Effects of water pretreatment on properties of pellets made from beech particles

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Abstract

Particles of beech wood were treated with hot water at the temperature of 150 °C, during 60 min, prior to the pelleting process. The applied hot water pretreatment affected the chemical composition and heating value of particles. Two groups of pellets, designated as PT 10 and PT 20, were produced from treated beech particles, with the moisture content of particles being 10.5 and 20.5 %, respectively. Pellets from nontreated beech particles (PNT) served as controls to assess the hot water pretreatment effects on the pellet properties. Both, the applied pretreatment, and the particle moisture content, affected properties of the obtained pellets. The heating value of PT 10 ad PT 20 pellets has increased for ~6 and 1 %, respectively. The mineral (ash) content in treated pellets decreased for about 24 % in comparison to that in PNT pellets. In addition, the bulk (apparent) density of pellets has increased for 21 % (PT 10) and 10 % (PT 20), as a consequence of the hot water pretreatment of particles. The specific density of PT 10 pellets was for 16 % higher, while the equilibrium moisture content (after conditioning at RH 68 % and 20.1 °C) was for about 32 % lower in comparison to the respective properties of PNT pellets.

Keywords: hot water pretreatment; chemical composition; pellet properties; heating value.

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1. INTRODUCTION

By compressing the comminuted wood material under high pressures (300 to 450 bar), without the addition of adhesives and additives, one can produce pellets as a biofuel of uniform composition and size [1]. Quality of the pellets depends on the processing parameters as well as on the characteristics of raw material, such as: the moisture content, chemical composition, and particle size [2]. The moisture content has a significant influence on friction characteristics of the raw material during pelleting. Besides the applied pressure, the moisture content of raw material also affects the consolidation (density) and the pellet strength [3,4]. Water molecules act as plasticisers, increasing mobility of polymer chains, and decreasing the glass transition temperature [5-7]. The presence of moisture is also significant for formation of bonds between particles in pellets, which is important for the pellet's quality [2]. Water molecules increase the contact surface and participate in formation of van der Vaal's interactions and hydrogen bonds between particles [8-10].

The chemical structure of biomass, which includes three biopolymers, cellulose, hemicelluloses and lignin, is significant for the pelleting process itself, while its elemental composition is important for the processes of thermal decomposition [11]. According to the elemental composition of these three structural compounds in wood, for all wood species, lignin has the highest heating value of 26.7 MJ/kg [12], while both cellulose and hemicelluloses have lower heating values of 17.3 and 16.2 MJ/kg, respectively [11-13].

Some properties, such as high oxygen content, low bulk density, relatively low heating value, hydrophilic nature and high moisture content, are not suitable for application of such biomass as fuel [14]. The initial biomass chemical structure can be changed by different pretreatments such as: steam explosion, torrefaction [15], hydrothermal carbonisation (HTC

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treatment) [16,17], and liquid hot water treatment (LHW) [12,18]. By the torrefaction process, biomass can be converted into a fuel exhibiting more favourable properties [19]. Although there is a high mass loss during torrefaction, the obtained solid product has 80-90 % of the initial energy content [15]. Pelleting of biomass that was torrefied beforehand, produces pellets with lower moisture contents, higher heating values, and higher resistance to biological degradation [20]. In the published literature there are opposite reports on the effects of torrefaction on mechanical properties of pellets, some studies showing improvements [14,21], while the other worsening [22-24]. The process of hydrothermal carbonisation (HTC treatment) of biomass has enabled production of pellets with higher bulk and energy densities, more favourable physical properties (higher moisture resistance and dimensional stability), greater mechanical stability, as well as increased resistance to biodegradability [16,17]. Use of steam explosion of wood before pelleting, results in pellets with higher density [25,26], increased impact and abrasion resistances, and with a lower content of alkaline metals [26].

The liquid hot water treatment (LHW) is one of the proven pretreatment methods for extraction of soluble components in wood. Water is a suitable extraction having wide applications in industry due to non-toxicity and low cost [27]. It can be also applied prior to the conversion of wood into paper, fuel or other products [18]. For example, pre-extraction of hemicelluloses with water is applied before sulphate cooking of wood chips in the production of Kraft pulp [28]. The hot water extraction or liquid hot water treatment (LHW) removes extractive and mineral materials soluble in water. It also removes a part of hemicelluloses [28], which decreases amounts of oxygen and hydrogen in biomass, while the carbon share increases, resulting in an increase in the biomass heating value [4]. By the LHW treatment, it is possible to produce pellets of improved properties - higher thermal power and lower affinity to moisture, with simultaneous removal of hemicelluloses sugars, that can serve as a raw material for a variety of different products such as xylitol, furfural, furfuryl alcohol [29,30], biodegradable plastics and various chemicals currently obtained from petroleum [31-33].

