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## PROCEEDINGS

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## OBTAINING LIGNOCELLULOSIC MICROPARTICLES USING ENERGY SAVING PRE-TREATMENT METHOD

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### ABSTRACT

In this work, aspen sawdust, a by-product of the mechanical processing of aspen wood, was studied as a feedstock for obtaining microparticles as a filler for polymeric composites. It is known that, due to enhanced energy requirements, milling of untreated wood is not economically beneficial. With the aim to partially destruct and activate the lignocellulosic matrix for the following modification, low temperature acid hydrolysis of aspen sawdust under mild conditions was carried out. The effect of the acid concentration, the hydrolysis duration and the hydromodulus on the components and fractional composition of milled hydrolysed aspen sawdust was investigated.

### I. INTRODUCTION

Lignocellulose is the most abundant renewable biomass, consisting of three polymers, namely, cellulose, hemicellulose and lignin, which all provide its perfect mechanical properties. In Latvia, aspen trees, along with pine and birch ones, annually give the highest wood yield. By-products, i.e. sawdust, bark and other wood biomass residues that are formed during forest management and wood mechanical processing are used mainly for energetic needs. At the same time, waste lignocellulosics are a feedstock for obtaining various value-added products. In recent years, intensive studies have been carried out on the application of lignocellulosics as a filler in wood-polymer composites [1-3] due to their renewability, easy availability, low cost, biodegradability, light mass, enhanced filling degree, etc. The obtaining of wood-polymer composites occurs by incorporating lignocellulosics in the form of fibres or particles in a polymer matrix. For the wood polymer composites filled with lignocellulosic fibres, their length and orientation in the polymer matrix are very important. The properties of the composites, containing wood microparticles, depend on the particle size, as well as size distribution, shape and charge. In most cases, smaller sizes of wood particles promote their compatibility with the polymer matrix and decrease the melt viscosity of the wood-polymer blend during the processing. For obtaining microparticles, wood has to be milled. However, due to the enhanced energy requirements, the milling of untreated wood is not economically beneficial, because it requires considerable energy consumption and energy input. With the target to facilitate and decrease the required energy for chemical and enzymatic processing of wood, various pre-treatment technologies are offered [4]. The acid hydrolysis of wood for production of ethanol and other chemicals is well known [5, 6]. The hydrolysis for bioethanol production can be realised using dilute or concentrated acids. As a rule, the dilute acid hydrolysis technology applies high temperatures (> 100°C) and enhanced pressures. The acid pre-treatment of wood at high temperature is used for energy saving in wood thermomechanical pulping [7, 8]. On the other hand, very scarce information is available on the effect of low temperature hydrolysis (< 100°C) with dilute acids on the wood composition and properties. Such information is useful for obtaining wood finest particles for wood-polymer composites, with simultaneous decreasing the energy input at wood milling and grinding. The cleavage of ether linkages at the wood surface is accompanied by changes in its functional groups' composition. The latter enhances the specific surface of the lignocellulosic matrix and facilitate its accessibility for chemical modifiers.

The aim of the study was to investigate the effect of acid hydrolysis parameters (acid concentration, duration, hydromodulus) at a low temperature (< 100°C) on the changes in the aspen wood components and fractional composition after milling, as well as on the time of milling that is equivalent to energy input. The hydrolysis served as the first step for obtaining wood microparticles for their following modification.

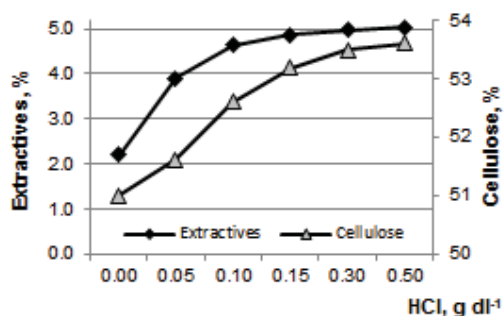
### II. EXPERIMENTAL

The aspen sawdust represented a by-product of the mechanical processing of aspen wood (*Populus tremula*). The main part of its fractional composition consisted of particles with a size from 1 mm to 0.5 mm (67 mass %). The elemental composition of the sawdust was determined by an Elementar Analysensysteme GmbH

