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The Study of Birch Lignin Isolated from Hydrolyzate Imitating Wastewater of Veneer Production

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Abstract: **Hydrothermal treatment of wood in a special water basin is employed before its mechanical processing for veneer production. Due to the wood autohydrolysis, the wastewater of the hydrothermal treatment is dramatically polluted, mainly with low-molecular lignin fragments, hemicelluloses and extractives. The waste biomass from the plywood basins may serve as a raw material for the development of new products with a value-added benefit. In this work, a chemical structure of lignin isolated from laboratory birch wood hydrolysate, imitating wastewater of plywood production, as well as its compositional features in comparison with commercial alkaline lignin has been studied.**

Keywords: **wood, veneer production, hydrothermal treatment, birch lignin, wastewater**

I. INTRODUCTION

During recent years in Latvia wood product industry has a tendency to increase. One of the most significant wood processing areas is the production of plywood. During 2008 plywood production reaced 180.000 m^3 which contributed to approximately 15% of total wood production in Latvia [1, 2].

One of the veneer production stages is wood hydrothermal treatment, and, as a result, a considerable amount of low-molecular lignin fragments, hemicelluloses and extractives passes to wastewater [3]. These organic substances are responsible for the high chemical oxygen demand and the colour of wastewater of the wood hydrothermal treatment and have a considerable negative effect on the environment.

One of the most effective solutions of this problem may be the regeneration of wastewater biomass and its further application in national economy. It is known that lignin, being a part of the biomass, could be used as a raw material in manufacturing of various products. Along with its traditional application as an energy source, nowadays it is also used as surface active agent, binder or fillers, soil improving agent or for other purposes [4-7].

The aim of this work was to investigate the chemical structure of lignin isolated from the laboratory wood hydrolysate imitating wastewater of plywood production, as well as to reveal its compositional features in comparison with a commercial lignin.

II. MATERIALS AND METHODS

Treatment of birch wood sawdust (cellulose – 40.3 %, lignin – 25.2 %, extractives – 3.9 %) was performed in a weak alkaline water solution with the hydromodulus 1/50 (sawdust/water) at the temperature of 90ºC for 4 h. For comparison industrial wastewater sample from the hydrothermal basin of plywood manufacturing was taken.

Birch lignin was isolated from the obtained wood hydrolysate by using 20% sulphuric acid solution [8]. The commercial lignin Curan 100 was supplied by Borregaard LignoTech, Sweden.

Elementary analysis of samples was determined using Elementar Analysensysteme Vario MACRO CHNS. Functional analysis was performed by analytical methods according to [8, 9]. Potentiometric and conductometric titration methods were used for analysis of functional composition. Surface tension at the water-air interfaces was measured by the Wilhelmy plate method, using the tensiometer KRUSS 9K, after 24 h storage of lignin's solutions at room temperature. FT-IR spectra were obtained in a range of 450–4000 cm^{-1} on a spectrophotometer Perkin-Elmer Spectra One, using KBr tablets. UV spectra were obtained by a Genesys 10UV spectrophotometer in a range of 220–420 nm. Sizes of the lignin particles were determined, using a ZETASIZER NANO ZS Malvern Instrument. The supramolecular structure of the isolated lignin was examined with a scanning electron microscope.

III. RESULTS AND DISCUSSION

The comparison of the elemental and functional compositions of the dry matters derived from the obtained hydrolyzate (WH) (Table 1), which imitates the real hydrothermal treatment of wood in the veneer production, and the industrial wastewater (WW) shows that there are no significant differences.

The birch lignin (IBL) isolated from WH is a brown fine disperse powder that does not dissolve in a distilled water, but forms a suspension in it with a particle size of 1100 – 1200 nm (Fig. 1). At the same time IBL dissolves in alkaline media.

The SEM image of the IBL indicates the high association degree of its macromolecules in water solution (Fig. 2). The revealed supramolecular structure represents the extended clusters, consisting of globules with different sizes.

