



Wood Biomass from the Model Wastewater and Its Fractionation

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Abstract. The production of veneer in Latvia and many countries of East Europe is accomplished by the hydrothermal treatment of hardwood in special water basins. As a result, formed effluents contain wood-originated pollutants, which are responsible for the enhanced chemical oxygen demand and the intensive colour of the wastewater. Keeping in mind the volume of the polluted effluents formed annually at the Latvian plywood plants, it is very important to extract qualitatively and quantitatively the formed biomass from the effluent. The choose of an effective method of the waste biomass extraction depends on chemical characterisation of the effluent. In this work, for imitating woodworking wastewater, birch sawdust was hydrothermally treated in mild alkaline conditions at 90°C. The yield of the solid biomass did not exceed 7% and contained, mainly, hemicelluloses in the polysaccharide form and lignin. The applied instrumental analysis (FTIR-, UV-, Raman spectroscopy) testify the dominant content of hemicelluloses in the obtained biomass. The fractionation of the biomass was performed using concentrated sulphuric acid and ethanol. As the obtained results have shown, the content of lignin, hemicelluloses and water-soluble degraded wood products in the solid biomass corresponded to the following mass ratio: 1.2 /6.7 /1.0, respectively.

Keywords – biomass, hemicelluloses, hydrothermal treatment, fractionation, lignin, wastewater.

I INTRODUCTION

Biomass pre-treatment, directed to the destruction of the lignocellulosic matrix, occupies a leading position in lignocellulosic biorefinery for obtaining biofuels and chemicals from cellulose, hemicelluloses and lignin [1-3]. The production of veneer in Latvia and many countries of East Europe is accomplished by the hydrothermal treatment of hardwood in special water basins for 16-18 h at a temperature lower than 100°C and a normal pressure [4]. Depending on the conditions of the hydrothermal treatment, a different yield of wood hydrolysis products occurs due to the hydrolysis of the lignocellulosic matrix [5]. As a result, the formed effluents are polluted with lignin, hemicelluloses, extractives and degraded products from these wood substances, which are responsible for the enhanced chemical oxygen demand and the intensive colour of the wastewater. The chemical indexes of the effluents depend on many factors, namely, the wood species, temperature, pH, etc. Keeping in mind the volume of the polluted effluents formed annually and the zero waste policy for rational use of bioresources, it is very important to extract qualitatively and quantitatively the formed biomass from the effluents for more rational its utilisation than the dilution with pure water to maximum allowable concentrations and then to discharge to natural water basins. It is known that sewage sludge can be used successfully for soil improvement [6], and for producing building materials [7] and sorbents [8]. Evidently, the proper selection of methods for effective extracting of wood biomass from the wood processing effluent is based on its chemical composition and, mainly, on the content of lignin and hemicelluloses.

The aim of the study was to assess the content of lignin- and hemicelluloses-containing fractions in the model solution imitating wastewater of veneer production.

II MATERIALS AND METHODS

Hydrothermal treatment of 60 g of sawdust (< 1.00 mm) was performed with 0.04% NaOH solution at the hydromodulus 1/50 (mass ratio of the oven dry sawdust to water) and a temperature of 90°C for 4 h, using a 5 l three-neck flask equipped with a return condenser, a thermometer and a stirrer. After hydrolysis, the cooled hydrolysate was separated from the treated sawdust by filtration, and the obtained biomass was dried to a constant mass, at first, at room temperature and then in an oven at 40°C. The treated sawdust was washed with distilled water to remove the adsorbed hydrolysed degraded products and dried to a constant mass, at first, at 60°C and then in an oven at 105°C. The characteristics of the treated sawdust and the obtained hydrolysate are represented by their average arithmetic values.

The elemental composition of the sawdust and was determined with the Elementar Analysensysteme GmbH (Germany). Inorganic matter (ash) was found according to Obolenskaya and co-authors [9]. The composition of birch sawdust - lignin, hemicelluloses, cellulose and extractives, before and after hydrolysis, was determined according to analytical chemical procedures. The content of lignin and cellulose was determined by Klason and Kürschner methods, respectively. The content of hemicelluloses was determined as a difference between the content of holocellulose found by treatment with sodium chlorite and glacial acetic acid and cellulose. The content of

extractives represented the sum of the content of the wood substances dissolved in acetone, using a Soxlet extractor, and in boiled water (100°C) during 3 h [9]. The found content of cellulose, lignin, hemicelluloses and extractives in the birch wood residue was the following: 40.3%, 25.2%, 29.2% and 3.9%, respectively. Biomass component composition was identified by Fourier Transform Infrared (FTIR), Ultraviolet-Visible (UV) and FT Raman spectroscopy. For FTIR- and UV-spectroscopy, a spectrophotometer (Perkin-Elmer Spectrum One, USA) with KBr tablets and a UV-VIS Spectrometer Genesys™ 10 (Thermo, USA)¹⁸ were employed.

