Scientific paper

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Hot water pretreatment in wood biorefining processing

ABSTRACT

Wood can be processed to create various products or components that can cover a wide range of purposes. As a natural reservoir of organic matter, wood is also an important raw material for the production of chemicals and fuels. The limited reserves of fossil resources, environmental pollution and climate change make it necessary to obtain energy and chemicals from renewable raw materials. In this context, there is a growing demand for wood as a renewable and available raw material, which also emphasizes the importance of its optimal use. Namely, the end products made from wood often contain elements that do not significantly enhance the quality of these products, or may even have negative effects. In addition, degradation and permanent loss of valuable wood components can occur during the chemical processing. The introduction of hot water pretreatment in wood processing can be a way to biorefine wood and a solution for a more rational use of its ingredients. In this way, some valuable products such as hemicelluloses, saccharides or extractives (e.g. tannins) and other compounds can be extracted from the wood before the main process. The type and amount of products separated depend on a number of factors such as the wood species and the pretreatment conditions (temperature, pressure and duration of the process). At the same time, changes in its chemical composition can improve some properties of the wood after pretreatmentor facilitate its further processing. This paper shows the influence of hot water pretreatment on some properties of wood, such as dimensional stability and heating value. The possibilities of using water-treated wood for the production of wood products with improved properties are also shown.

Keywords: wood, hot water pretreatment, dimensional stability, heating value

1. WOOD AS A RAW MATERIAL

Wood is a natural raw material with a wide range of uses. Wood is used for the manufacture of numerous products, such as structural elements, windows and doors, furniture, veneers, particle boards and fiberboards and others. Wood is also used as an energy source, in its natural form (logs) or in modified form, as charcoal, briguettes and pellets. Chemical processing of wood can produce carbohydrates cellulose and with different molecular weights such as glucose and xylose and their derivatives, aromatic compounds from the lignin, tannins, turpentine, acetic acid, tar and many other products [1]. The properties and use of wood anatomical depend on its and chemical composition.

1.1. Chemical composition and wood properties

The cell walls of wood consist of three biopolymer compounds: cellulose, hemicelluloses and lignin. Cellulose, hemicelluloses, and lignin have completely different structures and properties [2]. Wood also contains a large number of different organic compounds with a lower molecular weight, such as fats, waxes, polyphenols, alkaloids, monosaccharide's, proteins and others. These compounds are referred to as extractives. Their content in wood is usually 3 to 5%, but can be higher in some species. Wood contains up to 1% inorganic substances. After burning the wood, they remain as a non-combustible residue (ash) [2].

Cellulose is the structural material of the cell walls of wood and other plants. Cellulose is a linear homopolymer of β -D-glucose that makes up half namely 40 – 50% of the dry mass of wood [3]. In the cell walls of wood cellulose molecules group into bundles called microfibrils and fibrils. Within the microfibrils, there are highly ordered (crystalline) and less ordered (amorphous) regions [3]. Due to its high crystallinity, cellulose is more

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resistant to the effects of chemical reagents than other structural components [4]. Hemicelluloses heteropolymers (hetero-polysaccharides). are Hemicelluloses contain many different monosaccharides as well as their derivatives. The content of hemicelluloses in wood is 20 - 35% [2]. Hemicelluloses have no crystalline structure, and are therefore the most reactive component of the cell wall [5]. The hydroxyl groups (-OH) of hemicelluloses contribute greatly to the hydrophilic properties of wood [6-8]. Lignin is complex, branched, cross-linked phenolic biopolymer with a high molecular weight. Depending on the wood species, the lignin content in wood is 17 - 35% [3].

The content and properties of the structural cell wall molecules and the relationships between them have a significant influence on the wood properties [9,10].

Hemicelluloses and amorphous regions of cellulose microfibrils contain a large number of available -OH groups, which make the wood hygroscopic. As a result, wood exchanges moisture with itsenvironment. Changes in the moisture content of wood lead to changes in the dimensions of the wood. The hemicelluloses are the most hygroscopic component of wood, while lignin has the lowest hygroscopicity [8]. In addition, the available hydroxyl groups of wood play an important role in the chemical aspect of adhesion and the formation of an adhesive bond [11,12].