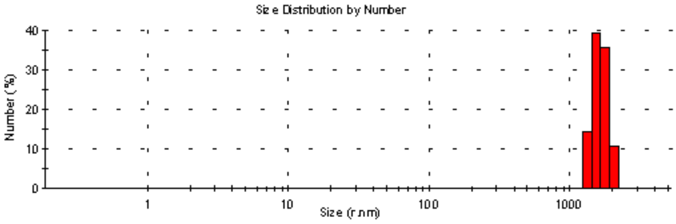

Fig. 1. Particle-size distribution pattern of IBL distilled in water

The chemical composition of IBL significantly differs from WH (Table 1), because WH besides the lignin contains also hemicelluloses fragments and extractives. IBL is characterized by a higher content of carbon, mainly, due to a relatively higher content of aromatic fragments in comparison with the dry matter of WH. At the same time, Curan 100 is characterized by the increased content of methoxyl groups (11.70 %) in comparison with IBL (7.53 %). The comparatively moderate content of OCH_3 groups in the composition of the studied lignin may testify the presence, besides syringyl units, of a considerable amount of guaiacyl and para-oxiphenyl fragments in its macromolecules.

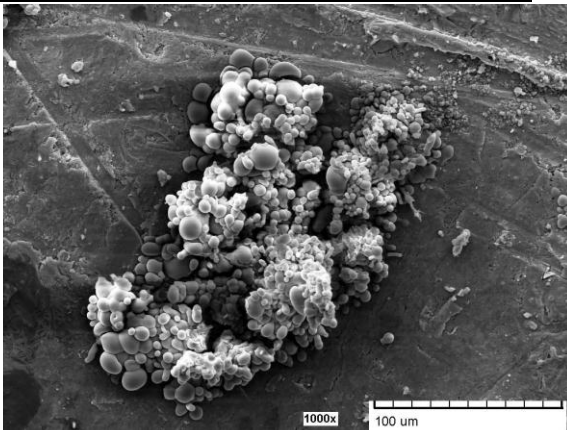

Fig. 2. SEM image of IBL obtained from alkaline water solution

TABLE 1
ELEMENTAL AND FUNCTIONAL COMPOSITION

Samples	C %	H %	N %	O %	S %	OCH_3 %	CO %	OH %
WW	42,33	5,35	0,74	51,00	0,58	1,86	1,05	9.25
WH	37,36	4,68	0,30	57,52	0,14	2,29	1,50	10,15
IBL	53,36	6,63	0,61	39,03	0,37	7,53	4,76	11,24
Curan 100	64,90	5,59	0,11	26,90	2,50	11,70	3,10	11,00

