ANALYSIS OF THE INFLUENCE OF PRE-TREATMENT WITH LIQUID HOT WATER (LHW) ON THE CHEMICAL COMPOSITION OF WOODEN CHIPS

Aleksandar D. Drpić[1,2*], Jasmina J. Popović[1], Mlađan M. Popović[1], Milanka R. Điporović- Momčilović[1]

[1]University of Belgrade- Faculty of Forestry, Belgrade, Serbia
[2]Institute IMS, a.d., Belgrade, Serbia

(ORIGINAL SCIENTIFIC PAPER)
UDC 674.8.031.931.2:66.093
DOI 10.5937/savteh2202040D

The goal of this paper is to analyze the chemical composition of untreated and treated wooden chips from the native narrow-leaved ash (*Fraxinus angustifolia Vahl. ssp. Pannonica Soó & Simon*). In order to determine the effect of pretreatment with liquid hot water (LHW) on changes in chemical composition, the content of moisture, cellulose, lignin, minerals (ash), extractives soluble in hot water, extractives soluble in organic solvents, for treated and for untreated wooden chips was determined. This was done in accordance with TAPPI and ASTM standard methods. The properties of wooden chips, treated for 30 min and 60 min at a temperature of 100 °C, are compared to untreated wooden chips and changes in the chemical composition that occurred are defined as a result of the applied treatments. The research was performed under controlled conditions in a laboratory, and the results of treatments were the subject of comparative analysis. Applied treatments had a statistically significant effect on decreasing the content of extractives. The content of cellulose and hemicellulose increased in the treated wooden chips compared to untreated wooden chips, while the lignin content did not significantly change.

Keywords: native narrow-leaved ash; pretreatment with liquid hot water (LHW); analysis of the chemical composition of treated and untreated wooden chips

Introduction

Liquid hot water treatment (LHW) or autohydrolysis or hydrothermal treatment is often used in wood processing processes. Liquid hot water (LHW) pretreatment has become one of the leading pretreatment technologies utilizing no other chemicals except liquid water at decreased temperature and pressure [1,2]. LHW leads to increased cellulose accessibility and minimises the production of potentially inhibitory products [3]. In LHW pretreatment, water acts as a solvent and also as a catalyst accompanied by released organic acids from biomass to help disrupt the cell wall matrix [4]. The major changes include the dissolution of hemicellulose, partial removal and relocation of lignin, limited deconstruction of cellulose, and minimal carbohydrate degradation. Hemicelluloses are reported to be almost completely solubilized and deconstructed from biomass in liquid hot water pretreatment at 200 °C for 50 min [5]. Grénman et al [6]. measured hemicellulose sugars extracted from softwood at 150–170 °C during LHW and reported that the dissolution of hemicelluloses depends on the pretreatment temperature, while its degradation was strongly influenced by the pH of the system.

LHW treatment is used to change the structure of biomass by removing hemicelluloses and changing the structure of lignin, which will make cellulose more accessible for the further process of enzymatic hydrolysis [7]. LHW pretreatment of wood leads to various chemical changes. Water penetrates biomass at a certain temperature and under high pressure, and in that case, carbohydrates (hemicelluloses and cellulose) and water-soluble lignin are subjected to depolymerization reactions. Hemicelluloses are hydrolyzed into water-soluble oligomers or monomeric sugars (auto-hydrolysis) [8]. Carbohydrates from hemicelluloses can be separated in the form of oligosaccharides from insoluble cellulose and lignin fractions [9].

Acetic acid is released during LHW treatment from O-acetyl groups in the polysaccharides, which lowers the pH of the extract to the range of 3-4 [10]. The hemicelluloses are then dissolved as oligomers after acid hydrolysis of the polymeric structures. Subsequently, the hemicellulose oligomers in the solution are partially further hydrolyzed to monomer sugars and sugar degradation products. Sugar degradation products include hydroxymethylfurfural (HMF) formed from hexose sugars and furfural formed from pentoses and uronic acids [10]. Lignin is partially depolymerized and solubilized, but complete delignification is not possible using hot

***Author address**: Aleksandar D. Drpić, Institut IMS, a.d., Bulevar vojvode Mišića 43, 11000, Belgrade, Serbia, email: aleksandar.drpic@institutims.rs
The manuscript received: July 5, 2022.
Paper accepted: September 26, 2022.

water alone, because of the recondensation of soluble components originating from lignin [11].

Pressure is applied during the LHW treatment when water needs to boil at increased temperature (160 °C to 240 °C) [7].

The effectiveness of LHT pretreatment depends on the conditions of operation (temperature, duration of the treatment), as well as on the type of treated biomass (softwood, hardwood) [12], and also depends on different properties of water (such as ionic strength, pH, and viscosity). Water at high temperatures acts as an acid, reducing the pH to slightly acidic levels, causing hydration of the cellulose, significant solubilization of hemicellulose, and, depending on the substrate, partial or no degradation of lignin [13].

Different treatment durations (30 min treatment and 60 min treatment at a temperature of 100 °C) are analyzed in this paper, as well as the changes in the chemical composition of treated wooden chips compared to untreated wooden chips from the native narrow-leaved ash.

