CHEMISTRY AND TECHNOLOGY OF WOOD PROCESSING

УДК 630*863

V. S. Boltovski, D. Sc. (Engineering), professor (BSTU)

THE COMPOSITION OF HYDROLYTIC LIGNIN FROM DUMPS OF JSC "BOBRUISK PLANT OF BIOTECHNOLOGIES" AND RATIONAL DIRECTIONS OF ITS USE

The composition of a hydrolytic lignin from dumps of JSC Bobruisk Plant of Biotechnologies is investigated. It is shown that long storage of lignin resulted in the reduction of the total content of polysaccharides at significantly smaller degradation of the actual lignin. The main directions of use of a hydrolytic lignin are considered, and recommendations about the most perspective and rational directions of its utilization are made: receiving fuel briquettes and pellets, organo-mineral fertilizers and sorbents.

Introduction. Lignin of cellular tissue of plant biomass is a high molecular natural polymer with aromatic structure, which when processed as a result of hydrolytic polycondensation transformations forms a three-dimensional reticulate structure. It is a complex comprising secondary aromatic structures (actual lignin significantly changed at hydrolysis), a part of non-hydrolyzed polysaccharides and unwashed monosaccharides, substances of the complex of lignin-humic group, mineral or organic acids, ash elements and other substances [1, 2].

The problem of hydrolytic lignin utilization has existed since the creation of the industry, and has not been fundamentally solved yet, despite the numerous methods of its processing, including those realized in industry.

The main areas in the processing of hydrolytic lignin [3] are: its use in-natural form (in ferrous and nonferrous metallurgy, in the production of lightweight refractory products – as burnable additives in the preparation of household fuel, as an adsorbent, etc.). It is also used after thermal processing (receiving lignin's active and granular coals), after chemical processing (receiving nitrolignin and its modifications, a collectivit, biologically active substances – ammonium salts of polycarbonic acids and lignin stimulating fertilizers, medical and lignin "polyphepanum" applied as an enterosorbent for prophylaxis and treatment of diseases of the gastrointestinal tract of animals and humans instead of an absorbit), and as power fuel as well.

A significant amount of hydrolytic lignin sufficient for industrial processing has accumulated

in the territory of the Republic of Belarus in the dumps, which occupy large areas and are a danger to the environment.

The data published in literature characterize chemical composition and properties of hydrolytic lignin obtained after hydrolytic processing of vegetable raw materials. For qualified decisions on the most efficient ways to use lignin from dumps it is necessary to determine its properties and to select the most promising directions of its processing.

Main part. For the analysis we have used samples of hydrolytic lignin, which are selected according to the requirements of TU BY 004791190. 005-98 and taken from a dump of JSC "Bobruisk Plant Biotechnology", located in the settlement of Titovka on industrial pilot site of field drying of lignin.

Determination of the chemical component composition of hydrolytic lignin samples and made of it briquettes and pellets was performed by the analysis methods accepted in chemistry of wood and cellulose [4] and hydrolyzing production [5].

Thermogravimetric analysis of pine, birch and hydrolytic lignin samples was performed on a TA-4000 METTLER TOLEDO (Switzerland) device under the following conditions: a shot of sample 30 mg, temperature rise rate of 5°C/min in the range of 25–500°C, air blowing 200 ml/min.

The results of determination of the main components in the hydrolytic lignin samples are shown in Table 1.

Comparison of the results of analysis of hydrolytic lignin from dumps with average composition of the lignin obtained immediately after the hydrolytic processing of wood (Table 2) shows that the decrease of the total content of polysaccharides at substantially less degradation of the actual lignin occurred as a result of long-term storage.

At the same time, hydrolytic lignin contains the same basic components as the timber (Table. 3), but smaller amount of polysaccharides and larger quantity of non-hydrolyzed actual lignin at hydrolytic processing, i. e. represents timber after the hydrolysis treatment (plant biomass).