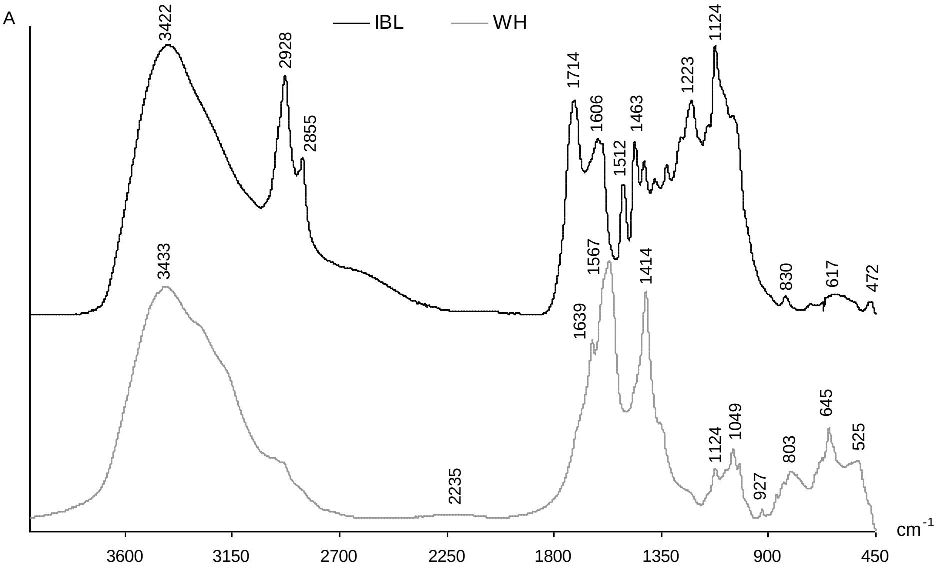

Fig. 3. FT-IR spectra of WH and IBL

The results of chemical analysis of WH and IBL are confirmed by the analysis of the obtained FT-IR spectra of WH and the isolated birch lignin (Fig. 3). According to them, WH contains not only lignin, but also hemicelluloses and extractives. Bands between 1125 and 1000 cm^{-1} are typical of hemicelluloses derivatives. The band at 1049 cm^{-1} in hemicelluloses is due to the C–O, C–C stretching or C–OH bending [10]. Tannins can absorb in a range of 3390-3600 cm^{-1}. Lignin differs from the other wood components by a higher variety of functional groups. In the FT-IR spectra of IBL (Fig. 3), the typical bands can be seen, which are common for hardwood lignins: 3410 cm^{-1}, attributed to the hydroxyl groups in phenolic and aliphatic structures, and the bands 2917 cm^{-1} and 2847 cm^{-1}, caused by CH stretch vibrations in methoxyl, methyl and methylene groups. 1591 cm^{-1}, 1503 cm^{-1} and 1417 cm^{-1} are assigned to skeletal vibrations and C = O stretching in the S and G aromatic rings. The relatively higher intensity of the band at 1591 cm^{-1} in comparison with the band at 1503 cm^{-1} may be caused by the presence of a great amount of syringyl derivatives in the lignin macromolecule and condensed aromatic structures, favouring the increase in the intensity of this absorption band. A broad band in a range of 1715-1625 cm^{-1} may be assigned to the presence of unconjugated and conjugated carbonyl and aromatic carboxyl groups in lignin macromolecules. A shoulder at 1378 cm^{-1} may be caused by the presence of phenolic OH and aliphatic C–H in methyl groups. A band at 1323 cm^{-1} and a band at 821 cm^{-1} are assigned to syringyl rings, the latter band is characteristic also for C–H vibration in S units. The higher intensity of the band at 1219 cm^{-1}, in comparison with the band at 1262 cm^{-1}, may be determined by the presence of both syringyl and a considerable amount of para-oxiphenyl derivatives [11]. A very strong band at 1121 cm^{-1} may be caused by C–H deformation in the syringyl units as well as in the secondary alcohols or by C=O stretching vibrations. The strong band with a maximum at 1036 cm^{-1} is complex and may be governed by both the deformation vibrations of C-H in the aromatic structures with predominating guaiacyl units, and the deformation vibrations C-O in primary and stretching vibrations of unconjugated C=O groups. Thus, it may be assumed that the isolated birch lignin fragments represent the guaiacyl-syringyl type, containing a lot of the p-hydrophyphenyl units.