The advantages of applying liquid hot water pretreatment are the following: prevention of corrosion, prevention of sediment formation (for example, on the reactor walls), reduction of total process costs, and under normal conditions, there is no large amount of cellulose degradation [14].

Materials and methods

Sample preparation

As material in this paper, a sampled tree from the native narrow-leaved ash (*Fraxinus angustifolia Vahl*. *ssp. Pannonica Soó & Simon*) was used. The sampled tree was cut into logs about 1 m long and hand-debarked. The samples were chopped into chips. Subsequent grinding of the chips into the required particle size was done by using a laboratory hammer mill (Type LHM 18A). According to the instructions of the TAPPI standard method T 257 sp-14 [15], the fraction of wooden particles suitable for chemical analysis was isolated. For the research, it was necessary to prepare wooden particles in dimensions sized from 1 mm to 0.5 mm, because it was determined that these particle dimensions are most suitable for complete penetration of chemical agents into wooden raw materials [16-18]. Accordingly, the grinded wooden chips are fractionated on a series of five vibrating sieves with dimension openings of: 1.5 mm; 1 mm; 0.5 mm, 0.4 mm and zero sieves. The required amount of wooden chips necessary for the research was obtained in the controlled procedure of treating wooden chips with water at 100 °C in periods of 30 min and 60 min (TW 30 and TW 60), in an autoclave-device brand “Stalsvets" (Sweden). After cooling the autoclave to room temperature, the treated wooden chips are washed with water.

Analytical methods for the chemical composition of wooden chips

The chemical composition of treated and untreated (Contr) wooden chips is analyzed: moisture, ash, cellulose, lignin, extractives soluble in hot water and extractives soluble in organic solvents.

All results of the content of chemical components are expressed in relation to the absolute dry mass of wood as mean values (arithmetic mean) of three consecutive repetitions.

During the analysis of the chemical composition, all masses were measured on a Sartorius semi-automatic analytical scale with an accuracy of 0.1 mg. The dishes for the measurements (weighing bottle, filter flasks) were previously dried to a constant mass, and then, after cooling in a desiccator, their mass was measured.

All test results were processed by using statistical analysis (one-factor ANOVA).

Determination of moisture content

The moisture content of samples of wooden chips from the native narrow-leaved ash was determined gravimetrically in accordance with the standard TAPPI method 264 cm-97 [19], by measuring the difference between the mass of samples before and after drying at 103 ± 2 °C to the constant mass. The procedure includes drying of weighing bottles to a constant mass (103 ± 2 °C for 5 hours) and cooling in a desiccator, with repetition until the difference in mass is less than 0.001 g. About 1 g of wet wooden raw material is poured into the completely dry weighing bottles previously prepared, the mass is measured and the procedure is repeated.

Determination of cellulose content by the Kurschner-Hoffer method

The cellulose content in the samples was determined by the Kurschner-Hoffer method [17]. For this analysis, an apparatus consisting of a water bath, an Erlenmeyer flask and a condenser was used. Erlenmeyer flasks with a mixture of raw materials and a solution of nitric acid and ethanol (20% HNO_3: 80% C_2H_5OH) were immersed halfway into a boiling water bath, and constant cooling of the condenser with water. The reaction lasts for 2 h from the moment the mixture in the Erlenmeyer flasks began to boil. The cellulose was washed until a neutral pH value was achieved. Then the filter flasks with the cellulose were placed in an oven (103 ± 2 °C), dried to a constant mass and then measured.

Determination of the content of extractives soluble in liquid hot water

Determination of the content of extractives soluble in liquid hot water was performed in accordance with the standard TAPPI method T 207 cm-99 [20]. The procedure was the following: the raw wooden material was poured into Erlenmeyer flasks, into which 100 ml of distilled water was added; then the Erlenmeyer flasks were connected to cooling condensers and immersed (up to

half) in boiling water baths. After 1 h of extraction, the extracted wooden chips were filtered using distilled water in a vacuum bottle. Finally, the filter flasks with the extracted wooden raw material were dried in an oven at a temperature of 103 ± 2 °C, to a constant mass.

Determination of the content of extractives soluble in organic solvents

Determination of the content of extractives soluble in organic solvents was performed in accordance with the standard method ASTM D1107-96 [21]. The procedure is based on the extraction of wooden raw material in a mixture of toluene and ethanol in a volume ratio of 2:1 ($C_6H_5CH_3$: C_2H_5OH = 2:1) in a Soxhlet apparatus. The measured filter flasks of raw material are placed in the extraction part of the Soxhlet apparatus. After extraction, all the extractives are dissolved in the extraction mixture in the flask of the Soxhlet apparatus, and the raw material in the filter flask was extracted. After drying it at room temperature, it was used as the starting material for isolating Klason lignin. The mixture with the dissolved extractives from the flask was transferred to the evaporation dishes. The extraction mixture was evaporated in a sand bath at a temperature below 50 °C. After evaporation, extractives remained at the bottom of the evaporating dishes. The evaporating dishes with extractives were dried in an oven at a temperature of 103 ± 2 °C to a constant mass and measured after cooling in desiccators.