The results of thermal gravimetric analysis of wood and hydrolytic lignin (mass loss and the differential thermal gravimetry characterizing the rate of weight loss), showed that the thermal decomposition of pine and birch wood and hydrolytic lignin was similar:

– the removal of free water (mass loss of pine and birch is 6.2–6.4%, respectively, mass loss of hydrolytic lignin is- 3.8–4.2%) takes place in the temperature range of 25–100°C;

– at temperatures above 100 up to 300°C there is a desorption of the combined water with the mass loss of the wood 4.2–4.3% and hydrolysis lignin 4.1–5.5%;

– the maximum rate of mass loss of wood, accompanied by its active thermal decomposition and mass loss is observed at 300°C, maximum rate of mass loss of hydrolytic lignin is 280°C, i. e. the main components of the original wood and wood after hydrolysis processing (hydrolytic lignin) burn down almost in the same temperature interval;

– further increase in temperature leads to a deeper destruction, loss of weight and carbonation with the formation of oil carbon sludge in the amount of 2.3–5.5% when burning wood and 3.9–5.9% – when burning hydrolytic lignin.

The results of thermogravimetric analysis confirm the results and the conclusions drawn on the basis of determining the chemical component composition of wood and lignin hydrolysis and that hydrolytic lignin is a timber after the hydrolysis treatment and is similar in properties during the combustion of wood.

Table 1

The content of the main components in the hydrolytic lignin from the dump, % of the bone dry solids

Name of the component	The average values in the samples taken at depth, m		
	2	4	6
Total polysaccharides, including: – easy- hydrolysable – – hard hydrolysable	21.51 1.63 19.88	19.61 1.65 17.96	17.67 1.80 15.87
Cellulose	18.86	17.04	19.95
Lignin	47.94	52.71	49.32
Ash	9.56	5.65	10.61
Acidity (in terms of $H_2 SO_4$)	0.1	0.1	0.1

Table 2

The content of the main components in timber after hydrolysis treatment (lignin hydrolysis)

Name of the component	Content, % by weight of bone dry matter	
	[2]	[7]
Polysaccharides	12.6–31.9	19.9
Actual Lignin	48.3–72.0	57.1
Acidity (evaluated in H_2SO_4	0.4–2.4	–
Ash content	0.7–9.6	–

Note. In reference [7] there are the data on the determination of hydrolytic lignin of Bobruisk hydrolysis plant; as polysaccharides – only cellulose content.

Table 3

Chemical composition of different wood species [1]

Name of the component	Content, % by weight of bone dry matter			
	spruce	pine	birch	asp
Total polysaccharides, including: – easy- hydrolysable – hard hydrolysable	65.3 17.3 48.0	65.5 17.8 47.7	65.9 26.5 39.4	64.3 20.3 44.0
Cellulose	46.1 (44.2)	44.1 (43.3)	35.4 (41.0)	41.8 (43.6)
Lignin	28.1 (29.0)	24.7 (27.5)	19.7 (21.0)	21.8 (20.1)
Ash	0.3	0.2	0.1	0.3

*In the parentheses there is a cellulose content without hemicellulose and lignin, according to reference [6].

Hydrolytic lignin has variety of application. Promising uses for industrial production are, for example, products based on its high sorption properties (sorbents, including enterosorbents of medical purpose – medical lignin and polyphepanum) [4], active coals, long-acting fertilizers and other products [3]) and its calorific value, (as fuel). The calorific value of hydrolytic lignin at a humidity of 60% is 7,750 kJ /kg, at 65% – 6,150 kJ/kg and 68% – 5,650 kJ/kg. The average calorific value of absolutely dry lignin is 24,870 kJ/kg [2].

Currently, the subordinated enterprise JSC "Bobruisk plant biotechnology" organized production of fuel briquettes (TU BY 700068910.019-2008) and pellets of hydrolytic lignin.

The results of determination of the main components of the briquettes and pellets made of hydrolytic lignin are shown in Table 4.

As Table 4 shows the briquettes and pellets from hydrolytic lignin do not differ from those made from the timber, but have a smaller content of polysaccharides and a larger one of lignin.

