

WOOD HYDROLYSIS INDUSTRY IN THE SOVIET UNION AND RUSSIA: A MINI-REVIEW

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*Dedicated to the memory of Vassily I. Sharkov,
founder of the Soviet hydrolysis industry*

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The main objectives, feedstock, processes and spectra of products (commodities, specialties, fine chemicals, including pharmaceuticals as by-products of lignin) manufactured by the Soviet and Russian hydrolysis industry for over 75 years are briefly overviewed. The limitations and the difficulties that might have affected this type of industry are also considered. The history of the Soviet/Russian hydrolysis industry clearly shows that, without state subsidies, the production of commodities, such as ethanol or fodder yeast, from lignocellulosic raw materials, can survive only if it also involves the production of heat and electric power from lignin and value-added products, which requires special techniques and equipment, along with a pre-developed market niche.

Keywords: Russia, wood saccharification, hydrolysis industry, percolation hydrolysis, hydrolysis ethanol, lignin utilization, environmental effect

Historical overview

The growth of the Soviet automotive industry at the beginning of the 1930s led to an enormous increase in rubber consumption. Because of the lack of natural rubber sources, the production of butadiene rubber, based on ethanol as a feedstock, was developed (by the Soviet chemist Sergei V. Lebedev). At that time, the Soviet population strongly suffered from hunger, so that cereals, potato or sugar beet molasses could not be used as a starting raw material. That is why, in 1931, a new Chair of Wood Hydrolysis was established at the Leningrad Academy of Forest Technology, under the scientific supervision of Dr. Vassily I. Sharkov. In 1934, the Cherepovets pilot plant, equipped with six 1 m³ reactors, was built to test and optimize different hydrolysis technologies, of which that of Sharkov proved its highest reliability. A year later, the first 50 students graduated from Sharkov's

Chair and, by the end of 1935, the Leningrad demo/industrial plant, with a set of 18 m³ reactors, became operational and started the production of ethanol by dilute-acid hydrolysis of softwood. Until 1985, 18 ethanol, 16 fodder yeast and 15 furfural/xylitol hydrolysis plants were built, operating not only in the forest regions of Belorussia, Ural, Eastern Siberia and Far East, but also in Central Russia, Ukraine and Uzbekistan, where they processed different agricultural wastes. Actually, since the mid-1950s, the Soviet agriculture produced sufficient amounts of potato instead of softwood as a feedstock for ethanol production and, consequently, the production of furfural, fodder yeast and other animal forage, as well as of xylitol as a dietetic sweetener, became the priority task of the hydrolysis industry.^{1,2} However, since the 1960s, all Soviet hydrolysis plants

permanently suffered from irregular feedstock supply.

By the end of the 80s, the combined production capacities (including the idle one) of the Soviet hydrolysis industry comprised:

- up to 500000 metric tons/year fodder yeast (30% of the combined production in the USSR) at plant capacities from 10000 to 60000 tons/year;
- up to 50 million gallons/year (MMgy) ethanol or 4-5% of the combined production in the USSR (at plant capacities from 1 to 4 MMgy);
- up to 65000 tons/year of furfural;
- up to 7000 tons/year of xylitol;
- 25000 tons/year of food-grade carbon dioxide;
- 4000 tons/year saccharified fodder wood.

The annual feedstock demand of the hydrolysis industry was estimated as:

- 8 million m³ of solid wood, including 80% waste wood and 20% fuel wood (at a softwood:hardwood ratio of 3:2);
- 0.7 million tons of agricultural wastes (35% cotton husk, 24% corn cobs, 18% sunflower seed hulls, 13% rice hulls).³

As shown in Table 1, after the subsidies provided by the state or local authorities ceased, most of the hydrolysis plants went through bankruptcy and were sold for \$1-7 million as, in spite of the cheaper feedstock, they could not compete with the plants that used grain or potato.

Dilute acid percolation hydrolysis as a robust and reliable process

During the long history of the Russian hydrolysis industry, several wood hydrolysis approaches have been extensively tested at a semi-industrial scale, among which special mention should be made of:

1. Scholler Tornesch-like percolation hydrolysis at 130-190 °C, by dilute sulfuric acid in stationary packed

bed reactors of different volumes, developed and improved by V. I. Sharkov, S. V. Chepigo, I. I. Korol'kov and colleagues.

2. Continuous counter-current wood hydrolysis by dilute sulfuric acid in 380 m³ column titan alloy reactors, processing 8-12 tons/hour oven dry wood (odw).
3. Continuous mechano-chemical sawdust saccharification by 75% sulfuric acid (1:1.5 w/w), the so-called Riga hydrolysis process, developed by P. N. Odintsov and colleagues and tested at the end of the 1950s - beginning of the 60s. Non-recoverable sulfuric acid was proposed for the simultaneous production of phosphate fertilizer (precipitate) from apatite minerals.
4. Bergius-Rheinau Holzchemie-like hydrolysis process with 41% hydrochloric acid, developed by N. V. Lebedev, N. V. Chalov and colleagues, to produce crystalline glucose from prehydrolyzed wood, performed in a battery of 10 m³ diffusers by the Kansk hydrolysis plant since 1957 until 1974, consuming ca. 13 m³ solid wood per 1 ton of crystalline glucose produced.

However, of these and many other pilot hydrolysis alternatives tested in the USSR since 1934, only the Scholler Tornesch-like percolation hydrolysis, with some variations and improvements, has proven its industrial reliability, in spite of certain well-known limitations.