Pu *et al.* studied the effects of temperature (150, 160, 170, and 180 °C) and residence time (1 and 2 h) during the LHW treatment of hardwood chip blends on the heating value [18]. It was found that the heating values of solid residues have increased with the increase in the treatment temperature. However, the total energy content is not always higher, since the mass loss of solids occurs simultaneously. At the extraction temperature of 150 °C and 1 h treatment duration, the energy content of the solid residue was 95 % of that of the initial wood, while at the temperature of 160 °C, only 75 % of the total energy was retained in the solid residue [18]. At the same time, the presence of arabinose, rhamnose, galactose, glucose, xylose, mannose, and other by-products such as acetic acid, formic acid, furfural and HMF (hydroxymethylfurfural) were found in the extract of water treatment. With the increase in the treatment temperature, extraction of hemicelluloses and cellulose is more extensive, resulting in increased lignin concentration in the extracted wood particles [18]. In another study, influence of the LHW treatment was investigated on various biomass samples by changing the treatment conditions such as: temperature (150, 160 and 170 °C), water to biomass ratio (4:1, 5:1 and 6:1), and the treatment duration (30, 45 and 60 min) [12]. It was found that a portion of 10-20 % of the initial biomass has been removed during the LHW treatment, primarily hemicelluloses and ash. As a result, the energy density was increased for up to 25 %, and 50-70 % of the initial ash content was eliminated [12], depending on the treatment conditions. Also, durability, compressive strength and wet integrity of pellets produced from LHW treated biomass have been improved [12].

However, introduction of LHW treatments in the pellet production process increases consumption of energy and water, which increases the cost of the process. Accordingly, use of sugars dissolved in the extract was proposed for the production of furfural, xylitol and other derivatives in order to make this process economically feasible [12].

Water treatment is environmentally favourable and it also provides possibilities for recovery of materials dissolved during this process. Possibilities for such an increase in biomass utilization, which is in accordance with the principles of modern bio-refinery processes, were one of the key motives for this particular research. Yet, the main goal was to explore potentials of water treatment to improve pellet properties. Beech wood particles were selected as the main raw material for production of pellet samples, based on two reasons: 1) there is a lack of data concerning the effects of the LHW treatment on the properties of pellets produced from this wood species, and 2) it is a dominant wood species in Serbia [34], frequently used in the pellet production. Hence, in this work, the influence of hot water pretreatment of beech wood particles, as well as the effects of the moisture content of treated particles on the properties of pellets, have been studied.

2. MATERIALS AND METHODS

2. 1. Materials

The starting material to produce pellets consisted of debarked residues from sawmill processing of beech wood (*Fagus moessaca* (Domin, Maly.) Czecz.). The moisture content of these wood residues was 34.02±0.08 %, as measured upon receiving at the pellet production plant (Amarant d.o.o., Belgrade, Serbia). The residues were hammer milled into particles at the same production site. Care was taken to prevent excessive heat accumulation during the milling process. Particles used in this research were randomly sampled from the produced batch. The fractional composition of the sampled particles was: 27.51±4.72 % of particles larger than 1.2 mm, 8.16±0.94 % in the range 1.0 - 1.2 mm, 17.62±0.84 % in the range 0.5-1.0 mm, 8.20±0.22 % in the range 0.4-0.5 mm, and 38.51±6.23 % of particles smaller than 0.4 mm.

2. 2. Pretreatment of wood particles

Comminuted beech wood particles (regardless the size) were treated with distilled water during 60 min in 6 separate autoclaves at a temperature of 150 °C. The ratio wood:water was 1:4 (w/w), taking into account the moisture present in the wood particles. Pretreatment conditions were selected based on literature data [12,18]. After pretreatment, particles were washed with tap water and air dried in order to achieve two different levels of moisture content of approximately 10 and 20 %. Three batches of treated particles were washed with distilled water and after air drying, they served for particle characterization. The proportion of wood substance dissolved in the reaction mixture during pretreatment was determined by the mass loss of wood.

2. 3. Pellet production

A handmade pellet press was used for the pellet production, with a flat matrix of 40 mm in thickness, and 6 mm diameter of openings (Fig. 1). Three groups of pellet samples were produced under the same processing conditions. Two groups of pellet samples were produced from treated beech wood particles, distinguished by the particle moisture content: 10.54±0.25 % (PT 10) and 20.46±0.18 % (PT 20). The third pellet group was produced from non-treated beech wood particles with the moisture content of 14.87±0.21 % (PNT) and served as a control (Fig. 2). During the pelleting process, the matrix temperature reached a value of about 97 °C. Temperature of the pellet press was measured at the matrix die, using the non-contact thermometer (*Smart Sensor, Intel Instruments, China*).

