakeyama, Y. Tsujimoto, M. Ya. Zarubin, S. M. Krutov, and T. Hatakeyama, *J. Therm. Anal. Calorim*., **101**, 289 (2010).

[76] O. N. Baklanova, G. V. Plaksin, V. A. Drozdov, V. K. Duplyakin, N. V. Chesnokov *et al*., *Carbon*, **41**, 1793 (2003).

[77] I. B. Kapustina, T. G. Matyushonok, N. M. Pozylova, M. E. Khololovich, L. N. Moskaliuk, *Chem. Sustainable Dev*., **14**, 17 (2006).

[78] L. A. Belovezhets, Ph.D. Thesis, Irkutsk State Univ., Irkutsk, Russia, 2007.

[79] L. A. Belovezhets, I. V. Volchatova, S. A. Medvedeva, *Agrokhimiya* (*Agrochem*.), **1**, 38 (2005).

[80] Russian Patent RU2412583, 2011.

[81] Russian Patent RU2059354, 1996. 264 pp.

[82] M. L. Rabinovich, A. V. Bolobova, V. I. Konrdashchenko, "Teoreticheskie Osnovy Biotekhnologii Drevesnyh Kompozitov", (Theoretical Backgrounds of Biotechnology of Woody Composites), Nauka, 2001, vol. 1,