Due to the high fluorescence, for obtaining the spectral characteristics of the biomass, a Multiram FT Raman spectrometer by Bruker with laser power of 125 mW was used.

Monosugars in the hemicelluloses fraction were determined by a high performance liquid chromatography (HPLC) using a liquid chromatograph (LC) SHIMADZU LC-20A (Shimadzu, Tokyo, Japan) with a refraction index detector. HPLC grade acetonitrile (Sigma-Aldrich, Germany) and water (distilled and deionised) were used for the HPLC analysis. Xylose, arabinose, rhamnose, mannose, glucose and galactose were reference standards. The column configuration was an Alltech Platinum Amino column (100Å 5u, 250x4.6 mm) with a Platinum Amino (NH₂) guard column (5u, 7.5x4.6 mm). The flow rate was 1.5 ml/min and the separation was performed at 35°C. The mobile phase consisted of a degassed filtered mixture of acetonitrile and water (80:20 %v/v). For measuring, a 1.0% biomass water solution in 0.01M NaOH was prepared and filtered through a 0.45 µm membrane filter before injection, filed in 1.5 ml bottles with caps and placed in an auto-injector. All samples were tested three times.

Z potential of the hydrolysate was measured with Malvern Nanosizer SZ (UK). Indexes of COD and colour for the obtained hydrolysate were determined according to ISO 6060:1989 [10] and ISO 7887:1994 [11].

III RESULTS AND DISCUSSION

As shown in Table 1, the obtained hydrolysate was characterised by a moderate alkaline pH value, a low concentration of dry matter, representing the sum of wood degraded products passing to the hydrolysate, a moderate value of chemical oxygen demand (COD) and a pronounced colour associated with the presence of lignin and lignin-like substances in the hydrolysate.

TABLE 1.
PARAMETERS OF THE OBTAINED HYDROLYZATE

Sample	pH	Dry solids, g l ⁻¹	Density, kg m ⁻³	COD, mg O l ⁻¹	Colour, mg Pt l ⁻¹
Hydrolyzate	9.02	1400	0.998	1285	746

The average yield of the solid biomass from the hydrolysate was 7.1±0.2% relative to the initial sawdust mass. The yield calculated from the sawdust mass loss was a little higher than that of the dried biomass, which may be associated with a partial adsorption of the formed degraded wood products at the sawdust surface. The defined elemental composition of the dried biomass was the following: 37.75% C; 4.78% H; 56.69% O; 0.30% N; 0.14% S, 0.34% of inorganic matter. A SEM image (Fig. 1) characterised the obtained lignocellulosic biomass as an amorphous one without pronounced morphological features.

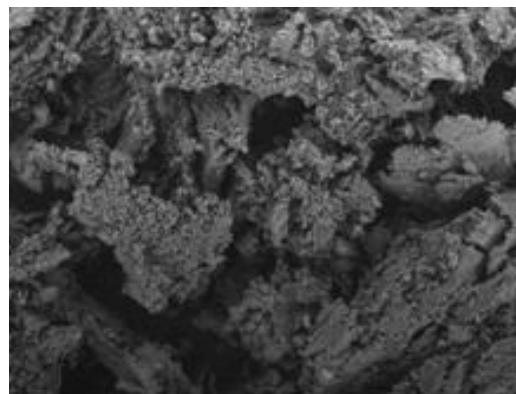


Fig.1. SEM image of the biomass.

The biomass had an enhanced ratio O/C close to 1.5±0.1 that indicated the presence of a great amount of oxygen-containing groups including hydroxyl, carbonyl and carboxyl groups in the hydrolysed wood products. The zeta potential value of the hydrolysate close to -30 mv testified the high content of these groups in the biomass. With decreasing pH to 2.0, the Z potential value of the hydrolysate fell to -10 mv, reflecting the decrease in the ionisation degree of the hydroxyl and carboxyl groups in lignin and hemicelluloses fragments.