Figure 1. The pellet press (a), flat die with rollers (b) and the produced pellets (c) [Amarant doo]

Figure 2. Images of the pellet samples (PNT - pellets produced from non-treated beech particles. PT10 and PT20 - pellets produced from treated beech particles with ~10 and 20 % water content, respectively)

2. 4. Conditioning of wood particles and pellets

The samples of non-treated (NT) and treated beech particles (T), as well as the pellet samples (PNT, PT 10 and PT 20), were air-conditioned in a desiccator over the saturated solution of ammonium nitrate (NH_4NO_3, *Centrohem D.O.O, Serbia*) until achieving the constant mass, according to ISO 3129:2012(en) [35]. Conditions in the desiccator were monitored by a digital thermo-hygrometer (*Data Logger LOG32, TFA, Germany*). The mean humidity in desiccator was 68 %, while the mean temperature was 20.1 °C.

2. 5. Characterization of wood particles

Three sample series of wood particles were randomly selected from both treated (T) and non-treated (NT) particles. Since the particle size distribution in different particle samples (T and NT) can affect the treatment process, the fractional composition of wood particles was determined on a laboratory vibrating sieve (*Friedrich Geyer K.-G., Ilmenau/Thuringen, Germany*). The modular sieve system included the sieves of the following sizes: 1.2, 1.0, 0.5 and 0.4 mm (16, 18, 35 and 40 mesh, respectively), and a bottom pan. In addition to the basic information on particle size distribution, this process also enabled selection of the fraction intended for the chemical composition analysis. Hence, the particles retained on a sieve size of 0.5 mm (35 mesh) were used for this latter purpose [36].

The moisture content of particles was determined gravimetrically (TAPPI T 264 cm-97) [37], as well as the particle equilibrium moisture content (EMC), after conditioning (68 %, 20.1 °C).

The chemical characterization of particles (NT and T) included determination of: the cellulose content by the Kurschner-Hoffer method [36]; extraneous matter dissolved in the organic solvent toluol:ethanol = 2:1 v/v (TAPPI T 264cm-97) [37] and in hot water (TAPPI T 207 cm-99) [38]; ash content (TAPPI T 211 om-02) [39]; Klasson lignin content (TAPPI T 222 om-11) [40] and the acid-soluble lignin content at a wavelength of 205 nm by an UV-spectrophotometer *Vision-600* (*Thermo Electron Scientific Instruments LLC, USA*), according to TAPPI T UM 250) [41]. The hemicelluloses content is calculated as the difference between the wood mass (100 %) and the sum of contents of the other wood components.

2. 6. Characterization of pellets

Diameter of the pellet samples was measured according to the standard method EN 16127:2012 [42], after conditioning (68 %, 20.1 °C). The EMC and density were determined according to EN 14774-1:2011 [43] and SRPS EN 15150:2012 [44], respectively. Dimensional stability of the pellets was calculated based on the change in diameter (d_{w-0}) after drying of conditioned samples until reaching the constant mass at the temperature of 105±2 °C, according to the equation (1):

$$d_{W-0} = \frac{d_W - d_0}{d_W} 100 \tag{1}$$

where: d_w is pellet diameter at EMC (68 %, 20.1 °C) and d_0 is pellet diameter after drying.

The bulk density of pellet samples was determined according to EN 15103:2009 [45]. The Vickers microhardness of pellets was determined by using a microhardness tester Buehler Indentamet 5101 - Series Micro Vickers Indentation Hardness Tester (*Buehler MicroMet 5101, USA*) with a load of 0.245 N. The indentation time was 10 s. The mechanical durability of the pellets was determined according to EN 15210-1:2011 [46]. This is essentially a tumbling test in which the sample of pellets is subjected to controlled shocks by collision to each other and against the wall of rotating test chamber. The durability is the measure of the resistance of densified fuels towards shocks and/or abrasion in consequence of transport and handling processes. The value of mechanical durability is calculated according to the equation (2):

$$D_U = \frac{m_A}{m_E} 100 \tag{2}$$

where: m_E is mass of pre-sieved pellets before the tumbling treatment (g) and m_A is the mass of sieved pellets after the test and free from abraded and broken pieces (g).

For determination of elemental composition and the higher heating value (HHV), both particle and pellet samples were prepared by grinding to the fraction smaller than 200 µm and bringing to the EMC state in the laboratory. The elemental and calorific measurements were performed in the laboratory under controlled conditions and according to the appropriate standards [47,48]. The elemental composition was determined by combusting the samples in a stream of pure oxygen (99.995 %) (*LECO elemental analyser, model CHN 628 - LECO Corporation, Michigan, USA*), in accordance to the EN 15104:2011 [47]. The carrier gas was helium (99.995 %). Calibration was checked before each measurement with the use of the certified reference material – ethylenediaminetetraacetic acid (EDTA). The oxygen fraction was determined by calculation (100% minus the contents of the other elements and ash). The upper heating value (HHV) of the samples was determined by combustion of about 0.5 g of the sample in a calorimeter IKA - model C200 (*IKA®-Verke GmbH & Co. KG, Germany*) at using the isoperibolic regime, in accordance with the standard method SRPS EN ISO 18125 [48]. The calorimetric vessel was filled with oxygen of 99.5 % purity (*Messer Tehnogas AD Belgrade, Serbia*), up to the pressure of 30 bar in order to achieve complete combustion. The calorimeter device was checked using the reference sample - benzoic acid tablet of the known heating value.