The heating value (HV) of wood is a combination of the heating values of its components and their proportions [13]. The heating value of lignin is the highest (26.7 MJ/kg) [14]. The heating value of cellulose is 17.3 MJ/kg, while hemicelluloses have the lowest heating value at 16.2 MJ/kg [13]. Therefore, the chemical composition of wood has a major influence on the heating value of wood [13]. A high content of mineral substances and high moisture content have a negative effect on the HV of wood [13,14].

2. BIOREFINING

Nowadays, chemicals and energy are obtained by processing fossil raw materials, such as oil. The consequence of the high consumption of fossil raw materials is ever increasing environmental pollution, global warming and other climate changes. This is the reason why the production of chemicals and energy from renewable sources is necessary, as well as the increasing demand for energy and materials in modern society.

Biomass, such as forest and agricultural biomass, is the only renewable resource from which solid, liquid and gaseous fuels, as well as chemicals, can be produced [1,15-20]. Wood, as the most abundant renewable source of

lignocelluloses, has a high potential for utilizationin a biorefinery for the production of chemicals and fuels [3,15,17,19,21,22]. For these reasons, the demand for wood as a raw material is constantly growing and it's more efficient and rational use is necessary.

In the traditional chemical processing of wood. the components of wood are not optimally utilized (Fig. 1). When chemical processes are used to produce pulp, for example, the wood components are not optimally utilized. The hydrolysis products of the hemicelluloses are found in the black liquor together with the degradation products of lignin and together with small amounts of extractives [23-28]. Black liquor, containing dissolved degradation products of hemicelluloses and lignin, is combusted in the regeneration of chemicals and energy although the heating value process, of carbohydrates and their degradation products is low compared to that of lignin [1].



Figure 1. Diagram of traditional wood processing

By applying biorefining in the chemical processing of wood, wood components such as hemicelluloses or extractives (e.g. tannins) are removed before the main process [23-28]. In this way, the wood components can be more optimallyused. Biorefining is an approach that offers the possibility of producing not only the main product, but also a wide range of valuable secondary products such as fuels (e.g. ethanol), chemicals (such as carbohydrate derivatives and also lignin-based chemicals), extractives andothers [1,15,17,28].

2.1. Pretreatments

Various chemical pretreatments play an important role in biorefinery processes based on [17,29-32]. lignocellulosic feedstocks The application of pretreatments usually aims to change the original chemical composition of the wood and thus enable further processing (e.g. hydrolytic decomposition) and at the same time a more optimal utilization of the wood. Depending on the conditions of the treatment applied (pH value, temperature and treatment duration) the following effects can be achieved in addition to the partial removal of hemicelluloses, removal of part of lignin [29], reduction of crystallinity and degree of cellulose polymerization [33], removal of acetyl groups, etc. [6,29].

Chemical pretreatments include two phases: solid, resulting in wood with an altered chemical

composition and properties, and liquid resulting in hydrolysate or extract resulting in dissolved wood degradation products that can be further converted into the desired chemicals, biomaterials or biofuels (Fig. 2) [15,34-38].



Figure 2. Diagram of wood processing with pretreatment

2.2. Water pretreatments of wood

Water pretreatments have the greatest utilization potential because water is non-toxic and non-flammable, inexpensive and available; it is a good solvent, easy to handle and environmentally friendly [1,4,22]. Water pretreatments causes less corrosion to equipment compared to utilization with other chemicals [4] and does not require special equipment, so the costs are not high. In addition, no significant cellulose degradation occurs during treatment [1,39,40].

The effects of water pretreatments depend on the treatment parameters, such as temperature, which is the most important parameter, pressure and extraction time, as well as on the properties of the wood samples, such as chemical composition, porosity, surface area to volume ratio, size and mass [1,4,22,41]. Water pretreatments at high temperatures, or Hot water extraction under (HWE), or Pressurized pressure hot-water extraction (PHWE) is carried out at temperatures ranging from 100 to 374 °C and is the most commonly used pretreatment [16,42,43]. During this process polar and non-polar wood components are dissolved, and the main reaction in this process is the depolymerization and removal of significant amounts of hemicelluloses from the wood [30,44-46]. Higher temperatures and a longer extraction time at HWE lead to degradation of the hemicelluloses [47].