Indeed, at 130-200 °C, the pseudo-first order rate constants of dilute acid cellulose hydrolysis and glucose decomposition are almost equal to each other (Fig. 1). Therefore, a rapid elution of the soluble sugars released from the hot reactor zone is a prerequisite of a higher sugar yield. However, a 100% conversion of cellulose to glucose can not be obtained principally by this process.

Table 1
Major hydrolysis plants in USSR and CIS

Year	Location/profile	Feedstock	Equipment, product spectrum, yield, annual capacity	Current state
1935	Leningrad/hydrolysis	Softwood (till 1992)	18 m ³ reactors, ethanol, 1941-43 – food-grade hydrocellulose, baker's yeast, 1992 – alcohol-based disinfectants, mineral water	Since 1992 – A/S “Petrospirit”, St. Petersburg
1936	Belorussia, Bobruysk/hydrolysis,	Softwood, corn, grain, molasse	Ethanol, fodder yeast, neutralized and hydrolysis lignin, CO ₂ , 1990 – fuel briquettes, disinfectants, plant-defense and veterinary compounds	Joint venture “Greenfield Ethanol”, Bobruisk (Belorussia – Ireland)
1939	Far East, Khor/hydrolysis	Softwood, grain from Siberia (2003)	Ethanol, 1944 – fodder yeast, 1946 – furfural Food-grade ethanol, fodder yeast Planned: biofuel (butanol)?	2003 – local authority plant “Lazovsky spiritovik”, 2007 – bankruptcy (\$2.5 M) 2008 – negotiations with the State Biotech Corp.
1940	Arkhangelsk/hydrolysis	Softwood	Ethanol, up to 4 MMgy, fodder yeast, CO ₂	1997-2004 – closed, 2003 – A/S “Arkhangelsk plant of technical grade alcohols”
1941	Saratov/hydrolysis	Hardwood	Fodder yeast, 15000 t	1990s – divided into 3 plants, 2008 – animal fodder plant bankruptcy
1943	Siberia, Kansk/biochemical	Softwood	Ethanol, up to 4 MMgy, 1946 – furfural, fodder yeast, 1957-1974 – crystalline glucose (hydrolysis by 41% HCl) 250 kg/t, 600 t Planned: biofuel (butanol)?	Kansk bioethanol plant 2009 – bankruptcy, bought by the State Biotech Corp.
1943	Ural, Tavda/hydrolysis	Softwood, grain (1990s)	Ethanol, 2-4 MMgy, 1946 – furfural, fodder yeast, lignin, CO ₂ Perfume, cosmetics, cleaning compounds Planned: biofuel (butanol)?	2004 – closed, since 2004 – “Tavda microbiology combine”, bankruptcy Area of interests of the State Biotech Corp.?
1943	Siberia, Krasnoyarsk/biochemical	Soft/hardwood Oil paraffines	Ethanol, up to 4 MMgy, 1946 – furfural, fodder yeast, CO ₂ , fodder yeast on paraffines, alcohol-based pharmaceuticals, enterosorbent lignin. Planned: biofuel (butanol)?	2004 – bankruptcy Area of interests of the State Biotech Corp.?
1944	Ural, Lobva/biochemical	Softwood	Ethanol, 180 L/t, 1-2 MMgy, 1964 – fodder yeast, 44 kg/t, 4000 t, 1971 – furfural, 5 kg/t, 220 t, 1972 – CO ₂ liquid, 60 kg/t, 4000 t Planned: biofuel (butanol)?	2009 – bankruptcy, sold for \$1 M Area of interests of the State Biotech Corp.?
1944	Stalingrad/biochemical	Hardwood, grain (1992)	Fodder yeast Currently – baker's yeast, food-grade ethanol, CO ₂	Currently – Borden, Volgograd

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1949	Siberia, Tulun/ hydrolysis	Soft/hardwood	Ethanol, 1965 – fodder yeast, 1969 – furfural Planned: biofuel (butanol, 30000 t; pellets, 100000 t)?	Bankruptcy, bought by the State Biotech Corp. currently – East-Siberian Biotech Combine
1946	Uzbekistan, Fergana/ furan chemical	Cotton hulls	1946, 1993 – ethanol, 1947 – furfural, 1959 – xylitan, 1962 – collactivite (charcoal from hydrolysis lignin), xylitol, 1963 – trioxoglutarate, 1967 – xylitol, 1960, 1968 – furfuryl and tetrahydrofurfuryl alcohol, THF, 2003 – cotton cellulose, alfa-cellulose. Planned: CM-cellulose	2008 – bankruptcy 2009 – 33% capacity
1952	Siberia, Biryusinsk/ hydrolysis	Soft/hardwood	Ethanol, up to 4 MMgy; fodder yeast, up to 12000 t, 1962 – furfural Planned: biofuel (butanol)?	2006 – bankruptcy, bought by the State Biotech Corp.
1954	Onega/ hydrolysis	Soft/hardwood, molasse (1997)	Ethanol, 1959-1996 – fodder yeast, 1974-1994 – furfural, 1997 – ethanol for beverages, 1999 – beer	2003 – bankruptcy
1955	Siberia, Khakas-ky/ hydrolysis	Hard/softwood	Fodder yeast, 28000 t; ethanol, up to 3 MMgy; furfural, CO ₂ , lime	A/S Mibiex, 2009 – bankruptcy
1959	Krasnodar, Kropotkin/ chemical	Corncoobs, sunflower and rice hulls	Furfural, furan, furfuryl and tetrahydrofurfuryl alcohol, THF	2006 – bankruptcy
1960	Ural, Ivdel/hydrolysis	Hard/softwood	Fodder yeast, ethanol	2005 – bankruptcy, closed
1963	Siberia, Zima/ hydrolysis	Soft/hardwood	Ethanol, up to 2.5 MMgy; fodder yeast, furfural Larchwood dihydroquercetin, charcoal	2003 – bankruptcy, closed Area of interests of the State Biotech Corp.?
1972	Far East, Lesozavodsk/ biochemical	Hardwood, grain from Siberia	Fodder yeast, 28000 t; furfural, ammonized lignin, Ginseng extracts	Hydrolysis division closed
1972	Kirov/ biochemical	Hard/softwood	80 m ³ reactors, fodder yeast, up to 60000 t; furfural, 1979 – furfuryl alcohol, 1980 – fodder hydrolysis sugars, 1997 – ethanol, 2008 – E-85 blend, 2008 – fuel pellets, 36000 t, with Syktyvkar subsidiary 72000 t. Production capacities of 36000 m ³ H ₂ daily	Ltd., the only stably working hydrolysis plant
1973	Belorussia,	Hardwood	Tannin extracts, furfural, neutralized lignin, 1982 – saccharified fodder	2009 – bankruptcy