Determination of lignin content using the Klason method

The lignin content in the samples was determined by the modified Klason method T 222 om-11 [22]. Hydrolysis of wooden substances is a reaction on glycosidic bonds and refers to their hydrolytic breaking with the presence of sulfuric acid. The procedure includes hydrolysis at room temperature for 2.5 hours, and hydrolysis after exposure to increased temperature (120 °C) for 1 hour. Hydrolytic decomposition reactions of polysaccharides of wooden mass in the acidic environment, i.e. the conversion of cellulose and hemicelluloses into simple sugars, which are dissolved in the reaction mixture and removed by filtering through the filter flask, while the lignin remains in the filter flask as an undissolved precipitate. The lignin is carefully transferred from the Erlenmeyer flasks into the filter flasks, by using distilled water and washed until a neutral pH value is achieved. After washing, the lignin in the filter flask is dried at a temperature of 103 ± 2 °C to a constant mass, and then the mass of the filter flask with lignin in an absolutely dry state is measured.

Determination of acid-soluble lignin content by UV spectrophotometric method

The content of acid-soluble lignin using the UV-spectrophotometric method was determined according to the instructions of the TAPPI standard method T UM 250 [23]. The procedure was the following: the required solution was prepared by pouring distilled water into Erlenmeyer flasks with Klason lignin in it; after 24 h of lignin precipitation, 1 ml of the undiluted filtrate from the Erlenmeyer flask was taken with a pipette and transferred to previously prepared test tubes, and 15 ml of 3% H_2SO_4 was added with a pipette. Afterwards, the necessary dilution of the filtrate was achieved. UV-absorption of the prepared solution was measured on a UV - spectrophotometer Vision-600, using quartz cuvettes with a width of 1 μm.

Determination of the mineral content

Mineral content in the test samples was determined in accordance with ASTM method D 1102-84 [24]. According to this method, the mineral content is determined by burning wooden raw materials in a furnace. During burning, all organic components turn into carbon dioxide and water vapour, and substances of mineral origin remain in the form of non-combustible residue, i.e. ashes.

Results and discussion

Moisture content of wooden chips

After air drying the untreated (Contr) samples and samples of wooden chips from the native narrow-leaved ash treated at a water temperature of 100 °C for 30 min (TW 30) and 60 min (TW 60), the absolute and relative moisture content, as well as the dryness coefficient, were determined. The results are presented in Table 1.

Table 1. Absolute moisture content (W_{aps}), relative moisture content (W_{rel}) and coefficient of dryness (K_s)

Treatment	W_{aps}	W_{rel}	K_s
Contr	6.90±0.04	6.45±0.04	0.94
TW 30	8,63±0,05	7,95±0,04	0,92
TW 60	8,70±0,09	8,01±0,08	0,92

TW 30- water treatment for 30 min at 100 °C; TW 60- water treatment for 60 min at 100 °C

Table 1 shows that the absolute moisture content of air-dried samples of wooden chips from the native narrow-leaved ash treated with water for 30 min is 8.63% (TW 30) and treated with water for 60 min is 8.70% (TW 60). These values are slightly higher compared to the moisture content of untreated (Contr) samples.

Pretreatment effects on the content of main components of wooden chips from the native narrow-leaved ash

Pretreatment effects on cellulose content

The content of cellulose for untreated (Contr) sam-

ples and samples of wooden chips from the native narrow-leaved ash treated with liquid hot water at a temperature of 100 °C for 30 min (TW 30) and 60 min (TW 60), determined by the Kurschner-Hoffer method, are shown in Figure 1.

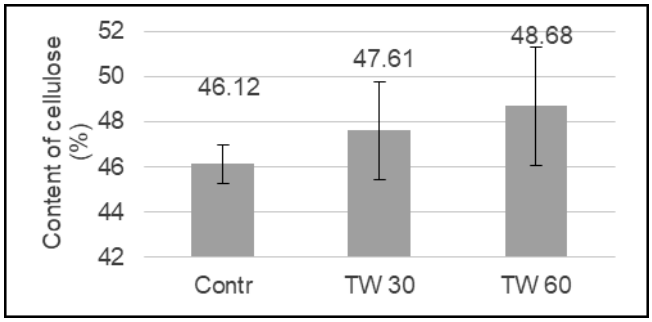

Figure 1. Content of cellulose for untreated (Contr) samples and samples of wooden chips from the native narrow-leaved ash with standard deviation, treated with water at 100 °C (TW 30- water for treatment 30 min; TW 60- water treatment for 60 min)

Figure 1 shows that the cellulose content of samples of wooden chips from the native narrow-leaved ash, treated with water for 30 min is 47.61% (TW 30) and treated with water for 60 min, is 48.68% (TW 60). These values are slightly higher compared to the untreated (Contr) sample which is 46.12%. This means that applied treatments led to an increase in the participation of cellulose in the tissue of the treated samples. According to literature, water treatments, as well as treatments with dilute acid solutions, led to hydrolytic degradation of glycosidic bonds in amorphous regions of cellulose microfibrils [18,25,26]. Laurová and Kačik (2009) noticed that D-glucose originating from glucomannan, as well as from amorphous regions of cellulose, was the main product in the hydrolysate from the liquid hot water treatment of wooden chips from the narrow-leaved ash (*Fraxinus exelsior* L.) at temperatures of 100 - 140 °C [27]. In the extract from the treatment of wooden chips from native narrow-leaved ash with water at 100 °C for 60 min, Popović (2015) noticed the presence of 2.06% glucose, as the main product, which originates from glucomannan and amorphous areas of cellulose [28]. It can be assumed, according to the data from literature, that treatments applied in this paper caused cellulose hydrolysis reactions, but to a lesser ratio compared to other degradation reactions of wood tissue, which caused a relative increase in cellulose participation in treated samples.