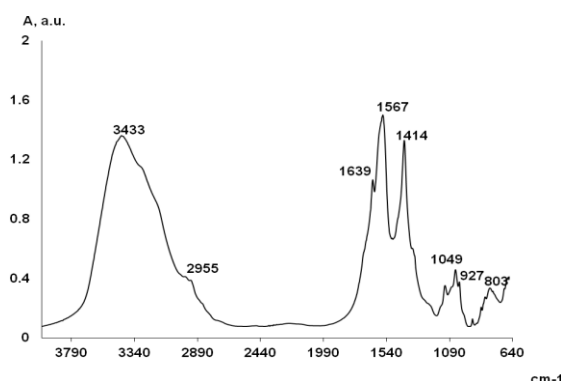


Fig.2. FT-IR spectrum of the biomass.

For fuller characterisation of the chemical composition of the biomass, the FT-IR, UV and FT Raman spectroscopy were applied. The interpretation of the obtained results was based on the literature data concerning the studies of lignin and hemicelluloses by

the methods [12-14]. According to the FT-IR spectrum of the biomass (Fig. 2), the strong broad band at 3433 cm^{-1} is attributed to both aromatic and aliphatic hydroxyl groups. The band at 2955 cm^{-1} is caused by C-H stretch vibrations in the methoxyl, methyl and methylene groups present in the aromatic and saccharide structures of the hydrolysed products. The narrow bands at 1639 cm^{-1} and 1567 cm^{-1} may be assigned to the presence of ketones, carbonyls and ester groups in the biomass lignin and hemicelluloses. At the same time, in the spectrum, the pronounced bands corresponding to the aromatic skeletal vibrations of lignin structures, namely, 1600 cm^{-1} and 1505 cm^{-1} [15] are absent. The presence of lignin structures in the biomass is testified by the absorbance at 1414 cm^{-1} , assigned to skeletal vibrations and C=O group stretching in the syringyl and guaiacyl aromatic rings. The CH_2 deformation vibrations appear at 1351 cm^{-1} and may be caused by both lignin and hemicelluloses structures. The bands in the region of $1115\text{--}803\text{ cm}^{-1}$ are typical for hemicelluloses. This region contains C-C ring vibrations, overlapped with the stretching vibrations of C-OH side groups and the C-O-C glucosidic band vibrations. The band at 1115 cm^{-1} may be caused by the presence of pectin. The band at 1047 cm^{-1} is attributed to the C-O-C stretching in glucosidic linkages, which is typical for xylan. The small bands at 927 cm^{-1} and 803 cm^{-1} are characteristic of the β -glucosidic bonds between the sugars units.

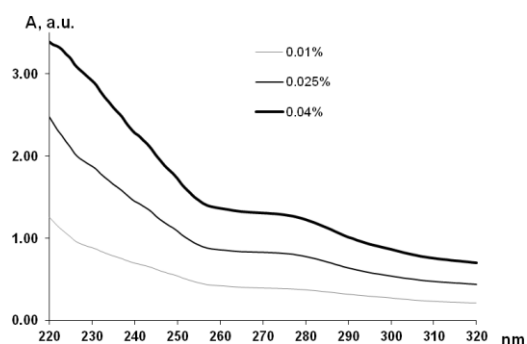


Fig. 3. UV spectra of the biomass water solutions at pH 9.0.

Fig. 3 shows UV-spectra of 0.01-0.04% solutions of the biomass with pH 9.0. The obtained spectra testify the presence of aromatic fragments in the biomass, namely, the absorption at 280 nm is typical for lignin. At the same time, the relatively low value of the calculated extinction coefficient ($3.89\text{ l g}^{-1}\text{ cm}^{-1}$) at this band indicates the dominant content of the non-aromatic structure in the dried biomass.

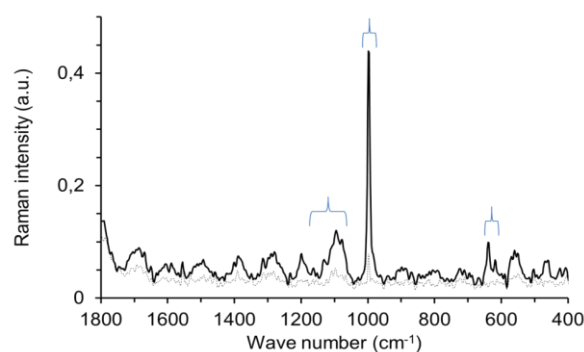


Fig. 4. FT Raman spectrum of the biomass.