It may be stated that large-capacity utilization of hydrolytic lignin is in agriculture as organic fertilizer (in natural form), organic-mineral fertilizer (mixed with mineral components or waste of microbiological industry – spent cultural liquid after fermentation of microorganisms, or in a mixture with various mineral substances-after composting – bio-humus), lignin-stimulating fertilizer (after modification by oxidative degradation in various ways with simultaneous enrichment by nitrogen and microelements.

Use of fertilizers based on hydrolytic lignin provides:

– improvement of soil physical properties and conditions for the development of saprophytic fungi;

– the creation of a loose surface layer, ensuring a normal water-air exchange;

– activation of nitrification processes in the soil;

– the prolonged action, creating conditions for the retention of nutrients (due to high adsorption capacity of lignin) and their gradual consumption by plant root system and preventing their fast washing away by atmospheric precipitation and soil waters;

– growth acceleration and yield gain of agricultural plants (e.g., application of lignin in a mixture with ammonia or urea raises the yield capacity of winter rye by 16–17%, and lignin stimulating fertilizer in the amount of 0.4 t/ha leads to increase in potato crop capacity by 15–30% [3].

Derived from the hydrolytic lignin sorbents have the following advantages [5]:

– have a high sorption capacity. Specific surface of starting hydrolytic lignin containing 15.2% of cellulose, is 10.14 mg/g. And specific surface of enterosorbent of medical purpose (medical lignin obtained on its basis after appropriate treatment is 16.3 mg/g. A pore space of the starting lignin is 0.651 cm^3/g and that of a therapeutic lignin is 0.816 cm^3/g, [4]. The total pore space of polyphepanum is 0.8–1.3 cm^3/g. The distribution coefficients of cesium and strontium between their test solutions and enterosorbent reach 400–900, and the sorption of microorganisms from the cultural media – 108 cells/g of preparation;

– have a low prime cost, since they are the remains after the hydrolytic treatment of plant biomass;

– are a natural plant biomass;

– have low ash content when burnt.

Possible fields of application are:

– cleaning of technogenic (man-made) solutions, industrial and storm sewage water;

– medical use as enterosorbent;

Sorption of liquid low- and medium-radioactive waste;

– use for the purification of gases of radionuclides and heavy metals;

– the use in the individual and collective devices for water purification;

– isolation of rare -earth, precious and nonferrous metals;

– other applications as natural phytosorbents.

Table 4

The main components in the produced lignin hydrolytic briquettes and pellets, % by weight of bone dry solids

Name of the components	Briquettes	Pellets
Total polysaccharides, including:	19.25	19.67
– easy- hydrolysable	2.13	2.17
– hard hydrolysable	17.12	17.50
Cellulose	15.90	16.81
Lignin	46.41	44.73
Ash	8.97	9.30
Acidity (in terms of H_2SO_4)	0.1	0.1

Conclusion. The most rational its application (from the point of view of large-capacity processing of hydrolytic lignin in Belarus, besides the production of briquettes and pellets for use as fuel), is to obtain organic or organic-mineral fertilizers and sorbents, for industrial wastewater purification as well.

References

1. Холькин Ю. И. Технология гидролизных производств. М.: Лесная пром-сть, 1989. 496 с.

2. Безотходное производство в гидролизной промышленности / А. З. Евилевич [и др.]. М.: Лесная пром-сть, 1982. 184 с.

3. Эпштейн Я. В., Ахмина Е. И., Раскин М. Н. Рациональные направления использования гидролизного лигнина // Химия древесины, 1977. № 6. С. 24–44.

4. Оболенская А. В., Ельницкая З. П., Леонович А. А. Лабораторные работы по химии древесины и целлюлозы. М.: Экология, 1991. 320 с.

5. Емельянова И. З. Химико-технический контроль гидролизных производств. М.: Лесная пром-сть, 1976. 328 с.

6. Богомолов Б. Д. Химия древесины и основы химии высокомолекулярных соединений. М.: Лесная пром-сть, 1973. 400 с.

7. Леванова В. П. Лечебный лигнин. СПб.: Центр сорбционных технологий, 1992. 136 с.

Received 12.02.2014