Pretreatment effects on lignin content

The mean values results obtained for the determination of Klason lignin and acid-soluble lignin for untreated and for treated samples of wooden chips from the native narrow-leaved ash are shown by summary diagrams in Figure 2, where the values of acid-soluble lignin are marked with a lighter shade of grey, while the Klason lignin is marked with a darker shade of grey.

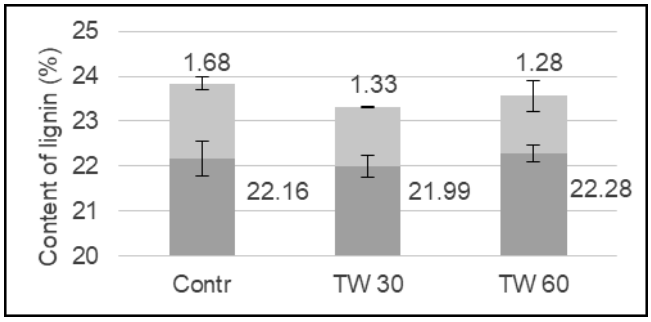

Figure 2. Content of lignin for untreated (Contr) samples and samples of wooden chips from the native narrow-leaved ash with standard deviation, treated with water at 100 °C (TW 30- water treatment for 30 min; TW 60- water treatment for 60 min)

The values of total lignin content in treated samples are 23.32% (TW 30) and 23.56% (TW 60) and are slightly lower compared to the total lignin content in untreated samples of wooden chips from the native narrow-leaved ash, which is equal to the value of 23.84%. Total lignin was obtained by adding acid-soluble lignin and Klason lignin.

Pretreatment effects on hemicelluloses content

According to the literature, the decomposition of hemicelluloses during treatment with liquid hot water at 100 °C is expected, but the content of hemicelluloses in the treated samples obtained by calculation increased from 19.78% (untreated) to 26.13% (TW 30) and 25.17% (TW 60) (Figure 3). This apparent increase in the content of hemicelluloses is probably a consequence of a great loss of other materials dissolved from wooden chips from the native narrow-leaved ash during treatment.

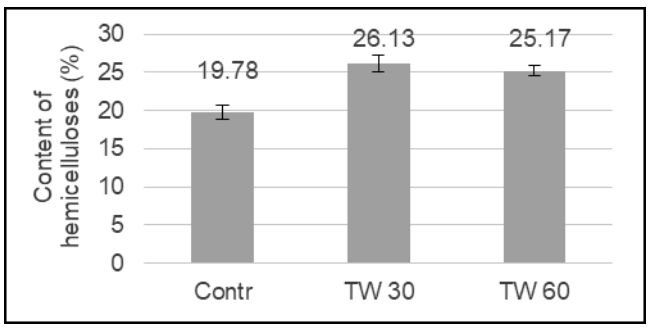

Figure 3. Content of hemicelluloses for untreated (Contr) samples and samples of wooden chips from the native narrow-leaved ash with standard deviation, treated with water at 100 °C (TW 30- water treatment for 30 min; TW 60- water treatment for 60 min)

Similar results were obtained by other researchers. D-glucose was detected as the main product of liquid hot water treatment for the narrow-leaved ash (*Fraxinus exelsior* L.) at temperatures of 100 - 140 °C, while the concentration of xylose at these temperatures is lower and increases with temperature and longer duration of treatment [29]. In the aqueous extract of narrow-leaved ash, the ratio of xylose/glucose concentrations in the extract at a temperature of 100 °C is 0.05 and increases to

0.289 when the extract is obtained at a temperature of 160 °C [29]. Based on the results from the literature, it is concluded that hydrolysis of hemicelluloses at a treatment temperature of 100 °C is present to a small extent, but when the temperature is increased and the duration of treatment is longer, reactions will get more intensive.

Content change of main components for wooden chips - An overview

Table 2 shows changes in the content of the main components for treated samples of wooden chips from the native narrow-leaved ash compared to the untreated (Contr) samples.

Table 2. Content change of main components of wooden chips from the native narrow-leaved ash during the treatment compared to untreated samples (TW 30- water treatment for 30 min; TW 60- water treatment for 60 min)

		Differences (%)	
Treatment	Contr	TW 30	TW 60
Content of cellulose	46.12	3.23	5.55
Content of Klason lignin	22.16	- 0.77	0.54
Content of acid-soluble lignin	1.68	-20.83	-23.81
Content of total lignin	23.84	-2.14	-1.17
Content of hemicelluloses	19.78	32.10	27.25

Table 3 shows results for the contents of the main components of wooden chips for untreated and treated groups of samples using statistical analysis (ANOVA).