	Rechitsa/pilot		wood, 4000 t	
1974	Volzhsk/ hydrolysis yeast	Hardwood, grain, bran	Fodder yeast, furfural; 1996 – fodder yeast, up to 36000 t	A/S VGDZ

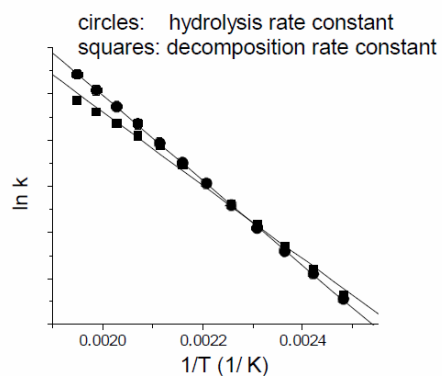


Figure 1: Arrhenius plot of the pseudo-first order rate constants of cellulose hydrolysis and glucose decomposition extrapolated to 1 N H₂SO₄

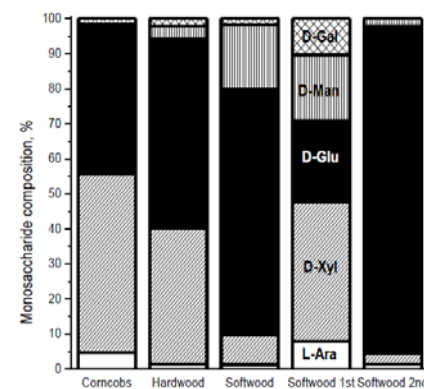


Figure 2: Comparative monosaccharide composition of dilute acid hydrolysates of different plant feedstocks. The composition of the two-stage softwood percolation hydrolysates (softwood 1st and softwood 2nd) is given in comparison with the one-stage percolation hydrolysate

Two opposite factors define the rate of sugar decomposition in the percolation process:

- Diffusion of sugars from insoluble particles slows down with the increase in particle size. This makes sawdust more preferable as a feedstock than wood chips (Table 2).
- Hydrodynamic resistance of the raw material increases with the decrease in particle size and the increase in the degree of cellulose conversion. This, in turn, means that the utilization of sawdust alone and/or the complete hydrolysis of the feedstock do not improve the yield of reducing sugars (RS).

In fact, the real RS yield at a sawdust fraction >50% is 1-3% lower than the calculated one (Table 2) because of hydrodynamic hindrance and increased sugar decomposition. That is why, besides wood chipper, the feedstock preparation facility of the hydrolysis plant includes sawdust sieving equipment, to obtain separate streams of wood chips and sawdust and to use them in an optimum one-to-one ratio. By transporter systems, the shredded wood is transferred to the storage facility, from which certain ratios of chips and sawdust are weighed on transporter balances and loaded into the hydrolysis reactor.

To minimize sugar decomposition, numerous attempts were made at increasing percolation velocity. They included different variants of the installation of the perforated acid-feeding pipe and outlet filters within the hydrolysis zone, to achieve the most efficient percolation – which may be ascending, descending, horizontal or combined.

The optimum one-stage percolation hydrolysis of softwood at a pulpwood chips to sawdust ratio of 1:1 can be characterized by the following average parameters:¹⁻⁶

- yield of reducing sugars: 45-46% odw (60-70% of the original polysaccharide content), *i.e.* consumption of 5-6 m³ solid wood/ton sugars;
- yield of residual solids: 35-37% odw (the so-called hydrolysis lignin,

which usually consists of 60-75% lignin and 15-25% residual cellulose);

- sulfuric acid consumption: 6-7% odw.

As shown in Table 3, about 40% of the working cycle duration in a typical percolation reactor is spent for non-productive operations (feedstock loading, steaming, lignin discharge). However, so far, all attempted arrangements of industrial scale continuous counter-current or percolation processes have been unsuccessful.

In fact, Russian hydrolysis plants are equipped with percolation reactors of different volumes and productivity (Table 4).

The most reliable reactors have been proven to be the steel ones, lined by acid-proof bricks and graphite or ceramic tiles, with a total volume of up to 80 m³ (d/h 0.25-0.35). Titan alloy reactors of higher volume (80-160 m³) were initially considered highly promising because they needed no internal acid-proof brick lining, which significantly reduces the working volume of the conventional steel reactors (Table 4). However, it was later established that, at high activity of hydrogen ions and high temperature, trace amounts of molecular hydrogen may be formed during hydrolysis. The absorption of hydrogen by titan makes the alloy fragile at certain temperatures and greatly increases the risk of reactor destruction during the operational cycle. For this reason, the titan alloy reactors were mostly replaced by the conventional ones, in spite of the relatively lower working volume of the latter, at the same size.