The ash content was determined in accordance with EN 14775:2010 [49].

Statistical analysis was performed with a single factor ANOVA test, at a confidence level of 95 %.

3. RESULTS AND DISCUSSION

3. 1. Characteristics of wood particles

3. 1. 1. Fractional composition of wood particles

Size fractions for both non-treated (NT) and treated (T) beech particles are presented graphically in Figure 3 and statistically in Table 1.

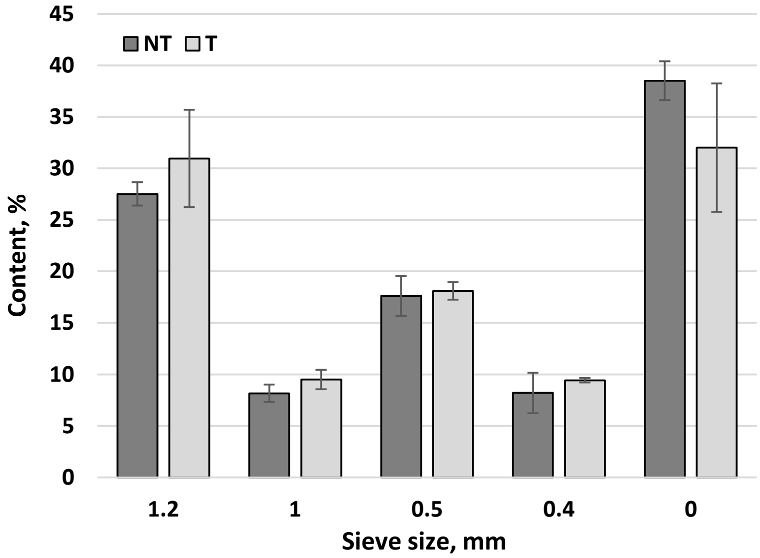

Figure 3. Size fractions of NT and T beech particles (average of n = 3)

Size fractions, of NT and T particles were not statistically significant at the confidence level of 95 %. However, the fractions of particles larger than 0.4 mm have slightly increased, while the smallest particle fraction (<0.4 mm) has been slightly reduced after the water treatment (Fig. 3). This could be expected due to the implementation of washing phase, applied on the T particles, during which the finest particles (wood dust) have been lost (washed out). This loss has also contributed to the total mass loss of particles, together with dissolved wood compounds [50]. This change in particle fractions could arguably affect the consolidation of wood material during the pelleting process and the compaction ratio of pellets, and by itself could present an interesting point to investigate the effects of the washing phase following the treatment. However, due to the non-significant difference between NT and T particle fractions (table 1), it was presumed that the change in size distribution of particles, will not significantly affect the quality of pellets [50].

Table 1. Statistical comparison (ANOVA) of the ratio of treated (T) and non-treated (NT) particles

Sieve size, mm	1.2	1.0	0.5	0.4	0
P-value	0.2865	0.1381	0.7117	0.3465	0.1591
F/F crit*	0.1959	0.4436	0.0204	0.1474	0.3873

*the relation between estimated F value and critical F value in ANOVA test

3. 1. 2. Mass loss of wood particles after the water treatment

The average mass loss of beech particles during the application of water treatment (150 °C, 60 min) was 10.56±0.11 %. Similar results were obtained by Pu *et al.* who reported the solid phase yield of 90 % after the hot water extraction of a wood chip mixture from different softwood species (maple, birch and oak), under the same treatment conditions [18]. The mass loss of wood, during the water treatment, results from the partial dissolution of extractive compounds in water and hydrolysis of structural compounds of wood, primarily hemicelluloses [51].

3. 1. 3. Chemical composition of wood particles

The cellulose content in beech particles have increased by 10.3 %, while the total lignin content increased for only 1.8 %, after the water treatment (Table 2). Pu *et al.* have determined the 31 % increase in the glucose content after the LHW treatment of a wood chip mixture (maple, birch, and oak), under the same treatment conditions, while the lignin content remained unchanged [18]. The content of extractives soluble in organic solvents increased by 17.4 %, while the hot water extracts and the minerals content have decreased by as much as 47.7 and 40.0 %, respectively, due to the high solubility of these substances in water. In addition, the content of other components has decreased by 10.0 % [50]. Pu *et al.* also recorded a decrease in the contents of xylose (21.6 %) and mannose (25 %), after the hot water extraction of a wood chip mixture and under the same treatment conditions [18]. Fisherova and Opalena have studied the effects of hot water and dilute oxalic acid solutions on the composition of beech wood extracts [52]. It was found that monosugars, particularly xylose, represent the largest portion of the hydrolyzed extracts, ranging from 65 % in hot water extracts to 88 % in a 0.165 % solution of oxalic acid [52]. According to these findings, we may suggest that the decrease in the amount of the other wood components, found in this research (10.0 %), could be attributed primarily to the loss of hemicelluloses.