This suggestion confirms the obtained FT Raman spectrum of the lignocellulosic biomass presented in Fig. 4. According to the known assignment of the vibration bands in FT Raman lignocellulosic materials [16], the strong pronounced bands observed in the interval of $1200\text{--}1000\text{ cm}^{-1}$ may be assigned to C-C and C-O stretching vibrations in hemicelluloses. At the same time, less manifested and weaker bands in the interval of $550\text{--}630\text{ cm}^{-1}$ may testify the presence of aromatic structures of lignin in the obtained biomass.

To fractionate the lignocellulosic biomass and calculate the content of lignin and hemicelluloses therein, the precipitation of the hydrolysate with concentrated sulphuric acid, with the following treatment of the formed filtrate with ethanol, according to Liu and co-authors [17] was employed. The scheme of the applied fractionation is given in Fig. 5. For the fractionation, the biomass dried at room temperature was dissolved in 0.1M NaOH for obtaining 50 ml of a 35% biomass solution. The concentrated hydrolysate was, at first, acidified with 20% sulphuric acid to a pH of 2.0 at room temperature with the following filtration and centrifugation of the obtained suspension for separating the lignin-containing fraction. The lignin precipitate was washed with distilled water to pH 5.5 and dried in an oven at 40°C . Anhydrous ethanol was added to the obtained filtrate at the volumetric ratio of ethanol/filtrate close to 4. After addition of anhydrous ethanol, the hemicelluloses-containing fraction precipitated and then was isolated by centrifugation, washed with the ethanol and dried in an oven at 40°C . The content of hemicelluloses- and lignin-containing fractions in the biomass was assessed from the masses of the obtained dried precipitates.

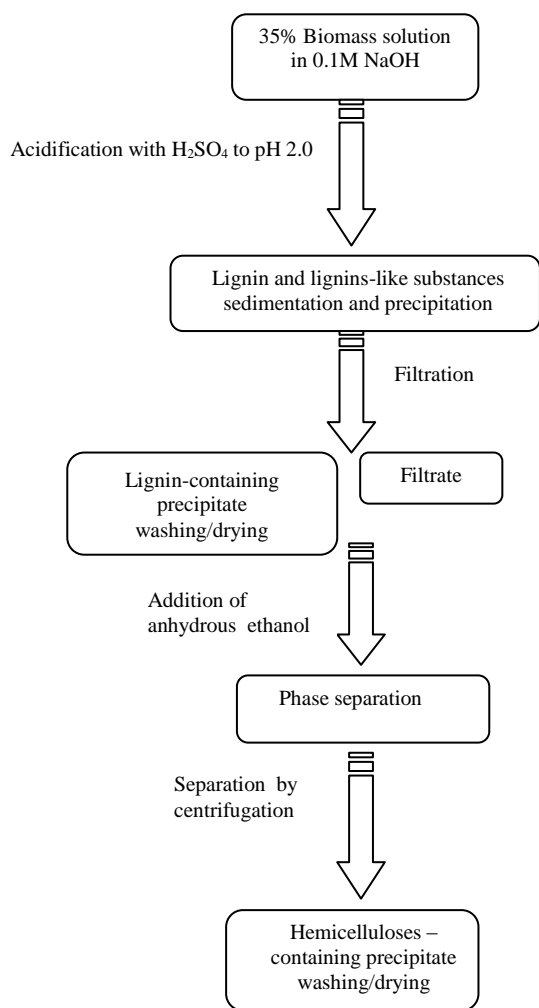


Fig. 5. Scheme of biomass fractionation

The FTIR spectrum of the isolated lignin and the isolated hemicelluloses are given in Fig. 6. In FTIR spectrum of lignin, typical bands can be seen, which are common for hardwood lignins, namely, a band at 1323 cm^{-1} and that at 821 cm^{-1} are assigned to syringyl rings. For FTIR spectrum of the isolated hemicelluloses, typical absorbance bands of glucosidic linkages in the $1200 - 800\text{ cm}^{-1}$ are observed.