2.3. Possible uses of the resulting extract after pretreatment

Increased energy consumption due to the introduction of pretreatment can be compensated for by the production of numerous valuable products from the hydrolysate. The hydrolysate contains mono-, oligo- and polysaccharides from hemicelluloses, which account for up to 60 - 80% of the total dissolved organic material, phenolic, aldehydic and other aromatic compounds from lignin, as well as various degradation products, extractives and acetic acid [1,15,34,48-51].

Various aromatic compounds resulting from lignin fractionation can be directly burned as fuel or converted into many valuable products, such as activated carbon or adhesives. Hemicelluloses can be used in polymeric form such as biopolymers or hydrogels [50]. Degradation products of carbohydrates can be converted into ethanol, xylitol, glycerol, sorbitol, arabinitol, furfural, hydroxymethylfurfural, acids such as fumaric, aspartic or levulinic acid, biobased protective films, stabilizers, emulsions and other derivatives that are used in the food, pharmaceutical and cosmetics industries [15,17,20,34,50,52].

3. PROPERTIES OF TREATED WOOD

Changes in the chemical composition of wood are reflected in changes in the physical, mechanical, thermal and biological properties of the original material [53,54]. Popović et al. [55] found that the mass loss of narrow-leaved ash (Fraxinus angustifolia Vahl. ssp. Pannonica Soó & Simon) wood panels (5 x 20 x 150 mm) during water pretreatments at 100 °C and 120 °C for 1 h was low, 0.90% and 0.92%, respectively. These values indicate that the water treatments at these temperatures did not lead to degradation of the structural compounds of the cell wall [55]. However, the mass loss of narrow-leaved ash wood particles (0.5 - 1 mm) treated at 100 °C of 4.90% is higher than the mass loss of panels treated under the same conditions [56]. The reason for this is the smaller dimensions and the larger contact surface of the wood particles with water during treatment. This leads to faster and more complete chemical reactions [4,22,41]. The mass loss of beech particles (≤ 1.2 mm) treated at 150 °C for 1 h is higher, 10.56% [57]. This indicates significant degradation of wood cell wall polymers (mainly hemicelluloses, but also lignin and cellulose) during treatment. As a result of the loss of mass during pretreatment, the density of the treated wood is lower, which is reflected in its lower mechanical properties [58,59]. However, some other properties of the wood can be improved, which can result in better properties of the final product.

3.1. Water uptake and volumetric swelling

The degradation of hemicelluloses during water pretreatment reduces the number of accessible -OH groups. This leads to a reduction in the hygroscopic character, lower water absorption and higher dimensional stability of the treated wood samples [6,7,48,60].

Popović [56] investigated water uptake as a function of time during 48 hours immersion in water (20 °C) of water-treated (100 and 120 °C, 1 h) narrow-leaved ash wood panels, as well as volumetric swelling. In the first 10 hours of immersion, both groups of treated samples absorb larger amounts of water compared to the control samples. After the first hour, the water uptake of the samples treated with water at 100 °C increased by 25.51% compared to the control samples [56]. The more intense water uptake of the treated samples during the first 10 hours indicates that the treatments increased the permeability and porosity of the ash wood. The reason for this could be the removal of extractives from the wood structure during the treatment [56]. After 10 hours of immersion, the intensity of water uptake decreases. The samples treated at 100 °C absorbed the least amount of water after 48 hours. This indicates that the applied treatments did not lead to a significant disruption of the cell wall structure and the appearance of new cavities of significant size, which is consistent with a low mass loss during the treatment [55].

Mohebby and Sanaei [61] found an increased moisture absorption of beech wood samples (*Fagus orientalis*) after hydrothermal treatment at 180 °C, as well as by Zhang et al. [60], who noted increased water absorption of pine strand samples after hot water extraction. Zhang et al. [60]and Paredes [62] explain the increased water absorption of the treated samples by the increase in the number and volume of pores and the appearance of micropores in the cells, which promote the capillary movement of water in the treated samples.