Besides the reactor, a standard hydrolysis facility includes a hydrolysis lignin pipeline with a pressure drop cyclone and a hydrolysate pipeline with several flashing tanks. In such tanks, furfural is evaporated along with the excessive steam pressure. A 1000 m³ inverter tank is used to complete the hydrolysis of soluble oligosaccharides and sugar sulfates formed during acid treatment at high temperatures, operating at 95-98 °C for 6-8 h, with simultaneous self-evaporation of furfural and other volatile components.

Table 2
Calculated yields of reducing substances (RS, % of oven dry wood (odw)) in percolation hydrolysis of standard softwood chips (35 mm long, 5 mm thick) and sawdust (particle size >1 mm) in different ratios

Sawdust fraction, %	0	10	20	30	40	50	60	70	80	90	100
RS Yield, %	43.9	44.5	45.1	45.8	46.4	47.0	47.6	48.2	48.9	49.5	50.1

Table 3
Parameters of one-stage softwood percolation (reactor working volume = 33 m³)

Stage	Duration, min	H ₂ SO ₄ , %	Pressure, MPa	T, °C	Hydrolysate, m ³
Sawdust+chips (1:1) loading (145 kg/m ³)	40	0.8-1	0.0	25-90	circulation
Steaming (200-210 °C), deaeration	30	-	0.9	175	-
Percolation	80	0.7-0.85	1.2	187	40-43
Washing	10	-	1.25	190	9-10
Squeezing out	30	-	1.3	195	7-7.5
Lignin discharge	10	-	0.6-0.7	160	-
Total	200	3.3-3.8% RS in hydrolysate			57-60

Table 4
Characteristics of percolation hydrolysis reactors produced in USSR

Volume, m ³		d/h	Hydrolysis duration, min	Yield of RS, kg/m ³	Productivity, kg RS/h m ³
Total	Working				
18	17	0.29	150-180	60-70	19-20
30	28	0.35	180-210	57-60	18-19
37	30-34	0.27	180-210	55-63	17-19
40	38	0.29	210-260	55-60	16-17
50	42	0.24	210-270	55-60	16-17 (up to 25*)
80	61-64	0.34	270-300	55-60	11-13
160	160**	0.17	450-600	50-60	5-7

*In the reactors with up-flow percolation; **Titan alloy AT-3 (3% aluminum)

The hydrolysate is further pumped through an intermediate holding tank in the neutralisation facility, where the neutralization of sulfuric acid with lime and organic acids with ammonia is performed. Further on, clarification is carried out removing gypsum and lignohumates, to improve the quality of the hydrolysate and to reduce its toxicity for yeast. Water and furfural vapors are cooled in the set of tube

and plate heat exchangers and then roughly separated into several condensers, operated at different temperatures. Further on, the recovered water and furfural streams are collected in separate tanks and furfural is pumped through the separate pipeline to the furfural purification facility.

After one-stage percolation, wood hydrolysates usually contain up to 2% glucose and 3% total hexoses, up to 1%

pentoses, 0.4% oligosaccharides (before inversion) and up to 0.6% sugar decomposition products, including furfural, hydroxymethyl furfural and levulinic acid. The content of volatile fatty acids, mainly acetic acid, may reach 0.65%. Because of a relatively high concentration of sulfuric acid, the pH of hydrolysates usually ranges between 1 and 1.4. Soluble lignohumates result mainly from the condensation of sugars, furfural and phenolics, giving the hydrolysate its dark color and inhibiting yeast growth. Among minor contaminants, methanol, formaldehyde and soluble phenolics are predominant. 2,4-dimethoxy-

phenol is the predominant constituent of volatile phenolics (Table 5).

According to Sharkov *et al.*,³ feedstock and energy consumption per 1 L of 100% ethanol (energy content as Lower Heating Value – 21.1 MJ) obtained by the hexose fermentation of such a hydrolysate comprised:

- 5.5-6.5 kg odw (softwood),
- 0.45 kg pure H₂SO₄,
- 0.51 kg pure CaO,
- 0.07-0.11 MJ steam (0.3 and 1.6 MPa),
- 0.42 kWh (1.51 MJ) electric energy.

Table 5
Average composition of acid wood hydrolysates from Russian plants

Major component	Concentration, %	Minor component	Concentration, mg/l
Glucose	1.3-2.0	Methanol	20-400
Σ Hexoses	1.75-2.8	Ethanol	5-25
Xylose	0.3-0.8	Formaldehyde	50-150
Σ Pentoses	0.4-1.0	Acetaldehyde	0.5-5
Uronic acids	0.1-0.3	Propionaldehyde	0.7-1.2
Oligosaccharides	0.1-0.4	Acetone	0.4-2
Furfural	0.02-0.12	Methyl formate	0.6-6
5-Hydroxymethyl furfural	0.03-0.18	Terpenes	0.1-5
Levulinic acid	0.1-0.3	Σ Phenolics	50-500
VFA as acetic acid	0.25-0.65	Volatile phenolics	2-20
Lignohumates	0.15-0.25	Phenol	0.4-1
Sulfuric acid	0.4-0.7	Guaiacol	0.3-2
Inorganic salts	0.1-0.3	2,4-Dimethoxyphenol	0.5-10