Table 3. Statistical comparison of untreated and treated groups of samples (ANOVA)

	Contr/TW 30		Contr /TW 60		TW 30/TW 60	
	P-value	F/Fcrit	*P-value*	F/Fcrit	*P-value*	F/Fcrit
Content of cellulose	0.0770	0.7465	0.0038	3.9180*	0.1222	0.4959
Content of Klason lignin	0.5562	0.0533	0.6484	0.0314	0.1839	0.3337
Content of acid-soluble lignin	0.0466	1.0583*	0.1329	0.4597	0.8452	4.46 E-03
Content of total lignin	0.1654	0.3724	0.4208	0.1041	0.3320	0.1577

*Denotes a statistically significant difference at the confidence level of 95%
TW 30- water treatment for 30 min at 100 °C; TW 60- water treatment for 60 min at 100 °C

Using the statistical analysis (one-factor ANOVA), it was concluded that 60 min liquid hot water treatment (TW 60) significantly affected the cellulose content, while 30 min water treatment (TW 30) had a significant effect on acid-soluble lignin content (Table 3). Based on the mentioned analysis, it was concluded that liquid hot water treatments for 30 minutes and 60 minutes did not have a significant impact on the content of Klason lignin and total lignin (Table 3).

Pretreatment effects on the content of auxiliary components of wooden chips from the native narrow-leaved ash

Pretreatment effects on the mineral content

The mean values of the mineral content for untreated (Contr) samples and samples of wooden chips from the native narrow-leaved ash treated with water at a temperature of 100 °C for 30 min (TW 30) and 60 min (T), expressed as the mineral content, are shown in Figure 4.

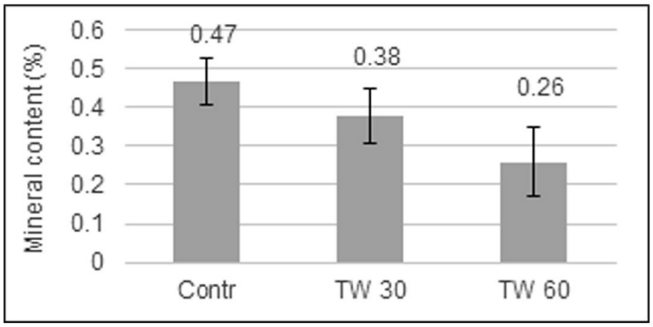

Figure 4. Mineral content for untreated (Contr) samples and mineral content for samples of wooden chips from the native narrow-leaved ash with standard deviation, treated with water at 100 °C (TW 30- water treatment for 30 min; TW 60- water treatment for 60 min)

The values of mineral content in treated samples are 0.38% (TW 30) and 0.26% (TW 60) and are slightly lower compared to the mineral content in untreated samples of wooden chips from the native narrow-leaved ash, which equals the value of 0.47%. Some parts of mineral materials present in the wood during the treatment are dissolved in the reaction mixture and removed with it. Statistical analysis showed that only liquid hot water treatment for 60 min (TW 60) significantly affected the mineral content (Table 4). Stevanović-Janežić (1993) stated that only a part of the mineral materials present in the wood is soluble in water, which is confirmed by the results of this paper [25].

Pretreatment effects on the content of extractives soluble in hot water

The mean values of extractives soluble in hot water for untreated (Contr) samples and samples of wooden chips from the native narrow-leaved ash treated with water at a temperature of 100 °C for 30 min (TW 30) and 60 min (TW 60) are shown in Figure 5.

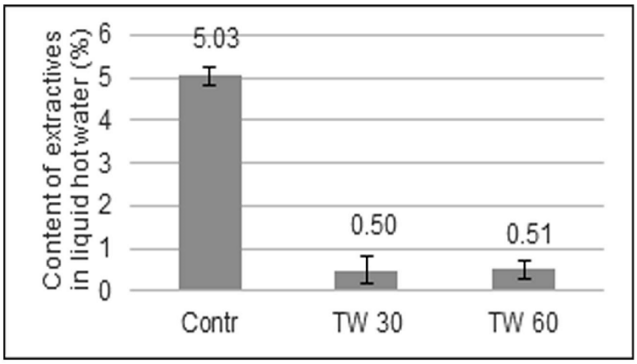

Figure 5. Content of extractives soluble in liquid hot water for untreated (Contr) samples and content of extractives soluble in liquid hot water of wood chips from the native narrow-leaved ash with standard deviation, treated with water at 100 °C (TW 30- water treatment for 30 min; TW 60- water treatment for 60 min)

Figure 5 shows that the content of extractives soluble in liquid hot water for samples of wooden chips from the native narrow-leaved ash treated with water for 30 min is 0.50% (TW 30) and treated with water for 60 min is 0.51% (TW 60). These values are significantly lower compared to the untreated (Contr) samples which is equal to 5.03%. Popović (2015) stated that the content of materials soluble in hot water in samples of wooden chips from the native narrow-leaved ash treated with water at 100 °C for 60 min was reduced by 75.52% [28]. Zhang et al. (2013) stated that the content of extractives was reduced by 67.42 % in mature wooden samples and by 69.42% in wooden samples from the narrow-leaved ash (*Fraxinus mandshurica Rupr.*), treated in an alkaline medium [30]. Such results are expected since the extractives are located in the lumens and micro- and macro-cavities of the cell walls, and are not bound by physico-chemical bonds to the macromolecular components of the cell wall. According to that state, as well as due to the relatively low molecular mass, extractives can be easily extracted from wood and are the first to be removed from wood tissue during treatment [31].