The obtained results of the biomass fractionation showed that the content of the lignin and hemicelluloses fractions in the solid biomass corresponded to 13.5% and 75.2%, respectively. At the same time, the low molecular products of the lignocellulosic matrix destruction that were not able to be

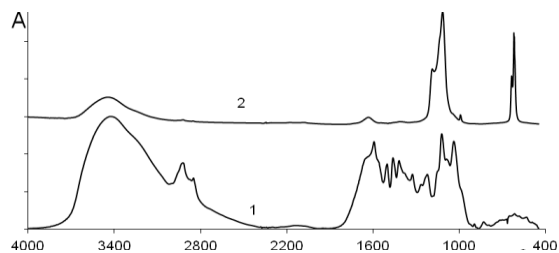


Fig. 6. FTIR spectra of biomass components: lignin (1), hemicelluloses (2).

precipitated by this procedure occupied 11.3% of the solid biomass. The measuring of the content of water-soluble lignin [9] in the filtrate obtained after the Klason lignin extraction corresponded to 5.89%, and the total content of lignin (Klason and water-soluble) in the biomass was 10.9%. As the obtained results have shown, the content of lignin, hemicelluloses and water-soluble degraded wood products in the solid biomass corresponded to the following mass ratio: 1.2/6.7/1.0, respectively.

TABLE 2.
WOOD COMPONENT COMPOSITION OF BIRCH SAWDUST BEFORE AND AFTER THE HYDROLYSIS

Sample	Holo-cellulose, %	Cellulose, %	Hemi-cellulose %	Lignin, %
Untreated	68.5	40.3	28.2	25.2
Treated	70.4	46.8	23.6	25.1

Simultaneously, the changes in the wood composition of birch sawdust due to its hydrolysis were assessed. According to the results listed in Table 2, the main changes in the wood composition caused by the hydrolysis took place for cellulose, i.e., its content increased by 6.5% and hemicelluloses, i.e., their content decreased by 5.6%, while the content of lignin diminished by only 0.1%. It is reasonable to assume that the gain in the cellulose content and the negligible alteration in the lignin content in the pre-treated lignocellulosic matrix were associated with the notable losses of hemicelluloses and water-soluble extractives during the hydrothermal treatment.

The chemical and morphological characteristics of the precipitated birch lignin were studied by Shulga and co-authors [18]. Hemicelluloses in the biomass were identified by a liquid chromatograph. The identifying HPLC analysis (Fig. 7) testified the presence of xylose, mannose, arabinose, rhamnose and glucose monomers in a 1.0% birch hydrolysate

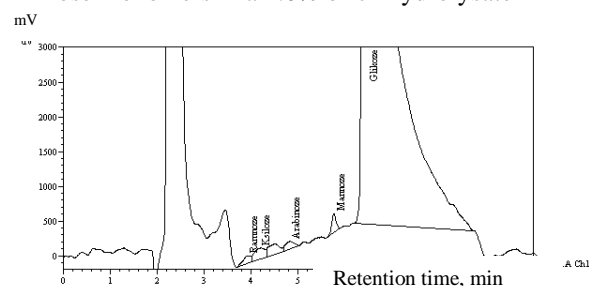


Fig. 7. HPLC chromatogram of a 1% biomass aqueous solution in 0.01M NaOH.

The obtained quantitative data analysis showed that the content of the first four sugars in the obtained hydrolysate was comparatively low and did not exceed 0.1%. This means that the hemicelluloses in the hydrolysate are represented mainly by polysaccharides. At the same time, the glucose content

in the hydrolysate was higher and close to 0.4%, which may be associated with the features of the birch lignocellulosic matrix degradation during the hydrolysis.

IV CONCLUSION

For imitating woodworking wastewater, birch sawdust was hydrothermally treated in mild alkaline conditions at 90°C. The yield of the solid biomass did not exceed 7% and contained, mainly, hemicelluloses in the polysaccharide form and lignin. The applied instrumental analysis (FTIR-, UV-, Raman spectroscopy) testify the dominant content of hemicelluloses in the obtained biomass. The study of the biomass with a high performance liquid chromatograph identified, along with xylose, glucose and mannose, also arabinose and rhamnose. The fractionation of the biomass was performed using concentrated sulphuric acid and ethanol. As the obtained results have shown, the content of lignin, hemicelluloses and water-soluble degraded wood products in the solid biomass corresponded to the following mass ratio: 1.2 /6.7/1.0, respectively.

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