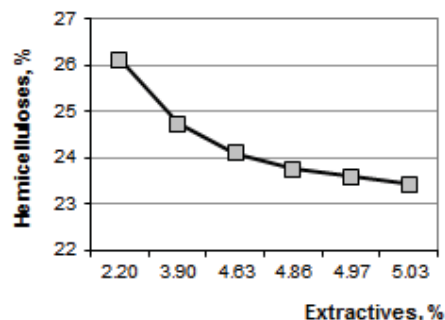
(Germany). The composition of the sawdust was determined according to analytical chemical procedures – Klason and Kirschner ones – for lignin and cellulose, respectively. The content of extractives in the sawdust represented the sum of the content of the wood substances dissolved in acetone, using a Soxhlet extractor, and in hot water (100°C) during 3 h. The elemental component composition of aspen wood was the following: 48.77% C, 6.25% H, 44.71% O, 0.11% N and 0.16% S. The content of cellulose, lignin, hemicelluloses, extractives and ash in aspen wood was 50.52%, 18.45%, 26.12%, 4.51% and 0.4%, respectively. Acid pre-hydrolysis was carried out by using a 5-L three-neck flask equipped with a return condenser, a thermometer and a stirrer under the following conditions: 0.05-0.5 g/dl HCl concentration, temperature 60°C and duration 1-7 h at a hydromodulus (sawdust/water mass ratio) of 1/10, 1/20 and 1/50. After the pre-hydrolysis, the treated sawdust was separated from the hydrolysate by filtration and dried, at first, at 60°C, and then at 105°C. The mass losses of the hydrolysed sawdust and the dry matter of the obtained hydrolysates were used for calculating the amounts of the degraded products. The hydrolysed sawdust milling was carried out with a planetary ball mill (Retsch, Germany) at 300 min<sup>-1</sup> during 15 min. The milled sawdust fractionation was performed by using Pulverizette 0 (Fritsch, Germany) with a set of sieves during 15 min. The size distribution in the particles < 100 µm was investigated with a laser particle granulometer (Annalizetto-22 NanoTec, Fritsch, Germany). The shape of the finest microparticles was fixed by transmission electron microscopy (Leo 912 AB Omega microscope, Carl Zeiss, Germany). The microstructure of the hydrolysed wood particles was examined using a scanning electron microscope (Tesla, Czech Republic). The UV-spectra of the obtained hydrolysates was performed with the help of an UV-VIS Spectrometer Genesys<sup>TM</sup> 10 (Thermo, USA).

### III. RESULTS AND DISCUSSION

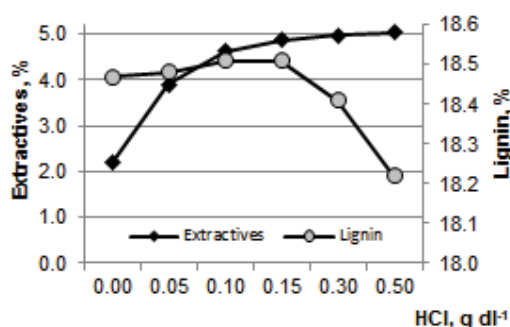
A study of the effect of the acid concentration on the yield of the extractives, consisting of water-soluble extractives and lignocellulosic degradation products (low molecular hemicelluloses and lignin fragments), as a result of the low temperature hydrolysis during 1 h at a hydromodulus of 1/20, shows that, with applying 0.05 g/dl HCl, the amount of the water-soluble products in the hydrolysate increases 1.6-1.8 times (**Figure 1**).



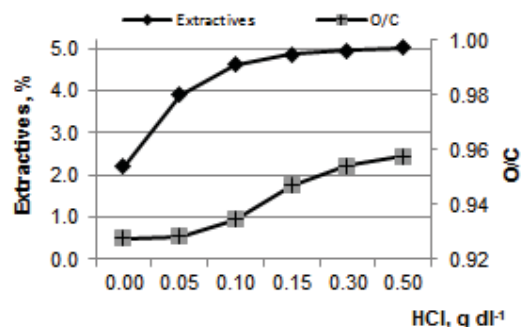
**Figure 1.** Effect of acid concentration on extractives amount in the hydrolysate and cellulose content in wood.