Pretreatment effects on the content of extractives soluble in toluene/ethanol mixture

The mean values of extractives content in organic solvents (toluene/ethanol mixture) for untreated (Contr) samples and samples of wooden chips from the native narrow-leaved ash treated with water at 100 °C for 30 min (TW 30) and 60 min (TW 60) are shown in Figure 6.

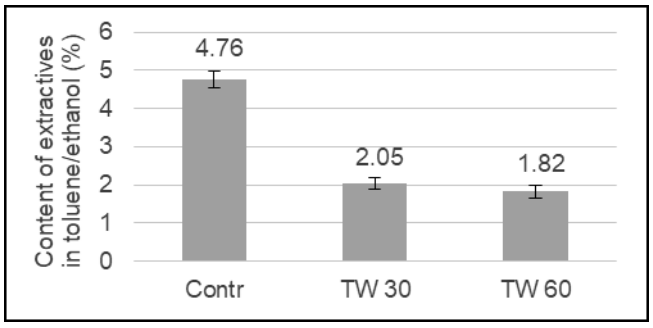

Figure 6. Content of extractives soluble in organic solvents (toluene/ethanol) for untreated (Contr) samples and samples of wooden chips from the native narrow-leaved ash with standard deviation, treated with water at 100 °C (TW 30- water treatment for 30 min; TW 60- water treatment for 60 min)

The content of extractives soluble in the mixture of toluene/ethanol for untreated samples was equal to 4.76%, and after treatment with water at 100 °C for 30 min decreased to a value of 2.05% and after treatment with water for 60 min decreased to a value of 1.82% at the same temperature. Popović (2015) also stated that the content of materials soluble in a mixture of toluene/ethanol in samples of wooden chips from the native narrow-leaved ash treated with water at 100 °C for 60 min decreased by 57.74% compared to untreated samples [28]. The slightly higher content of materials extracted with a mixture of toluene/ethanol for treated samples compared to the content of materials extracted with liquid hot water is due to the presence of compounds insoluble in water during treatment.

Content change of auxiliary components for wooden chips- An overview

Table 4 shows results for contents of auxiliary components of wooden chips for untreated and treated groups of samples using statistical analysis (one-factor ANOVA).

Table 4. Statistical comparison of untreated and treated groups of samples (ANOVA)

	Contr/TW 30		Contr/TW 60		TW 30/TW 60	
	P-value	F/Fcrit	*P-value*	F/Fcrit	*P-value*	F/Fcrit
Mineral content	0.09348	0.6626	0.00887	2.4235*	0.0916	0.6724
Content of extractives soluble in hot water	1.07 E-06	119.4677*	1.15 E-06	115.9552*	0.95072	5.61 E-04
Content of extractives soluble in toluene/ethanol mixture	7.85 E-09	3585.6162*	1.8 E-06	236.6094*	0.02712	1.5048*

*Denotes a statistically significant difference at the confidence level of 95%
TW 30- water treatment for 30 min at 100 °C; TW 60- water treatment for 60 min at 100 °C

Table 5 shows an overview of changes in the content of auxiliary components for treated samples of wooden chips from the native narrow-leaved ash compared to untreated (Contr) samples, expressed as a percentage.

Table 5. Content change of auxiliary components of wooden chips from the native narrow-leaved ash during liquid hot water pretreatment compared to untreated samples

		Differences (%)	
Treatment	Contr	TW 30	TW 60
Mineral content	0.47	-19.15	-44.68
Content of extractives soluble in hot water	5.03	-90.06	-89.86
Content of extractives soluble in toluene/ethanol mixture	4.76	-56.93	-61.76

TW 30- water treatment for 30 min at 100 °C; TW 60- water treatment for 30 min at 100 °C

Based on statistical analysis, it is concluded that 30 min water treatments (TW 30) and 60 min hot water treatments (TW 60) had a significant effect on the content of extractives soluble in a toluene/ethanol mixture (Table 4).

Table 5 shows that the applied treatments led to a decrease in the content of auxiliary components of wooden chips by 19 – 90%. A greater impact on the mineral content had a treatment with water for 60 minutes, which led to a decrease in the content of these materials by almost 45%, while treatment for 30 minutes decreased their content by only 19%. Water treatments decreased the content of extractives for wooden chips from the native narrow-leaved ash for about 90% (when dissolved in hot water), and by 57 – 62% (when dissolved in a mixture of toluene/ethanol). It is important to note that the porosity and permeability of treated wooden chips from the native narrow-leaved ash are increased after the removal of a significant amount of extractives.