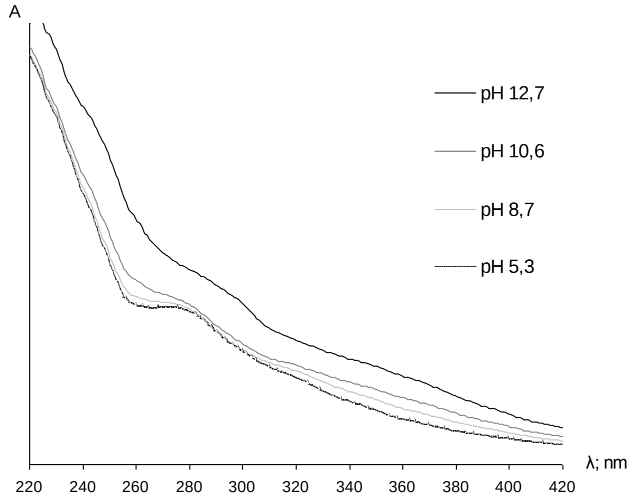

Fig. 4. UV spectra of BL aqueous solutions depending on its pH values

The UV-absorption curves of IBL only in a weak acid media had a pronounced maximum at 276 nm (Fig.4). In an alkali medium, they represented integrity of absorption bands in the form of strongly or weakly pronounced shoulders, reflecting the presence of different phenyl propane fragments in the macromolecule of birch lignin. The very pronounced shoulders at 242, 257, 280 and 312 nm on the ionization curve of BL in a strong alkaline medium could testify the presence of the biphenyl derivatives, as well as the aromatic structures, containing non-etherified hydroxyl groups, conjugated carbonyl groups and aromatic carboxyl groups in the lignin macromolecules. The values of the extinction coefficient of BL varied from 13.5 l $g^{-1}cm^{-1}$ ($\lambda = 276$ nm) at pH 5.3 to 16.8 l $g^{-1}cm^{-1}$ ($\lambda = 280$ nm) at pH 12.7. These indices were typical for the lignins of hardwood species [8].

The study of acidic functional groups of the lignins was performed by potentiometric and conductometric titration. It is known that soluble lignins, containing carboxyl groups, may be regarded as weak polymer acids. In order to compare the ability of the carboxyl groups of IBL and Curan 100 to dissociate in water solutions, their dissociation constants (Kα) were calculated based on the titration curves (Fig. 5). As the titration shows, the IBL carboxyl groups in comparison with Curan 100 ones are characterized by higher pKα values that may be gained by the presence of many biphenyl structures in the chemical composition of IBL (Fig. 3 and 4).

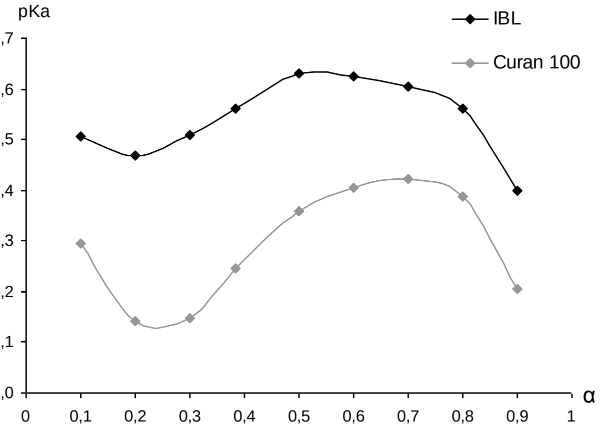

Fig. 5. pKα of carboxyl groups of IBL and Curan 100 versus their degree of dissociation

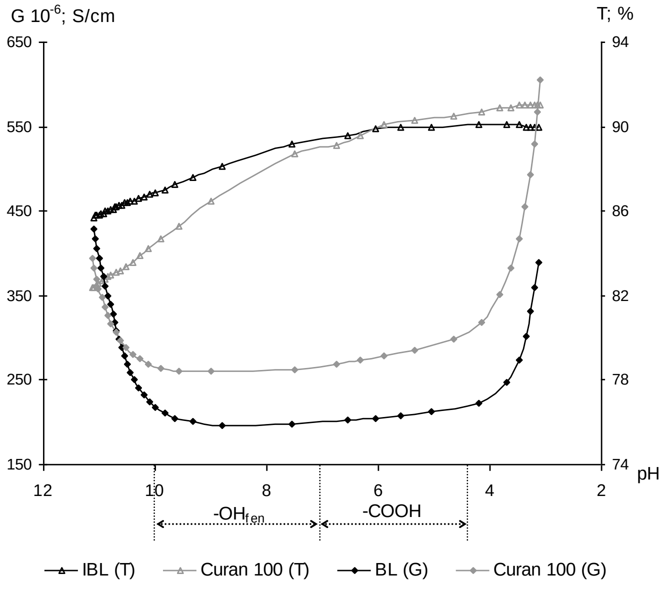

Fig. 6. Conductometric and spectrophotometric titration (540 nm) curves of water solutions of IBL and Curan 100