**Figure 2.** Hemicellulose content in sawdust versus extractives concentration in the hydrolysate.



**Figure 3.** Effect of acid concentration on lignin content in wood.



**Figure 4.** Effect of acid concentration on oxidation degree of wood.

The highest content of the degraded products is in the hydrolysate obtained by the treatment of the sawdust with the highest HCl concentration (0.5 g/dl): the amount of the degraded products in the hydrolysate increases more than twice in comparison with the case of the hydrolysis in water. At the same time, the correlation between the released extractives and acid concentration has a saturation character. According to **Figure 2**, the

main water-soluble degraded products passing to the hydrolysate are hemicelluloses fragments, the amount of which decreases in the lignocellulosic matrix with increasing concentration of the degraded products in the hydrolysate. The relative content of cellulose in the hydrolysed residue is enhanced with increasing HCl concentration (Figure 1). At a lower concentration of the acid, the transition of hemicelluloses' fragments to water is dominant, but, at the HCl concentration  $> 0.15$  g/dl, the amount of lignin aromatic fragments in the hydrolysate starts to increase (Figure 3). The cleavage of the glucosidic linkages in the lignocellulosic matrix influences the functional groups' composition. This testifies the increase in the values of O/C with growing applied HCl concentration (Figure 4).

The UV-spectrum of the hydrolysate obtained with the highest HCl concentration was characterised by pronounced absorbance bands at 238, 288 and 338 nm, indicating the presence of biphenyl derivatives and aromatic fragments, containing non-etherified hydroxyl groups, carbonyl and carboxyl groups.

According to Figure 1, the hydrolysis with the HCl concentration more than 0.15 g/dl does not lead to an essential change in the amount of the released water-soluble degraded products. However, the application of higher concentrations of HCl increases the content of low molecular lignin fragments in the hydrolysate that is not rational, taking into account the following modification of the obtained wood microparticles.

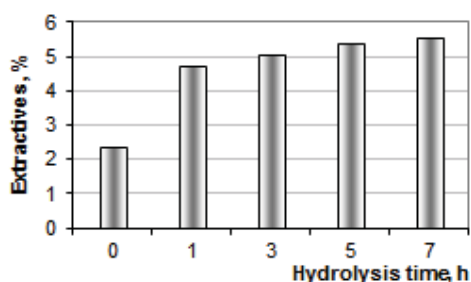


Figure 5. Extractives concentration in the hydrolysate *versus* hydrolysis time.

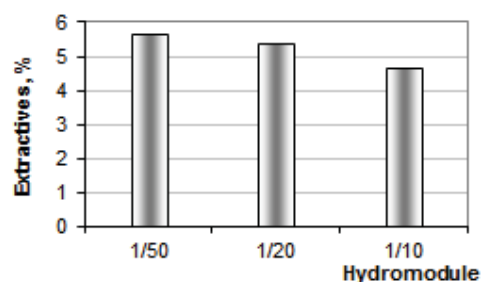


Figure 6. Extractives concentration in the hydrolysate *versus* hydrolysis hydromodulus.

The results shown in Figure 5 reflect the effect of the hydrolysis duration, using a 0.15 g/dl HCl concentration, on the yield of the degraded products. It is seen that, with increasing hydrolysis time, the concentration of the extractives in the hydrolysate grows. It is found that the relative content of cellulose increases, but the relative lignin content in the sawdust decreases after the hydrolysis time 5 h. The found correlation of the degraded products' concentration with time has the same saturation character as the dependence of the extractives on the acid concentration.

According to Figure 6, with decreasing hydrolysis hydromodulus (mass ratio of sawdust to water) from 1/10 to 1/50, the extractives concentration in the hydrolysate, obtained with a 0.15 g/dl HCl concentration at a hydrolysis duration of 5 h, remarkably enhances. The components composition analysis of the hydrolysed residue obtained at a hydromodulus of 1/50 showed that the extractives had mainly the hemicelluloses nature. However, the use of a hydrolysis hydromodulus of 1/50, in spite of the absent of a large amount of the lignin's fragments, is not beneficial, because the hydrolysis requires a considerable consumption of water.