Conclusion

The main goal of this paper was to determine the changes in the chemical composition of wooden chips of native narrow-leaved ash, which occurred during the applied liquid hot water pretreatments (LHW). It was concluded that liquid hot water pretreatments at a temperature of 100 °C led to changes in the content of auxiliary and main components of treated wooden chips from the narrow-leaved ash as follows:

- the cellulose content of wooden chips from the native narrow-leaved ash treated for 30 min and treated for 60 min at a temperature of 100 °C statistically increased significantly compared to the untreated (controlled) sample;
- the total lignin content for wooden chips from the native narrow-leaved ash treated for 30 min and 60 min at a temperature of 100 °C is statistically insignificantly lower compared to the untreated (controlled) sample;
- hemicelluloses content of wooden chips treated for 30 min and treated for 60 min at 100 °C statistically increased significantly compared to untreated sample;
- the content of mineral materials in the samples treated for 30 min and 60 min are statistically negligible lower compared to the control (untreated);
- the content of extractives soluble in hot water is statistically significantly lower in the treated samples 30 min and 60 min compared to the controlled sample;
- the content of extractives soluble in the toluene/ethanol mixture is statistically significantly lower in samples treated for 30 min and 60 min compared to untreated (controlled) samples.

By changing the treatment parameters (temperature, duration of treatment), it is possible to influence the change in the chemical composition of the treated wooden chips.

Acknowledgements

The results were obtained within the master's paperwork of Aleksandar Drpić, "THE INFLUENCE OF WATER PRETREATMENT ON THE PROPERTIES OF CHIPBOARDS" finished and defended at the University in Belgrade-Faculty of Forestry, Serbia

References

[1] Lishi Y, Ruoshui M, Liangzhi L, Jiaolong F. Hot water pretreatment of lignocellulosic biomass: an effective and environmentally friendly approach to enhance biofuel production. *Chemical Engineering Technology.* 2016, 39 (10), 1759–70. https://doi.org/10.1002/ceat.201600394

[2] Zhuang X, Wang W, Yu Q, Qi W, Wang Q, Tan X, Zhou G, Yuan Z. Liquid hot water pretreatment of lignocellulosic biomass for bioethanol production accompanying with high valuable products. *Bioresource Technology*. 2016, 199, 68–75. https://doi.org/10.1016/j.biortech.2015.08.051

[3] Youngmi K, Hendrickson R, Mosier NS, Ladisch MR. Liquid hot water pretreatment of cellulosic biomass. *Biofuels Methods and Protocols*. 2009, 581, 93–102. 10.1007/978-1-60761-214-8_7

[4] Mosier NS. Fundamentals of aqueous pretreatment of biomass. Aqueous pretreatment of plant biomass for biological and chemical conversion to fuels and chemicals. *John Wiley & Sons Ltd* , 2013, 129–143. https://doi.org/10.1002/9780470975831.ch7

[5] Nitsos CK, Choli-Papadopoulou T, Matis KA, Triantafyllidis KS. Optimization of hydrothermal pretreatment of hardwood and softwood lignocellulosic residues for selective hemicellulose recovery and improved cellulose enzymatic hydrolysis. *ACS Sustainable Chemistry & Engineering*. 2016, 4 (9), 4529–44. https://doi.org/10.1021/acssuschemeng.6b00535

[6] Grénman H, Eränen K, Krogell J, Willför S, Salmi T, Murzin DY. Kinetics of aqueous extraction of hemicelluloses from spruce in an intensified reactor system. *Industrial & Engineering Chemistry Research*. 2011, 50 (7), 3818–28. https://doi.org/10.1021/ie101946c

[7] Teixeira SSR, Silva SA, Moutta OR, Ferreira-Leitão SV, Barros ROR, Ferrara MA, Bon PSE. Biomass pretreatment: a critical choice for biomass utilization via biotechnological routes, 5th Congress of the Brazilan Biotechnology Society (SBBIOTEC), Brazil, 2014. https://doi.org/10.1186/1753-6561-8-S4-O34

[8] Parajó JC, Garrote GJ, Cruz M, Dominguez H. Production of xylooligosaccharides by autohydrolysis of lignocellulosic materials. *Trends in Food Science & Technology*. 2004, 15 (3-4), 115-120. https://doi.org/10.1016/j.tifs.2003.09.009

[9] Taherzadeh JM, Karimi K. Pretreatment of Lignocellulosic Wastes to Improve Ethanol and Biogas Production: A Review, *International Journal of Molecular Sciences*, 2008, 9, 1621-1651. https://doi.org/10.3390/ijms9091621

[10] Chen XW, Lawoko M, Heiningen van A. "Kinetics and mechanism of autohydrolysis of hardwoods," *Bioresource Technology.* 2010, 101 (20), 7812-7819. https://doi.org/10.1016/j.biortech.2010.05.006

[11] Alvira P, Tomás-Pejó E, Ballesteros M, Negro MJ. "Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review," *Bioresource Technology*. 2010, 101 (13), 4851-4861. https://doi.org/10.1016/j.biortech.2009.11.093

[12] Phuttaro C, Sawatdeenarunat C, Surendra KC, Boonsawang P, Chaiprapat S, Khanal SK. Anaerobic digestion of hydrothermally-pretreated lignocellulosic biomass: Influence of pretreatment temperatures, inhibitors and soluble organics on methane yield. *Bioresource Technology*. 2019, 284, 128–138. https://doi.org/10.1016/j.biortech.2019.03.114

[13] Kumar M, Oyedun OA, Kumar A. A review on the current status of various hydrothermal technologies on biomass feedstock. *Renewable and Sustainable Energy Reviews*. 2018, 81, 1742–1770. https://doi.org/10.1016/j.rser.2017.05.270

[14] Liu S. "Woody biomass: Niche position as a source of sustainable renewable chemicals and energy and kinetics of hot-water extraction/hydrolysis," *Biotechnology Advances*. 2010, 28 (5), 563-582. https://doi.org/10.1016/j.biotechadv.2010.05.006

[15] Test Method TAPPI T 257 sp-14: Sampling and preparing wood for analysis, 2014.