Table 2. Characteristics of nontreated (NT) and treated (T) beech particles with the results of statistical analysis (ANOVA)

Component	Content, %		Statistical analysis NT/T	
	NT	T	*P*-value	*F/F* crit****
Cellulose	41.12±0.46	45.34±1.24	0.0053	3.9485***
Klason's lignin	21.88±0.19	22.05±1.00	0.7833	0.0112
Acid-soluble lignin	1.37±0.05	1.63±0.28	0.1827	0.3362
Total lignin	23.25±0.20	23.68±0.20	0.3867	0.1222
Extractives in hot water	3.96±0.57	2.07±0.34	0.0078	3.1722***
Extractives (toluol/ethanol)	2.87±0.12	3.37±0.19	0.0199	1.8271***
Ash (mineral content)	1.25±0.41	0.75±0.36	0.1864	0.3290
Others* (supplement to 100 %)	27.55	24.79	/	/
EMC**	9.94±0.14	10.27±0.14	0.0150	1.8949***

*including hemicelluloses; **after conditioning of samples (68 %, 20.1 °C); ***denotes a statistically significant difference at the confidence level of 95 %; ****the relation between estimated F value and critical F value in ANOVA test

3. 1. 4. Equilibrium moisture content

The equilibrium moisture content (EMC) in T particles (10.27±0.14 %) was higher in comparison to that in NT particles (9.94±0.14 %). This difference was found to be statistically significant, suggesting that the hot water treatment has increased the affinity of beech particles towards moisture. We can assume that the treatment has increased the number of free −OH groups in the wood material, although the content of hemicelluloses decreased. Using the alkaline treatment procedure on jute fibres, Ray and Sarkar have found that the removal of hemicelluloses have increased the number of free hydroxyl groups on the fiber surface, thus providing a greater number of the active sites [53]. Consequently, one can conclude that the partial removal of hemicelluloses liberates many of the −OH groups at the fibril surfaces, which then become available for interactions with water. Hence, the EMC of treated beech particles increases.

3. 1. 5. Elemental composition and the heating value of particles

The treatment has affected the elemental composition of treated particles and therefore the heating value (Table 3).

Table 3. Elemental composition and the heating value of nontreated (NT) and treated (T) beech particles

Sample*	Element content, wt.%				C/O ratio	Higher heating value, MJ/kg
	C	H	N	O**		
NT	46.94±0.09	6.14±0.05	0.17 ±0.04	45.49±0.16	1.03±0.01	18.131±0.073
T	47.59±0.06	6.58±0.06	0.23±0.02	44.86±0.07	1.06±0.01	18.580±0.088

***** state of the equilibrium moisture content; **calculated value

Carbon and hydrogen contents in water treated beech particles increased by 1.4 and 7.1 %, respectively, while the fraction of oxygen decreased by 1.4 %. As a consequence, the carbon-to-oxygen (C/O) ratio increased by 2.8 % in treated beech particles. These changes had an impact on the heating value of treated particles, which is 2.5 % higher in comparison to that of the untreated beech particles. Under the same treatment conditions, Pu *et al.* reported an increase in the heating value of LHW-treated particles for 4.1 % [18]. In addition, results of the present research show that the elemental composition of treated particles was also affected by their higher EMC value.

3. 2. Characteristics of pellets

3. 2. 1. Physical and mechanical properties of pellets

Diameter and density of pellets were affected the most by the water treatment (Tables 4 and 5). It is interesting that the mean diameters of PT 10 and PT 20 pellets (6.07±0.04 and 5.95±0.18 mm, respectively), showed just a slight deviation from the nominal diameter of 6 mm (diameter of die openings). On the other side, the diameter of PNT pellets (made from non-treated particles) has significantly increased after conditioning (6.34 mm) [50].

Table 4. Physical and mechanical properties of PNT, PT 10 and PT 20 pellets (numbers after the±represents the standard deviation

	Sample				Test Method
Property	PNT	PT 10	PT 20	A1 class	
Diameter, mm *[50];	6.34±0.11	6.07±0.04	5.95±0.18	6 - 8 (±1)	EN 16127
EMC, % * [50]	10.40±0.21	7.08 ±0.17	10.60±0.23	/	/
Diameter change, % **	2.39±0.46	1.47±0.30	2.38±0.52	/	/
Bulk density, kg/m^3 [50]	605.13±4.37	729.63±8.57	667.11±4.84	750≥BD≥600	EN 15103
Pellet density, kg/dm^3 *	1.21±0.05	1.40±0.05	1.27±0.06	≥ 1.12	EN 15150
Mechanical durability, % ***	98.79	96.73	98.74	≥ 97.5	EN 15210-1

*after conditioning (68 %, 20.1 °C); **after drying of conditioned pellets until constant mass (103±2°C); ***percentage of initial particles (pellets)