Also, the decomposition of monosaccharides during dilute acid hydrolysis of plant feedstock increases¹⁻⁵ in the following order (values in parentheses represent the relative decomposition rates compared to glucose):

D-Glu (1) < *D-Gal* (1.1) < *D-Man* (1.5) < *L-Ara* (1.7) < *D-Xyl* (3)

That is why, various two-stage percolation protocols were developed to obtain a higher yield of pentoses and of other hemicellulose components. Actually, before a major percolation by 0.8-1% acid at 185-

190 °C for cellulose decomposition, mild prehydrolysis was proposed as a reasonable stage. The following variants were industrially tested to obtain a higher sugar yield, higher RS concentrations or to reduce water and acid consumption:

- percolation by 0.5% acid at 130-145 °C to obtain 3.5-4.2% primarily pen-tose hydrolysate (C5:C6 sugar ratio = 7:3) with a pentose yield up to 100%, then the major percolation step with a hexose yield up to 75% (2.5-3.2% RS, C5:C6 sugar ratio is 1:4);

- wood impregnation and percolation at 145 °C by the hexose hydrolysate from the major percolation stage, to finally obtain 4.5-5.3% combined pentose-hexose hydrolysate and to save up to 20% acid and 50% water;
- moist wood impregnation with 3-4% acid, squeezing out by steam (0.2-0.3 MPa) to obtain a final acid concentration of 1-1.2%, and subsequent washing with water. Under such conditions, the actual yield of pentoses reached the theoretical one, and the total sugar yield after the major percolation stage reached 50% odw or 77% of the polysaccharide content in the mixed softwood/hardwood feedstock.

The composition of monosaccharides in the one-stage percolation hydrolysate varies with the feedstock. Usually, the content of pentoses in the one-stage softwood hydrolysate does not exceed 10% of the total

monosaccharide content, whereas in hardwood and corncobs, they constitute 40 and 55% of the monosaccharides, respectively. Two-stage percolation allows production from softwood first-stage hemicellulose hydrolysate, containing almost equal amounts of hexoses and pentoses, whereas in the second stage, almost exclusively hexose hydrolysate with a residual pentose content <5% can be obtained (Fig. 1).

Taken together, dilute acid percolation hydrolysis of wood in acid-proof lined steel reactors of an appropriate volume and its geometry proved its reliability for high-yield prehydrolysis of the hemicellulose fraction, as well as for the production of hydrolysates containing up to 5-5.5% C5+C6 sugars, at a total monosaccharide yield of up to 80% and appropriate energy consumption.¹⁻⁶

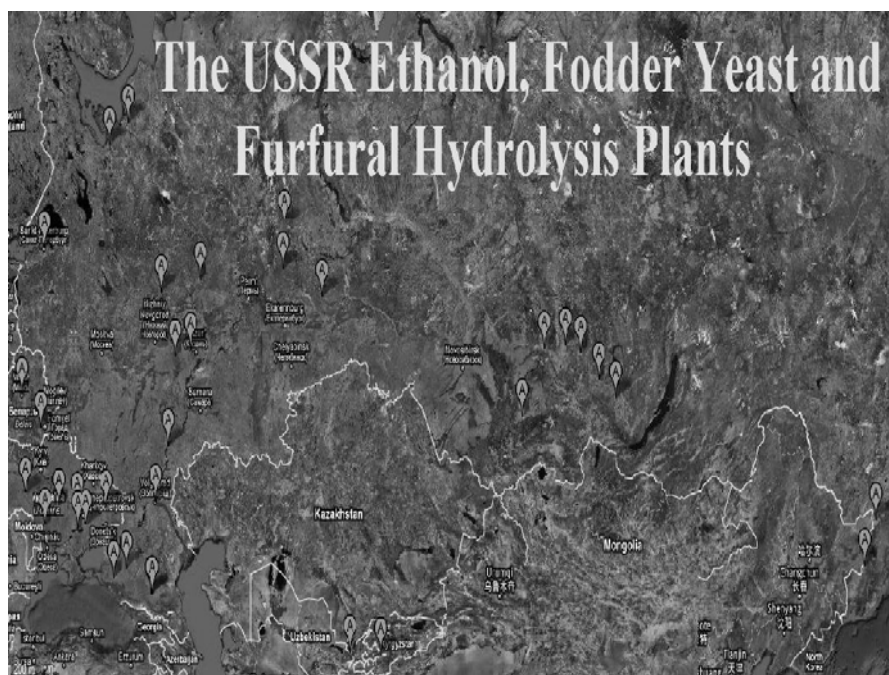


Figure 3: Location of the main hydrolysis plants in the former Soviet Union

Air emissions

A Russian yeast/ethanol-yeast plant of an average capacity produced 2000-5000 m³/h of air emissions, of which 80-90% contributed to inverters, neutralizers and dryers. Table 6 lists the major constituents of air emissions of the major production facilities (excluding boilers).

The combustion of hydrolysis lignin in

boilers represents another serious air pollution problem of this type of industry. Boilers provide ca. 60% of the air pollution of Russian hydrolysis plants. Their emissions usually consist of 20-25% dust, 20-25% SO₂ and 3-5% CO. In addition, they contain 8.5 kg flying ash per one ton of processed wood (odw).

By the end of the 1980s, the protesting

actions of the inhabitants from the surrounding areas, whose children strongly suffered from respiratory and allergic diseases, forced the former Minister of Microbiological and Medicinal Industry of the USSR to stop the ethanol and yeast production at the Kirishi hydrolysis yeast plant (St. Petersburg region) and to completely change the plant profile.