However, Hornus et al. [63] found that the equilibrium moisture content (EMC) of water treated (120, 140 and 160°C, 45 min) southern yellow pine (Pinus spp.) strands was reduced compared to control samples. Sattler et al. [64] investigated the effects of water treatment at 120, 140 and 160 °C for 20, 40 and 60 min on the physical and chemical properties of loblolly pine (Pinus taeda) wood flakes. They found that the EMC of flakes decreased with increases in temperature and treatment duration, indicating an increase in the dimensional stability of the samples [64]. Paredes et al. [48] also found that the EMC of OSB boards made from water-treated red maple chips at 160 °C was reduced, but that the water absorption of these boards was increased during immersion. The authors explained this disagreement with the consequences of the treatment [48].

Popović [56] also investigated the volumetric swelling of water-treated (100 and 120 °C, 1 h) narrow-leaved ash wood panels during immersion in water for 48 h (20 °C). During the entire immersion, the control group of samples showed higher swelling compared to both treated groups of samples, even though their water absorption was lower. Water absorption and swelling are usually strongly correlated, but the relationship changes when extracted wood is used [48]. Popović [56] concluded that pretreatments with water at 100 and 120 °C led to an increase in the dimensional stability of ash wood panel samples, despite more intensive water absorption in the first hours of immersion [56]. After the first hour of immersion, the samples treated with water at 100 °C showed 5.87% less swelling compared to the control samples. These samples showed a maximum decrease in volumetric swelling of 20.27% compared to the control samples after 24 hours of immersion [56]. An increase in dimensional stability indicates a decrease in the content of available -OH groups as a result of the treatment. During hydrothermal treatment, wood degradation processes already start at temperatures of 100 °C, during which small amounts of amorphous areas of cellulose dissolve the [65.66]. but also glucomannans [66].

3.2. Adhesion properties

The adhesion properties of wood are important for all processes that involve bonding, such as the manufacture of wood-based panels. Some of the factors that affect the chemical interaction between the wood and the adhesive can also change during pretreatment. Hydroxyl groups are potential sites for the formation of bonds between the wood and the adhesive [11]. Thus, as the number of available -OH groups decreases the number of bonds between the wood and the adhesive also decreases. In this way, the pretreatments affect the changes in the adhesion properties of the wood and the strength of the bond [67]. The removal of acetyl groups and extractives during pretreatment changes the pH value of the wood, which can also affect the curing of the adhesive.

Popović et al. [55] examined the tensile shear strength in the lap joint of water-treated (100 and 120 °C, 1 h) narrow-leaved ash wood panels. They found that the shear strength of the control and treated samples did not differ significantly. This indicatedthat the applied pretreatments did not have a significant influence on the structural compounds of the wood [55]. A slight decrease in the shear strength of the treated samples compared to the control is probably due to aslight decrease in the content of available –OH groups, which is due to the dissolution of small amounts of amorphous regions of cellulose and glucomannans [65,66].

Based on the results shown, it can be assumed that water pretreatment at temperatures of 100 and 120 °C did not significantly change the adhesion properties of the ash wood panels [55]. These results indicate that the applied treatments do not significantly affect the interaction of wood and adhesive in wood-based panels made from watertreated ash wood at 100 and 120 °C.

3.3. Heating value

The removal of hemicelluloses, whose heating value is low compared to lignin, can increase the heating value of treated wood [14,26]. Popović [56] found that heating value (HV) of ash wood particles increased slightly (by 0.17%), after water treatment at 100 °C. Laurová and Kačík [66] state that during hydrothermal treatment in the temperature range of 100-140 °C, glucomannans and the amorphous region of cellulose undergo autohydrolysis. Mamoňová et al. [65] also find that during hydrothermal treatment, wood degradation begins at temperatures as low as 100 °C, when small amounts of the amorphous region of cellulose dissolve, while xylans are stable at these temperatures.