[16] Browning BL. Methods of Wood Chemistry, Volume 1, *Interscience Publications Inc*, New York, London, 1967 a.

[17] Browning BL. Methods of Wood Chemistry, Volume 2, *Interscience Publications Inc*, New York, London, 1967 b. https://doi.org/10.1002/pol.1968.160061112
[18] Fengel D, Wegener G. Wood: Chemistry, Ultrastrukture, Reactions, *Walter de Gruyter GmbH*, 1984, Berlin, 97-100;
[19] Test Method TAPPI T 264 cm-97: Preparation of wood for chemical analysis, 2007.
[20] Test Method TAPPI T 207 cm: Water solubility of wood and pulp, 2008.
[21] ASTM D1107-96: Standard Test Method for Ethanol-Toluene Solubility of Wood, 2013.
[22] Test Method TAPPI T 222 om-11: Acid-insoluble lignin in wood and pulp, 2011.
[23] Test Method TAPPI T UM 250: Acid-insoluble lignin in wood and pulp, 2000.
[24] ASTM D 1102-84: Standard Test Method for Ash in Wood, 2007.
[25] Stevanović-Janežić T. Hemija drveta sa hemijskom preradom - Prvi deo: Hemija drveta, Jugoslavija publik, Beograd, 1993.
[26] Dumitriu S. Polysaccharides: Structural Diversity and Functional Versatility, *Marcel Dekker Inc*, New York, 2005, https://doi.org/10.1021/ja0410486
[27] Laurová M, Kačik F. Permanent Changes To Structure And Properties Of Beech And Ash Wood After Its Hydrothermal Plasticization. Part II, Chemical Changes, *Folia Forestalia Polonica*, 2009, Series B, 40, 15-22.
[28] Popović J. Efekti nekih predtretmana na hemijski sastav juvenilnog i zrelog drveta poljskog jasena (*Fraxinus angustifolia Vahl. ssp. Pannonica Soó & Simon*) i mogućnosti primene tako modifikovanog drveta, Doctoral dissertation, Faculty of Forestry, University in Belgrade, Serbia, 2015.
[29] Laurová M, Kačik F, Sivák J. Water Prehydrolysis Of Willow Wood (*Salix alba* L.), *Acta Facultatis Xylologiae*, 2009, 51 (1), 19−26.
[30] Zhang SY, Wang CG, Fei BH, Yu Y, Cheng HT, Tian GL. Mechanical Function of Lignin and Hemicelluloses in Wood Cell Wall Revealed with Microtension of Single Wood Fiber, *BioResources*, 2013, 8 (2), 2376- 2385; doi: 10.15376/BIORES.8.2.2376-2385
[31] Parham RA, Gray RL. Formation and structure of wood. The Chemistry of Solid Wood, R. M. Rowell (Ed.). *American Chemical Society*, Washington DC, 1984, 43-45.

Izvod

ANALIZA UTICAJA PREDTRETMANA VRELOM VODOM (LHW) NA HEMIJSKI SASTAV DRVNOG IVERJA

Aleksandar D. Drpić[1,2], Jasmina J. Popović[1], Mlađan M. Popović[1], Milanka R. Điporović- Momčilović[1]

[1]Univerzitet u Beogradu- Šumarski fakultet, Beograd, Srbija
[2]Institut IMS, a.d., Beograd, Srbija

(ORIGINALNI NAUČNI RAD)
UDK 674.8.031.931.2:66.093
DOI 10.5937/savteh2202040D

Cilj ovog rada je analiza hemijskog sastava tretiranog i netretiranog iverja drveta poljskog jasena (*Fraxinus angustifolia Vahl. ssp. Pannonica Soó & Simon*). U cilju utvrđivanja uticaja predtretmana vrelom vodom na promene hemijskog sastava, određivan je sadržaj vlage, celuloze, lignina, minerala (pepela), ekstraktiva rastvorljivih u vreloj vodi, ekstraktiva rastvorljivih u organskim rastvaračima, za tretirano i za netretirano drvno iverje pomenute vrste. Rad je urađen u skladu sa standardnim metodama TAPPI i ASTM. Svojstva drvnog iverja tretiranog 30 min i 60 min upoređena su sa netretiranim drvnim iverjom i definisane su promene u hemijskom sastavu koje su nastale kao rezultat primenjenih tretmana. Istraživanje je obavljeno u kontrolisanim uslovima u laboratoriji, a rezultati tretmana su bili predmet uporedne analize. Primenjeni tretmani su statistički značajno uticali na smanjenje sadržaja ekstraktiva. Sadržaj celuloze i hemiceluloza povećan je kod tretiranog drvnog iverja u odnosu na netretirano, dok se sadržaj lignina nije značajno promenio.

Ključne reči: poljski jasen, predtretman vrelom vodom, analiza hemijskog sastava tretiranog i netretiranog iverja.