Solid wastes and by-products of Russian hydrolysis plants

Ethanol, along with other valuable by-products obtained in the same process, namely, fodder yeast protein, furfural and food-grade carbon dioxide, constitutes less than one third of the dried softwood feedstock refined by this technology (Table 7). Another nearly one third constitutes wastes, such as sediment slime and

distillation solids. The rest is the so-called hydrolysis lignin, which constitutes up to 40% of the feedstock dry weight (Table 8). Lignin itself constitutes only 50-60% of the solids of hydrolysis lignin, of which one quarter is represented by the recalcitrant polysaccharide fraction. The rest consists of ash, residual amounts of sulfuric acid and soluble monosaccharides, as well as alkali-soluble lignohumates. Hydrolysis lignin directly from the reactor usually consists of only one third of solids, whereas the rest is moisture. For this reason, its heat capacity is 3-4 times lower than that of the oven dry hydrolysis lignin (Table 9). The utilization of unprocessed hydrolysis lignin as a fuel in usual boilers is limited, not only because of its high moisture content, but also because of the difficulties of drying and of the presence of residual sulfuric acid.

Table 6
Average air emissions of hydrolysis facilities, kg/t odw

Water vapor	Furfural	VFA	Methanol	Solids (mainly yeast and lignin dust)
1000-1500	3-6	1	0.5	2-3

Table 7
Yield of products and wastes (kg) from 1 ton odw softwood by ethanol production

Ethanol	Fodder yeast	Furfural	Hydrolysis lignin	CO ₂	Slime	Distillation waste
160-175	30-40	5-7	350-400	70-90	150-225	100-150

Table 8
Yield and content of hydrolysis lignin

Feedstock	Yield, % odw	Major contaminants	Oven dry mass, %
Softwood	38	Polysaccharides	15-30
Hardwood	32	Residual monosaccharides	2-10
Cotton hulls	37	Lignohumates (alkali-soluble)	5-15
Corncoobs	24	Sulfuric acid	0.5-2
Sunflower seed hulls	32	Ash	2-10

Table 9
Heat capacity of moist hydrolysis lignin

Moisture, %	0	60	65	68
Heat capacity, kJ/kg	24870	7750	6150	5650

The annual production of such hydrolysis lignin in the former Soviet Union reached 1.5 million tons by the end of the 1980s. However, only 30-40% of it was really utilized, whereas the rest formed giant landfills around the hydrolysis plants, creating serious environmental problems because of self-ignition. For example, the current lignin waste stocks in the Irkutsk region, where only four plants are located, exceed 20 million tons. However, some hydrolysis plants, like the oldest Bobruysk one in Belorussia, consider now their huge hydrolysis lignin landfills as possible fossil fuel resources and plan its combustion in the local heat power stations instead of, or along with turf.

Actually, during the long history of the Soviet hydrolysis industry, numerous lignin applications have been proposed and tested,⁷⁻³¹ such as:

- Hydrolysis lignin (60-65% moisture) as a fuel in specialized lignin/black oil boilers E-75-40K, which consumed 32 tons of moist lignin and produced 65-75 tons of overheated steam (440 °C, 4 MPa) per hour. Such a boiler was additionally equipped with a drying chamber heated by flue gas recirculation. These gases were initially produced by the side torch fueled by black oil. Dried lignin was then milled to dust, by a wet fan mill, and burned in a coal dust torch;
- Unprocessed lignin as a burning clay filler for the production of bricks;
- Lignobriquettes as domestic fuel or reductant for ferro-alloys (annual production of 17000 tons in the mid-1980s). Unfortunately, this application was limited by its relatively high production costs;
- Granulated lignin as a reductant in the production of crystalline silicon and alumo-silicide alloys, which replaced up to 30% of the wood coal;
- Lignin flour (powder) as a filler in the polymer industry;
- Nitrolignin (moist hydrolysis lignin nitrated by HNO₃) and nitrolignin saponificated by Na₂CO₃ (Igetan™) as surfactants by oil well drilling. Their combined annual production reached 15000 tons in the 1980s;
- Lignin rust remover paste (sulfate-, chloride-free ammonolyzed lignin+FeO or hydrolysis lignin+H₃PO₄, 1:1);
- Collactivite™ charcoal (lignin oxidized by 20% oleum), annually produced in amounts of 5000 tons in the middle of the 1980s and used by some hydrolysis plants for discoloration of hydrolysates by xylitol production;
- Carbonized (pyrolyzed) lignin for CS₂ production. Pyrolysis of hydrolysis lignin to produce coke was performed in a Biryusinsk hydrolysis plant, with a demonstration-scale installation capable of utilizing ca. 10000 tons/year moist lignin;
- Alkali-extracted solid residue of hydrolysis lignin alone and in combination with iodine as an enterosorbent Polyphapan™, used both as a medicine and veterinary compound, currently produced at St. Petersburg and Manturovo plants in amounts of ca. 300 tons/year;
- Lignohumate (oxidized alkaline extract of hydrolysis lignin) as a plant growth regulator;
- Simultaneous production of synthesis gases (70%, of which 38% CO, 17% CO₂, 3.5% H₂, 7.5% CH₄, 3% C₂H₆) and coke (30%), by combined gasification/pyrolysis of moist (50%) hydrolysis lignin;
- Humic acid-like immunostimulators Olipifat™, Ligfol™ (oxidized alkaline extract of hydrolysis lignin supplemented with pyrophosphate) with a broad spectrum of activities;
- Complex organomineral fertilizer for sandy or clay soils (90% hydrolysis lignin, 5% lime, NH₄NO₃, superphosphate, KCl);
- Molding composition from the 90% hydrolysis lignin and 10% heavy coal tar fractions;

- Oil-collecting absorbent (insoluble fraction of the alkali-extracted hydrolysis lignin);
- Hydrolysis lignin (20-40%) in combination with urea-formaldehyde for fiberboard production;
- Lubricant composition (25% hydrolysis lignin);
- Liquid fuel composition as a stabilized suspension of coal dust and moist hydrolysis lignin (1:1);
- Hydrolysis lignin as an additive in concrete mixtures;
- Heat-insulating compositions (molding of wood fiber, hydrolysis lignin and Na_2SiO_3).