The bulk density of pellets made from treated particles has increased by 20.6 % (PT 10) and by 10.2 % (PT 20) as compared to that of PNT samples [50], while the den sity values have increased by 15.7 % (PT 10) and 5.0 % (PT 20). Such results suggest that the PNT pellets have probably relieved a larger amount of residual stresses, which led to the higher level of spring-back effects, consequently increasing the diameter and reducing the density of these pellets. Spring-back properties of pellets were studied by evaluating some of the effects of the wood material (chemical composition, particle size and initial moisture content) and/or the effects of processing parameters (pressure, hold time, temperature and die geometry) [54,55]. Although these studies did not involve the pre-treatments of wood particles, both have emphasized the effects of chemical composition of the wood material on densification and spring-back properties of the resulting pellets. Accordingly, only slight deviation in the diameter and the increased bulk and pellet densities of PT 10 and PT 20 pellets are probably a consequence of the changed chemical structure of treated particles, due to the loss of hemicelluloses that contributes to the elasticity of the wood cell wall [4]. Lower elasticity improved compression of these particles and significantly reduced their expansion after the release of pressure, *i.e.* upon leaving channels in the press die. Hence, the samples PT 10 and PT 20 exhibited low diameter deviations from the nominal value, which is particularly reflected in the formation of a compact structure of pellet samples PT 10, which had the highest values of bulk and pellet densities. In addition, the EMC (7.1 %) and the diameter change after drying (1.5 %) of these pellets are for 32 and 38.5 % lower in comparison to the respective values of PNT pellets (Tables 4 and 5).

Table 5. Statistical comparison of physical properties of PNT, PT 10 and PT 20 pellets

Compared sample groups	PNT/PT 10		PNT/PT 20		PT 10/PT 20	
Property	P-value	F/F crit	P-value	F/F crit	P-value	F/F crit
Diameter	1.71 10^{-6}	10.9468*	2.18 10^{-5}	7.3116*	0.05874	0.9227
EMC	8.21 10^{-18}	318.0246*	4.6001	0.7068	4.52 10^{-16}	293.5752*
Diameter change	0.0002	5.2842*	0.9598	0.0006	0.0003	4.5797*
Bulk density	2.35 10^{-5}	65.1566*	7.96 10^{-5}	35.1770*	0.00039	15.7064*
Pellet density	1.63 10^{-7}	16.1676*	0.0262	1.3324*	0.00014	5.5154*

*denotes a statistically significant difference at the confidence level of 95 %

By comparing the properties of PT 10 and PT 20 pellet samples, it can be noticed that the moisture content of the treated raw material has also greatly affected physical properties of the pellets (Tables 4 and 5) [50]. PT 20 pellet samples have a significantly higher EMC, lower dimensional stability, as well as lower bulk and pellet densities as compared to those of PT 10 samples.

Presence of moisture in the raw material is necessary for the pelleting process. Moisture acts as a plasticizer, reduces friction in press channels and improves adhesion between particles in the pellet [3]. However, increase in the moisture content above optimal, reduces the density of pellets [2]. Accordingly, due to the high moisture content in the raw material, PT 20 pellet samples had for 8.6 % lower values of the bulk density and 9.3 % lower values of the pellet density when compared to those of PT 10 samples.

Softening of the amorphous matter in cell walls and their subsequent flow and redistribution occur as a consequence of the increased pressure and temperature during pelleting, as well as the presence of moisture in the raw material. This processes also lead to breakage of existing and formation of new intermolecular bonds [3]. It was stated that a certain amount of water is needed in the pelleting process to form hydrogen bonds, which increase the strength of mouldings [10]. However, excessive moisture is deposited in spaces between particles, increasing the distance between them, which prevents intermolecular interactions during the pellet formation and leads to reduction in their strength and density [9]. It can be assumed that this excessive moisture has evaporated after the pellet left the press channel, due to a sudden decrease in pressure, which resulted in a porous structure and a significantly lower density of PT 20 samples in comparison to PT 10 samples. Evaporation of excessive moisture, occurring after exiting the pellet press, may also explain the shrinkage of PT 20 samples and their slightly smaller diameter (5.95 mm) then the nominal (6 mm). In addition, after evaporation of moisture that occupies spaces between particles during pressing, according to literature [10], the −OH groups that remained within the pellets did not participate in the formation of hydrogen bonds between the polymers of the cell wall. These −OH groups are available for interactions with water molecules from air and can be the reason for a lower dimensional stability of PT 20 pellets in comparison to that of PT 10 pellets (Tables 4 and 5).

Mechanical properties of pellets are also especially important, particularly during the transport and manipulation. The results of mechanical characterization, in terms of mechanical durability, are shown in Table 4. The lowest values of mechanical durability were determined for PT 10 pellets. It was noticed that cracks appeared at very tips of some of these pellets, which was probably a result of the pellet press parameters that were not fully optimized for processing of the treated raw material, *i.e.* the same pelleting parameters were used for non-treated and treated particles.