Water treatment at higher temperatures resulted in more significant changes in the chemical structure [63-66]. Laurová and Kačík [66] and Sattler et al. [64] found that the concentration of carbohydrate degradation products in the hydrolysate increases with increasing temperature and treatment duration. However, Hornus et al. [63] found that the cellulose content in southern yellow pine (Pinus spp.) strands increases with increasing water treatment temperature from 120 to 160°C, while a significant loss of hemicelluloses occurs only at 160° C. The intensive hydrolysis of xylan starts at 140 °C [64,65] and is the dominant reaction at a temperature of 160 °C [66]. According to Pu et al. [26] and Runge et al. [14] the HV of wood increases after the removal of hemicelluloses. However, depending on the conditions, lignin degradation reactions also occur in the water medium. Laurová and Kačík [66] found that the concentration of lignin degradation products (syringaldehyde and vanillin) in the hydrolysate from hydrothermal treatment increases slowly with an increase in temperature from 100 to 140°C. owever, with increasing temperature (and duration of hydrolysis), the proportion of these substances in the hydrolysate increases and reaches maximum values at 160 °C [66]. Sattler et al. [64] reported a lignin loss of 1.24% during the 60 minute water extraction of loblolly pine (Pinus taeda) flakes at 160 °C. The decomposition of lignin at high treatment temperatures has an effect

on the reduction of the HV of the samples. Popović et al. [57] found that the content of hemicelluloses decreased and the content of cellulose in beech wood particles increased after treatment with water at 150 °C, while the content of lignin did not change significantly. These changes in the content of wood constituents led to an increase in carbon (C) content by 1.4% and a decrease in oxygen (O) content by about 1.4% in the treated samples. As a result, the C/O ratio and HV increased by 2.8% and 2.5% [57].

3.4. Viscoelastic properties of wood

The degradation of hemicelluloses, which contribute significantly to the viscoelastic properties of wood, reduces the elasticity of the wood and it becomes brittle and stiff. This facilitates the compression of wood particles in processes involving pressing, such as particleboards or the productionof pellets. This improves the contact between the particles, which promotes the formation of bonds and increases the strength and stiffness of the product, while the lower elasticity of the wood influences the reduction of the springback effect [68].

4. UTILIZATION POSSIBILITIES OF WATER-TREATED WOOD

Water-treated wood can be used to produce wood-based boards with improved properties, such as oriented strand boards (OSB) [48,63]. particleboards (PB) [56,68], fiberboards [69] or wood-plastic composites (WPCs) [70,71]. A lower EMC value for 6.2% of OSB made of red maple (Acer rubrum L.) strands extracted with water at 160 °C compared to the moisture content of control boards of 10.2% was established by Paredes et al. [48]. At the same time, water uptake was increased while the thickness swelling of OSB from treated strands was reduced [48]. OSB from of southern yellow pine strands treated with water (120, 140, and 160 °C, 45 min) showed lower water absorption and thickness swelling compared to control OSB while increasing modulus of elasticity (MOE) and bending strength (MOR) [63].

Popović [56] found that particleboards made from narrow-leavedash particles treated with water at 100 °C for 1 h had a lower density as well as a lower EMC at all applied ambient moisture conditions (32%, 65% and 90%, 20 °C) compared to control panels. This led to a reduction in thickness swelling of about 23% compared to the control panels [56]. Pelaez-Samaniego et al. [68] investigated the effects of HWE (160 °C, 90 min) of ponderosa pine (*Pinus ponderosa* Dougl. Ex Laws.) and sugar maple (*Acer saccharum* Marsh.) chips on the properties of particleboard. They find that HWE increases compressibility and reduces springback by 34% for maple chips and 44% for pine chips. The water absorption of PB panels from HWE samples was reduced by 35% (pine) and 30% (maple). This resulted in a reduction in thickness swelling by 39% for pine PB and 56% for maple PB after 24 hours of immersion in water. At the same time, the mechanical properties were not significantly affected [68].

The dimensional stability of wood-plastic composites (WPCs) made from polypropylene and extracted southern yellow pine (*Pinus* spp.) wood flour in cold water for 1, 3 and 5 days and in boiling water for 1, 3 and 5 hours was significantly improved compared to the corresponding WPCs made from untreated flour. In all treatment conditions applied, the water absorption and thickness swelling of the WPCs were lower than those of WPCs made from non-extracted wood [71].

Medium-density fiberboard (MDF) made from hydrothermally treated fibers at 120, 150 and 180 °C for 30 and 90 minutes showed increased dimensional stability. Although the hydrothermal treatment of the fibers did not affect water absorption, the thickness swelling of MDF made from treated fibers was significantly reduced. However, the mechanical properties were also reduced [69].