Obviously, it is not possible to adequately describe all tested hydrolysis lignin applications in a short review. However, one should observe that, in each case, the utilization of hydrolysis lignin requires a specially designed industrial facility.

Russian hydrolysis industry since 1991

In the Soviet Union, the wood hydrolysis industry occupied a well-established production niche, mainly because of the low efficiency of the collective agricultural sector, which could not harvest and store sufficient amounts of grain, potato and sugar beet for foodstuff, forage and technical needs.

Since 1992, the situation changed dramatically with the beginning of privatization and ceasing of state subsidies as fixed procurement prices. In the following ten years, all plants tried to resplace partially or fully the wood and lignocellulosic feedstock with grain, bran, molasses, to produce alcoholic beverages, alcohol-based medicines and extracts, cleaning compounds, as well as animal fodder premixes. Most plants producing hydrolysis lignin were penalized by the environmental control authorities. Until 2003, the local authorities tried to support this industry. However, in the last decade, most of the Russian hydrolysis plants went through bankruptcy and were sold for \$1-7 million (Table 1). The only positive example was the relatively new and large Kirov biochemical plant, originally built to produce fodder yeast and furfural derivatives. However, in 1997, it started the

production of ethanol, too, now currently producing E85 blend and 36000 tons lignin fuel pellets *per annum*. Moreover, it has equipped its subsidiary at Syktyvkar pulp mill (Komi Republic) to produce additional fuel pellets. The plant also developed industrial capacities for hydrogen gas production.

In 2008, following the global tendency towards biofuel development, the Russian government established a new State Biotechnology Corporation A/S, which developed “A Concept of Second-Generation Biofuels and Wood Biorefinery for the Russian Hydrolysis Industry”, namely 68 plants – including those utilizing hemicellulose hydrolysates from sulfite pulping. The list of tentative products includes butanol as the primary product of interest, as well as ethanol, acetone, hydrogen gas, food-grade carbon dioxide, animal fodder supplements, lignin fuel pellets, excessive heat power (from combustion of lignin as a fuel for plant boilers), diet food and pharmaceutical ingredients (for example, larchwood dihydroquercetin and arabinogalactan), etc. The planned production capacities included two East Siberian bankrupt plants in Tulun and Kansk, and the plant in Ust'ilimsk, built by the end of the Soviet era, but unoperational eversince. These plants will operate as the East-Siberian Biotechnology Kombinat A/S, which has already purchased Tulun plant for \$1.5 million with a governmental credit line. The State Biotechnology Corporation also considered purchase of the Far-Eastern Khor plant and the Ural bankrupt hydrolysis plants in order to make them operational again. The necessary investment in the first 3-4 plants was estimated to reach around \$200 million and is planned to be made between 2009 and 2011. The new Corporation announced an investment of \$1.5 billion, planned to be made during the next decade in 30 ethanol and fodder yeast plants under bankruptcy, in order to reach a combined production of 650 MMgy butanol as early as in 2017.

The major objective of the Corporation was to establish a demonstration plant in the East Siberian Tulun. The Corporation planned investments of \$60 million, to

achieve a production of 6-10 MMgy butanol, >1 MMgy acetone, about 60000 tons/year of lignin fuel pellets and 13000 tons/year of microbial fodder protein by the end of 2010. The annual feedstock consumption was expected to be of 290000 m³ solid wood.³² However, the financial crisis of 2009 has postponed these plans until better times.

CONCLUSIONS

Wood percolation with dilute sulfuric acid in acid-proof brick-lined steel reactors has proven its reliability and robustness, compared to other industrially tested processes in the USSR. The developed technique was also successfully used for the treatment of a variety of agricultural wastes, along with sewage sludge and cereal grain, as well as for steam cracking or mild acid prehydrolysis of hemicelluloses. The achieved ethanol yield (ca. 50 gallons per one ton of dried softwood) may be substantially improved (at least by 10%) by pentose-fermenting ethanol-producing organisms. The introduction of these organisms and of two-stage percolation into wide industrial practice would permit yields of above 55 gallons ethanol per one ton of dry plant feedstock, even with the existing facilities, regardless of the plant feedstock (softwood, hardwood or agricultural wastes). Under these circumstances, the yield of ethanol produced by Russian percolation hydrolysis plants might be quite comparable to the yields of the processes developed by Abengoa Bioenergy Biomass of Kansas, LLC or ALICO, Inc. of LaBelle, Florida. These companies, selected in 2007 by the US Department of Energy for federal financial support (<http://www.energy.gov/print/4827.htm>), are planning to produce 11.3 and 13.9 MMgy by an agricultural feedstock consumption of 700 and 770 tons per day, respectively. The existing industrial potential of Russia, along with the accumulated practical experience may be also used to produce dilute-acid pretreated and highly reactive plant feedstock for simultaneous saccharification and fermentation, provided that adequate modern techniques are used to prevent air emissions and water pollution by this type of industry.