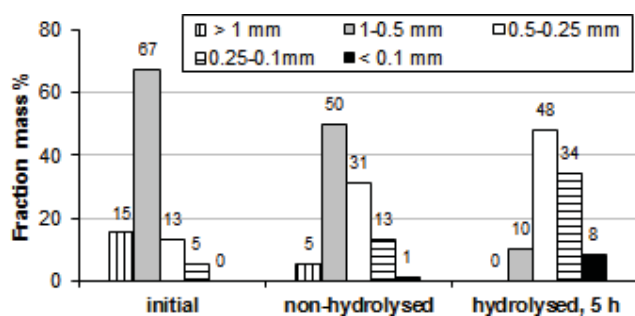


Figure 7. Fractional composition of milled initial, non-hydrolysed and hydrolysed aspen sawdust.

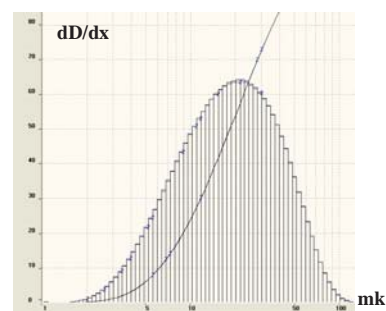
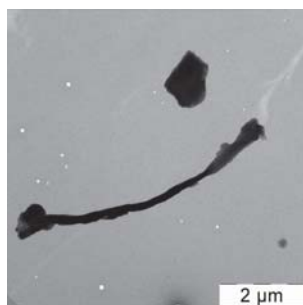


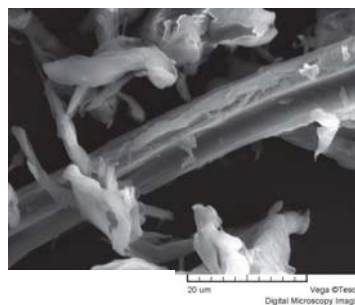
Figure 8. Size distribution histogram of hydrolysed aspen microparticles (< 100 mk).

The components composition changes in the lignocellulosic matrix lead to the reduction of its mechanical strength. This is testified by a pronounced shift in the fractional composition of the milled aspen sawdust, hydrolysed with a 0.15 g/dl HCl concentration for 5 h at a hydromodulus of 1/20, toward the content of the microparticles with the sizes  $< 250$  mk (Figure 7) and a 3-fold decrease in the milling time for obtaining the fine

particles ( $< 250$  mk), in comparison with the case of non-hydrolysed sawdust. The analysis of the particle size distribution within the fraction  $< 100$  mk showed that more than 50% of the fraction volume was occupied by the lignocellulosic particles with sizes of 10-30 mk (**Figure 8**).



**Figure 9.** TEM image of the obtained aspen microparticles.



**Figure 10.** SEM image of the obtained aspen microparticles.

The study of the obtained microparticles by TEM revealed the prevalence of two types of the microparticles' shape, namely, oval and extended ones (**Figure 9**) with average sizes of 1-2 mk and 6-8 mk, respectively.

The performed low temperature pre-treatment of wood with dilute HCl is gentle and thus has a negligible effect on the morphology of aspen wood fine fibres that is testified by their SEM image given in **Figure 10**.

#### IV. CONCLUSIONS

The optimal parameters of the low temperature hydrolysis of the aspen sawdust with dilute acid for reducing sawdust particle sizes, with the aim of their further chemical modification, are found. These parameters are compromised from the point of view of the lignocellulosic matrix destruction and the lignin content. The pronounced growth of the finest particles in the milled wood and the essential drop of the milling time were achieved mainly by the partial hydrolysis of hemicelluloses. At the same time, the performed hydrolysis is gentle and has a negligible effect on the morphology of aspen wood.

#### V. ACKNOWLEDGEMENT

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