Wood particles with increased HV after HWE can be used for the production of wood biofuels such as pellets. Pellets produced from beech particles water-treated at 150 °C (with a MC of 10%) showed a 5.84% higher HV and 24.24% lower ash content compared to control pellets [57]. In addition, due to the reduction of the springback effect caused by the loss of hemicelluloses, the diameter of pellets from treated wood particles showed a lower deviation from the nominal value, the density of pellets after conditioning (68%, 20.1 °C) increased by 15.70%, which resulted in an increase in bulk density by 20.57% compared to control pellets [57]. A pellet made from watertreated (170 °C, 60 min) poplar wood (Populus maximowiczii x nigra) chips showed a 5.8% higher HV, 12.1% higher density and 18.5% higher energy density compared to a pellet made from untreated wood chips of this type. The compressive strength and durability of pellets made from poplar chips treated with liquid hot water were also significantly higher [14].

5. CONCLUSION

Depending on the conditions of the process, water treatment leads to greater or lesser degradation of the wood. If the water treatments take place at lower temperatures, there is no significant degradation of the structural molecules of the cell wall.With an increase in the treatment temperature, the cell wall structural compounds primarily hemicelluloses and amorphous areas of cellulose microfibrils, but also lignin, are degraded.The products of wood decomposition are in the liquid phase of the treatment - the hydrolyzate, and they can be used to produce numerousvalue added products.

The changes that occur in the chemical composition are reflected in the physical, mechanical, thermal and other properties of wood. The degradation of hemicelluloses during water pretreatment reduces the number of accessible -OH groups. This results in a decrease in hygroscopic character and an increase in dimensional stability, despite the higher water absorption of water-treated wood samples, as well as an increase in thermal power. In addition, the elasticity of wood decreases, which is significant for wood products produced by pressing. Water treatments can also affect the adhesive properties of wood.

Water treatments at certain parameters can be applied for wood products with improved properties, such as wood-based panels (OSB, PB, MDF, WPCs) with improved dimensional stability, as well as for solid fuels such as pellets, with improved combustion properties (HV, ash and moisture content).

Considering the above, it can be concluded that liquid hot water pretreatment in wood biorefining processing can result in more efficient use of wood, with the simultaneous production of wood products with improved properties.

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IZVOD

PRIMENA PREDTRETMANA VRELOM VODOM U BIORAFINACIJI DRVETA

Drvo se može preraditi u razne proizvode ili poluproizvode sa širokim spektrom primene. Kao prirodni rezervoar organskih materija, drvo je, takođe, važna sirovina za proizvodnju hemikalija i goriva. Ograničenost rezervi fosilnih resursa, zagađenje životne sredine i klimatske promene nameću potrebu za proizvodnjom energije i hemikalija iz obnovljivih sirovina. U tom kontekstu potražnja za drvetom kao obnovljivom i dostupnom sirovinom sve više raste, a time i potreba za njegovim optimalnijim iskorišćenjem. Naime, u krajnjim proizvodima od drveta često se nalaze sastojci koji ne utiču značajno na njihov kvalitet, ili čak mogu imati negativan uticaj. Pored toga, tokom hemijskih procesa prerade može doći do degradacije i trajnog gubitka vrednih sastojaka drveta. Uvođenje predtretmana vrelom vodom u procese prerade drveta može biti jedan od načina biorafinacije drveta i racionalnijeg iskorišćenja njegovih sastojaka. Tako se, pre glavnog procesa prerade, iz drveta mogu izdvojiti vredni proizvodi kao što su hemicelulozni šećeri ili ekstraktivi (na primer tanini), ali i druga jedinjenja. Vrsta i količina izdvojenih proizvoda zavise od brojnih faktora kao što su vrsta drveta i uslovi izvođenja predtretmana (temperatura, pritisak i trajanje procesa). Istovremeno, usled promena u hemijskom sastavu, posle predtretmana mogu biti poboljšana neka svojstva drveta, ili se može olakšati njegova dalja prerada. U ovom radu prikazan je uticaj predtretmana vrelom vodom na neka svojstva drveta, kao što su dimenzionalna stabilnost i toplotna moć. Takođe su prikazane mogućnosti upotrebe drveta tretiranog vodom za proizvodnju proizvoda od drveta poboljšanih svojstava.

Ključne reči: drvo, predtretman vrelom vodom, dimenzionalna stabilnost, toplotna moć

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