3.2.2. Chemical properties of pellets

Effects of the water treatment and the moisture content in treated particles on chemical properties of produced pellets are shown in Table 6. Due to the higher carbon content in PT 10 and PT 20 pellets (5.3 and 1.2 %), and their lower oxygen content (4.4 and 1.1 %), the C/O ratio increased by 10.1 % (PT 10) and 2.3 % (PT 20) as compared to that of PNT samples.

Higher carbon fractions and lower fractions of hydrogen and oxygen in all pellet samples (Table 6) in comparison to those in relevant particles (Table 3), may be a consequence of the pellet formation mechanism. Namely, under conditions of elevated temperature and pressure, several processes occur, such as the movement and redistribution of cell wall molecules, breakage of existing intermolecular interactions, and formation of new bonds within the pellets. In these processes, water molecules have an important role in the formation of bonds between particles [8,9,10]. It is also important to notice that particles and pellets have shown different equilibrium moisture contents (Tables 2 and 4, respectively). Therefore, differences in the elemental composition between pellets and corresponding particles, as well as between the pellets obtained from treated particles (PT 10 and PT 20), can be partly attributed to differences in moisture contents in these samples.

Table 6. Elemental composition of PNT, PT 10 and PT 20 pellets

Pellet sample*	Element content, wt.%				C/O ratio***
	C	H	N	O**	
PNT	47.60±0.07	5.68±0.10	0.19±0.02	45.21±0.05	1.05±0.01
PT 10	50.11±0.06	5.48±0.09	0.17±0.02	43.24±0.07	1.16±0.01
PT 20	48.15±0.08	5.91±0.12	0.16±0.03	44.70±0.21	1.08 ±0.01

*state of the equilibrium moisture content; **calculated value; ***carbon-to-oxygen ratio

3. 2. 3. Thermal properties of pellets

Heating values and ash contents in pellet samples are presented in Table 7, indicating the influence of water treatment on the pellet heating value. These values increased for 5 and 1 % for PT 10 and PT 20 samples, respectively, corresponding to the increase in carbon contents in these pellets (Table 6). These results are in accordance with reported 5.8 % increase in the heating value of pellets made from LHW-treated poplar wood (170 °C, 60 min, 6:1) [12].

Table 7. Heating values and ash contents in PNT, PT 10 and PT 20 pellets [50]

Property	Sample			Classes		Method
	PNT	PT 10	PT 20	A1	A2	
Higher heating value, MJ/kg	18.266±0.099	19.332±0.253	18.445 ±0.218	16.3 ≤ Q ≤ 19		EN ISO 18125
Ash content, %	1.32±0.14	1.00±0.24	1.08±0.08	≤ 0.7	≤ 1.5	EN 14775

Again, the moisture content in treated particles significantly influenced heating values of the resulting pellets as it was the case for pellet physical and mechanical properties. Although PT 10 and PT 20 samples are made from raw materials of the same molecular structure, the heating value of PT 20 pellets was for 4.8 % lower as compared to that of PT 10 pellets, probably as a consequence of a large difference in EMC values (Tables 4 and 5). This finding confirms high influence of the moisture content in raw material on the properties of resulting pellets [50].

Ash, being an incompressible residue and the fuel ballast, is present at significantly lower fractions in PT 10 and PT 20 samples as compared to PNT samples (Table 7). This result was expected, since a large portion of the mineral matter was dissolved during the water treatment [50], as shown in Table 2. However, the ash content in PT 10 and PT 20 pellet samples (about 1 %, Table 8) increased in comparison to the ash content in treated particles (0.75 %, Table 2). This result is probably due to the relatively high hardness of water from the water supply, which was used for rinsing particles for the pellet production process. Particles used for the chemical composition analysis were washed with distilled water.

3. 2. 4. Stability in water

Pellet stability in water was tested during 24 h of immersion (Fig. 4).