Nevertheless, hydrolysis of wood and of

other lignocellulosic plant feedstock as a source of bulk chemicals, like ethanol, or for the production of animal fodder, was and still remains an industrial emergency. Without state subsidies or legislative privileges (*e.g.*, restrictions in biofuel production from food sources or fixed acquisition prices), the wood hydrolysis industry cannot be competitive, because of its lower yield and complex technology, as compared to the ethanol production from food feedstock. The recent financial crisis has clearly demonstrated that this type of industry suffers mainly from the high volatility of both oil and corn prices.³³

Complete utilization of non-hydrolysed residues is a prerequisite for successfully solving the major environmental problems of the acid hydrolysis of plant feedstock. However, the direct use of hydrolysis lignin as a boiler fuel or for any other needs requires special equipment and technologies and makes its utilization expensive. Some types of equipment were designed and tested at pilot and industrial scales, because Russian hydrolysis plants provide an ideal demonstrational range for such trials. Small-scale value-added products obtained by the alkaline treatment or extraction of hydrolysis lignin, such as veterinary compounds and medicines, absorbents, humic-like plant growth regulators, rust and corrosion inhibitors, have demonstrated their economic reliability in Russia. They significantly improve the overall economics of the commodities produced by lignocellulose hydrolysis, requiring equally substantial marketing efforts.

REFERENCES

- ¹ V. I. Sharkov, "Hydrolysis industry", Moscow-Leningrad, GLBI, Vol. 1, 1945, 288 pp.; Vol. 2, 1948, 490 pp., Vol. 3, 1952, 552 pp. (in Russian).
- ² A. K. Slavyansky, V. I. Sharkov, A. A. Liverovsky, A. V. Buevskoy, F. A. Mednikov, V. A. Lyamin, F. T. Solodky, E. M. Tsatska, O. A. Dmitrieva and B. F. Nikandrov, "Wood Chemistry Technology", Moscow, Goslesbumizdat, 1962, 576 pp. (in Russian).
- ³ V. I. Sharkov, S. A. Sapotnitsky, O. A. Dmitrieva and I. F. Tumanov, "Technology of the Hydrolysis Industry", Moscow, Lesnaya promyshlennost', 1973, 408 pp. (in Russian).
- ⁴ Yu. T. Khol'kin, "Technology of the Hydrolysis Industry", Moscow, Lesnaya promyshlennost', 1989, 496 pp. (in Russian).

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⁵ I. I. Korol'kov, "Percolation Hydrolysis of Plant Raw Materials", Moscow, Lesnaya promyshlennost', 1990, 272 pp. (in Russian).

⁶ V. A. Elkin, V. A. Vyrodov, V. V. Ryabov and M. M. Krechmer, "Equipment and Design of the Hydrolysis and Forest Chemical Industry", Moscow, Lesnaya promyshlennost', 1991, 205 pp. (in Russian).

⁷ M. I. Chudakov, "Industrial Lignin Utilization", Moscow, Lesnaya promyshlennost', 1983, 200 pp. (in Russian).

⁸ SU Patent 610854, Method of reprocessing hydrolysis lignin, 1978.

⁹ SU Patent 706120, Apparatus for flushing collactivity, 1979.

¹⁰ SU Patent 1010066, Process for producing nitrogen-containing derivative of hydrolysis lignin, 1983.

¹¹ SU Patent 907003, Method for preparing nitrogen- and sulfur-containing lignin derivatives, 1982.

¹² SU Patent 981323, Process for producing molding composition from hydrolysis lignin, 1982.

¹³ SU Patent 994548, Process for producing coal from hydrolysis lignin, 1983.

¹⁴ SU Patent 1578147, Method of processing hydrolysis lignin, 1990.

¹⁵ SU Patent 1663009, Method of producing carbon from hydrolysis lignin, 1991.

¹⁶ RU Patent 2109216, Process of burning of hydrolyzed lignin in boiler furnace, 1998.

¹⁷ RU Patent 2141334, Method of preparing "Olipifat" for the treatment of patients with non-oncological pathology in the body, 1999.

¹⁸ RU Patent 2130895, Method for producing granulated activated carbon, 1999.

¹⁹ RU Patent 2132361, Method of briquetting hydrolysis lignin, 1999.

²⁰ RU Patent 2132769, Method of preparing molding material for manufacturing facing layer of chipboards, 1999.

²¹ RU Patent 2183658, Liquid fuel composition and method of preparation, 2002.

²² RU Patent 2217463, Method for preparing huminic acid salts, 2003.

²³ RU Patent 2205166, Drilling solution, 2003.

²⁴ RU Patent 2209196, Hydrolysis lignin-based organomineral fertilizer, 2003.

²⁵ RU Patent Appl. 2003124410, Raw mix for manufacturing heat-insulation articles, 2005.

²⁶ RU Patent Appl. 2004131076, Sorbent for collecting oil and oil products, method for producing sorbent and method for collecting oil and oil products, 2006.

²⁷ RU Patent Appl. 2004133434, Composition for light concretes gluing and method for composition production, 2006.

²⁸ RU Patent 2291173, Corrosion modifying

agent, 2007.

²⁹ RU Patent 2302866, Enterosorbent and method for its preparatuion, 2007.

³⁰ RU Patent 2318013, Composition to reduce wear in wheel-rail friction pair, 2008.

³¹ RU Patent 2342339, Complex additive for concrete mixes and water mortars, 2008.

³² P. Stepanenko, *The Chemical Journal*, **9**, 34 (2008) (in Russian).

³³ M. L. Rabinovich, *Biotechnol. J.*, **4**, 1117 (2009).