The changes of specific conductivity of the IBL and Curan 100 solutions, depending on pH, are given in Fig. 6. It is seen that, in the studied pH range, the specific conductivity of the

Curan 100 solution is higher than that of the IBL one. This may confirm a higher state of charge of the acidic groups of Curan 100 in comparison with the isolated birch lignin. However, in a strong alkaline media at pH > 10.5, the state of charge of the IBL macromolecules becomes higher than for the molecules of Curan 100. This may indicate that IBL in comparison with Curan 100 contains a lot of the phenolic hydroxyl groups with higher pKα. The enhanced value of extinction coefficient of IBL at pH 12.7 (16.8 l $g^{-1}cm^{-1)}$ may confirm this suggestion.

With decreasing pH, light transmittance at 540 nm increases for both IBL and Curan 100 solutions (Fig. 6), which is gained by the decrease of phenolic hydroxyl groups ionization. However, the light transmittance coefficient for the Curan 100 solution is lower in comparison with the IBL one in alkaline and neutral media. It is known that a colour of lignins, to a great extent, depends on a conjugation degree of their chromophoric system. Generally, the higher the degree of conjugation, the darker lignin's water solution is. Evidentially, IBL is characterized by a less conjugated structure than Curan 100 due to its lower molecule mass as can be seen from the comparison of the carbon content in the chemical compositions of both lignins (Table 1) and the obtained viscometric data.

IV. CONCLUSIONS

The birch lignin (IBL) was isolated from the hydrolyzate, imitating wastewater of veneer production. It was a brown fine disperse powder with a particle size of 1100 – 1200 nm. The analysis of the obtained FT-IR and UV spectra indicated the presence of the biphenyl derivatives, as well as the aromatic structures, containing non-etherified hydroxyl groups, conjugated carbonyl groups and aromatic carboxyl groups in the lignin chemical composition. In comparison with the commercial alkaline lignin, it is characterized by a decreased content of methoxyl groups due to the presence, besides syringyl units, of a considerable amount of guaiacyl and para-oxiphenyl fragments in its macromolecules. The acidic groups (phenolic hydroxyl groups, carboxyl groups) of ILB in comparison with the commercial lignin are characterized by higher pKα values that may be gained by the presence of many biphenyl structures in its chemical composition. IBL is also characterized by a less conjugated structure than the commercial lignin due to its lower molecule mass.

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Sanita Skudra, Galija Suļga, Skaidrite Reihmane. No finiera ražošanas hidrotermiskās apstrādes modeļšķīduma izdalīta bērza lignīna pētījumi

Pēdējos gados Latvijā pakāpeniski ir palielinājusies kokrūpniecības produkcijas ar augstāku pievienoto vērtību ražošana un eksportēšana. Viens no nozīmīgākajiem koksnes pārstrādes veidiem Latvijā ir finiera ražošana. 2008. gadā tika saražoti ap 180 tūkst. m^3 saplākšņa, kas veido 15 % no kopējās koksnes produktu saražotās vērtības Latvijā. Viens no saplākšņa ražošanas posmiem ir koksnes hidrotermiskā apstrāde, kuras rezultātā ūdenī nonāk ievērojams daudzums zemmolekulāro lignīna savienojumu, hemiceluložu un ekstraktvielu. Šīs organiskās vielas ir atbildīgas par koksnes hidrotermiskās apstrādes notekūdeņu lielo ķīmiskā skābekļa patēriņu un krāsainību, kas būtiski ietekmē apkārtējo vidi. Viens no visefektīvākajiem risinājumiem varētu būt šīs notekūdeņu biomasas reģenerācija un tālāka pielietošana. Biomasas sastāvā esošais lignīns var kalpot kā izejviela dažādu produktu ražošanai. Darba mērķis bija no laboratorijas apstākļos iegūta koksnes hidrotermiskās apstrādes modeļšķīduma, kas imitē reālu saplākšņa ražošanas hidrotermiskās apstrādes procesu, izdalīt bērza lignīnu un izpētīt tā ķīmisko sastāvu, lai tālāk varētu meklēt tā potenciālās izmantošanas iespējas.