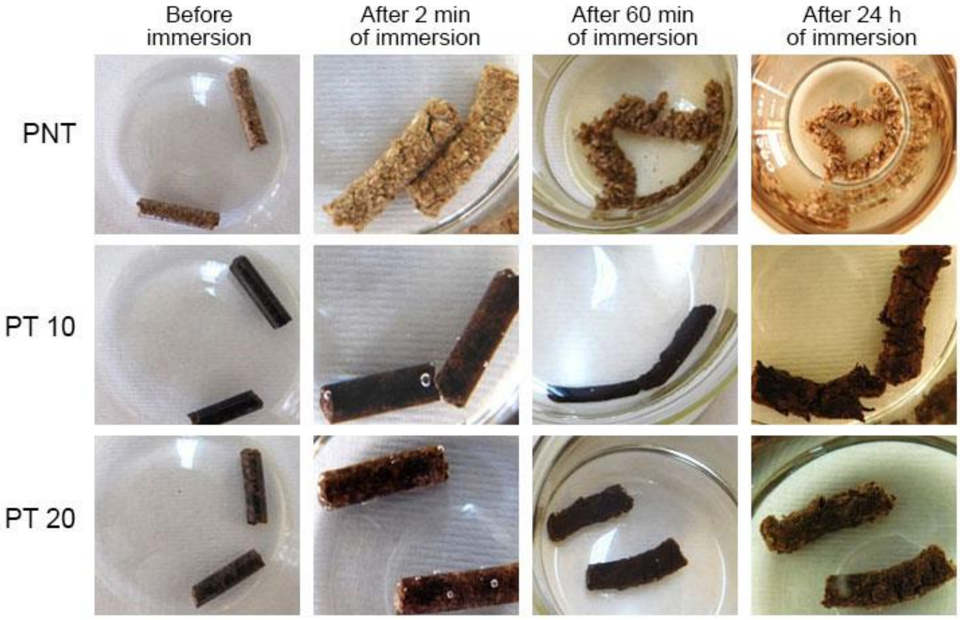

Figure 4. Stability of pellets in water

PNT pellets showed the lowest stability in water. Already after 2 min of immersion, the pellets started to swell and lose their compact structure, and after 60 min, the pellet structure was greatly disturbed. PT 20 pellet samples begin to swell only after 60 min. However, after 24 h of immersion, the structure of all samples was disrupted. Similarly, it was reported that the pellets made from LHW-treated particles of poplar, miscanthus, corn stover and switchgrass, showed better integrity in water then the pellets obtained from non-treated biomass [12].

4. CONCLUSION

The applied hot water treatment (150 °C, 60 min) has changed the chemical composition of beech particles used as a raw material in the pelleting process, and consequently it significantly influenced the resulting pellet properties. Pellet samples made of treated particles (PT 10 and PT 20) showed higher densities and heating values, while lower amounts of ash in comparison to PNT samples. Besides, the pellets obtained from treated particles showed lower diameter deviations from the nominal value, due to the reduced spring-back effect after leaving the matrix channels. This is the consequence of decreased elasticity of the particles, resulting from the extraction of hemicelluloses during the hot water treatment.

Effects of the initial moisture content of treated particles were evaluated by comparing PT 10 and PT 20 pellet samples. Generally, it was found that a lower initial moisture content in treated particles had positive effects on characteristics of the relevant pellets. Pellets produced from treated particles with a lower moisture content (PT 10) showed for ~33 % lower EMC value in regard to that of PT 20 pellets. PT 10 pellets also exhibited a notable decrease in the diameter change after drying. The initial moisture content of treated particles also affected the elemental composition of pellets. For instance, the C/O ratio in PT 10 pellets (10 %) was significantly higher then that in PT 20 pellets (2.3 %). By this particular effect, together with the lower EMC value, PT 10 pellets showed significantly higher heating value as compared to that of PT 20 pellets, thus confirming positive effects of the lower initial moisture content in raw wood materials.

It can be concluded that the application of water treatment and appropriate selection of the moisture content in treated particles can result in production of pellets with improved properties.

Further research should include evaluation of water treatment effects on other wood species used for pellet production. Another interesting aspect could be the chemical analysis of extracted hemicelluloses carbohydrates, together with the evaluation of possibilities for their utilization as well as the economical feasibility of introducing the LHW-treatment in pelleting processes.

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SAŽETAK

Uticaj predtretmana vodom na svojstva peleta izrađenog od iverja bukve

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(Naučni rad)

Polazna struktura iverja bukve namenjenog za izradu peleta, izmenjena je predtretmanom vodom na temperaturi od 150 °C u trajanju od 60 min, što se odrazilo na hemijski sastav i toplotnu moć iverja. Od tretiranog iverja bukve, čiji je sadržaj vlage iznosio 10.5 i 20.5 %, izrađene su dve grupe peleta: PT 10 i PT 20. Pelet izrađen od netretiranog iverja (PNT) poslužio je za procenu efekata tretmana vodom na svojstva peleta. Rezultati ispitivanja peleta ukazuju da su i primenjeni predtretman i sadržaj vlage tretiranog iverja imali uticaj na svojstva izrađenih peleta. Toplotna vrednost peleta PT 10 i PT 20 povećana je za oko 6 i 1 %, redom, dok je sadržaj pepela posle sagorevanja ovih uzoraka smanjen za oko 24 % u poređenju sa uzorcima peleta PNT. Pored toga, uzorci peleta izrađeni od iverja tretiranog vodom imali su za oko 21 % (PT 10), odnosno 10 % (PT 20) veću nasipnu gustinu, kao i manje odstupanje od nominalnog prečnika u poređenju sa uzorcima PNT. Jedinična gustina uzoraka PT 10 bila je veća za oko 16 %, a sadržaj ravnotežne vlage posle klimatizacije (68 %, 20.1 °C) za oko 32 % manji u poređenju sa uzorcima peleta od netretiranog iverja bukve.

Ključne reči: predtretman vrelom vodom; hemijski sastav; svojstva peleta; toplotna moć