Veiktie pētījumi parādīja, ka no modeļšķīduma izdalītais bērza lignīns (IBL) ir brūna smalki dispersa viela, kas nešķīst ūdenī, bet veido tur suspensiju ar daļiņu izmēriem 1100-1200 nm. FT-IR un UV spektru analīze liecina, ka IBL ķīmiskajā sastāvā ietilpst bifenil atvasinājumi, kā

arī aromātiskās struktūras ar neesterificētām hidroksilgrupām, konjugētām karbonilgrupām un aromātiskām karboksilgrupām. Salīdzinājumā ar komerciālo kraft lignīnu, izdalīto lignīnu raksturo mazāks metoksigrupu saturs, kas norāda uz to, ka tā makromolekulā bez siringilvienībām ietilpst arī ievērojams daudzums gvajacil un para-oksifenilpropānvienību. IBL skābās grupas raksturo lielākas pKα vērtības salīdzinājumā ar komerciālo lignīnu, kas varētu būt izskaidrojams ar lielāku bifenilstruktūru daudzumu IBL sastāvā. IBL raksturīga arī mazāk konjugēta struktūra nekā komerciālajam lignīnam, kas izskaidrojams ar IBL mazāku molekulāro masu.

Санита Скудра, Галия Шульга, Скайдрите Рейхмане. Изучение березового лигнина, выделенного из гидролизата, имитирующего сточные воды фанерного производства

Одной из ведущих отраслей деревопереработки в Латвии является производство клееной фанеры. В 2008 году было произведено почти 180 тыс.м^3, что составляет 15% от всей продукции, произведенной деревоперерабатывающими предприятиями. Для получения шпона, древесину подвергают гидротермической обработке, в результате которой в сточные воды попадает большое количество низкомолекулярных лигнинов, фрагментов гемицеллюлоз, экстрактивные вещества, которые обусловливают высокие показатели ХПК и окраску сточных вод. Одним из перспективных решений снижения загрязнения окружающей среды может быть регенерация биомассы из сточных вод с целью дальнейшего ее применения. Лигнин, находящейся в составе биомассы, может служить исходным сырьем для получения целевых продуктов с добавленной стоимостью. Целью данной работы было изучение химического состава березового лигнина, выделенного из лабораторного гидролизата березовой древесины, имитирующего сточные воды гидротермической обработки древесины в заводских условиях, а также выявления его особенностей в сравнении с промышленным щелочным лигнином.

Проведенные исследования показали, что березовый лигнин, выделенный из модельного раствора 20% серной кислотой, представляет собой коричневый мелкодисперсный порошок с частицами 1100-1200 нм. Химический анализ, Фурье- и УФ спектры выделенного лигнина свидетельствовали о присутствии в его составе бифенильных производных, а также ароматических структур, содержащих неэтерефицированные гидроксильные группы, конъюгированные карбонильные группы и ароматиические карбоксильные группы. В сравнении с промышленным лигнином, выделенный лигнин характеризовался пониженным содержанием метоксильных групп, что могло быть вызвано значительным присутствием в его составе фрагментов, содержащих пара-оксифенилпропановые единицы. Более низкие значения рK_a фенольных гидроксильных и карбоксильных групп березового лигнина, а также более высокие значения коэффициента светопропускания при 540 нм, относительно этих же показателей промышленного щелочного лигнина, обусловлены структурными особенностями его строения и более низкой его молекулярной массой.