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Preliminary Study of Chemically Pretreated Densification of Juniper Wood for Use in Bone Implants

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Abstract. Kraft cooking of juniper wood with NaOH/Na_2S aqueous solution has been used in the study for partial delignification at the temperature of 165ºC for different residence time (0-40 minutes) following by thermal compression for densification under a pressure of 5 MPa at 100ºC for 24 hours. The densified and natural juniper wood samples were characterized by chemical composition and mechanical properties. The results show that the density of densified juniper wood was increased by 96-127% reaching the value of 1170 kg/m^3 that is similar to conventional bone implants (1090 kg/m^3). Modulus of rupture and modulus of elasticity of densified juniper wood were increased by 85% and 621%, respectively, demonstrating a high potential of the material to be used as bone implants.

Introduction

Bone implants have been extensively studied in both material and medicine science for decades. There are thousands of scientific articles on the bone implants. Demand for non-metallic implant materials is growing rapidly, not only because of metal implants damage bone over time due to loosening and biocorrosion, but also because of increased use of modern medical diagnostic systems, e.g., nuclear magnetic resonance (NMR) [1]. Materials such as calcium phosphate, calcium carbonate and calcium sulphate are mainly studied as potential bone substitutes. Materials obtained directly from nature are also being studied, e.g., corals [2]. At the same time, wood as a natural material for bone implants has been studied insufficiently.

The main advantage of wood as a bone implant biomaterial is its structural similarity to bone structure. Internal structural similarity also leads to similar properties, e.g. density, anisotropy and fluid transport in cells. Previous studies have shown that wood have a good biocompatibility and osteoconductivity with no toxicity has been observed [3; 4].

The idea of the study is based on two previous investigations - use of *Juniperus communis* in bone implants by prof. dr. hab. med. E. Ezerietis [5] and a study on the delignification and compaction of wood to produce high-performance materials [6]. The above studies indicate that wood can be used successfully as a bone implant material. However, there are still a number of problems that prevent wood from using in bone implants. The main ones - wood has a variable density and composition depending on age, species and growing conditions; the density of wood is less than that of bone. These problems could be prevented by densification of wood leading to increased density and improved physical-mechanical properties.

The first studies on the wood densification have been presented in the early 1900 in the United States when the first patents of wood densification concept were submitted. The initial studies were not complete, they focused on the compression technique without evaluating the plasticization mechanism and the stability of the products. Between 1930 and 1960, research was carried out pre-treatment methods of wood densification, for example by using heat treatment or chemical compounds to impregnate the wood filling the porous structure of the cell wall. Recent research on wood densification has involved the pretreatment of a chemical or enzymatic modification by which chemical components (lignin, hemicelluloses, cellulose) in the cell wall structure are modified and partially destroyed and new covalent bonds are formed [7;8].

Song. et. al. [6] in 2018 initiated a new research direction of wood densification based on partial delignification of wood by chemical pretreatment with alkaline cooking in an aqueous solution of $NaOH/Na_2SO_3$ followed by hot-pressing. This method of densification has been used in several latest studies [6;8-11]. As it is known, $NaOH/Na_2SO_3$ aqueous solution is widely used in pulping process and is the second most popular method after the Kraft cooking. Kraft cooking results a lower yield of cellulose with stronger fibers for paper materials [8;12]. Based on this fact, our study performs namely Kraft cooking pretreatment using aqueous $NaOH/N_2S$ solution by following hot-pressing to obtain improved densified juniper wood.

Materials and Methods

The research was carried out on samples of solid juniper *(Juniperus Communis)* wood collected in a forest at Kegums, Vidzeme region, Latvia. Sodium hydroxide (>97%, Sigma-Aldrich), sodium sulfide hydrate (≥60%, Sigma-Aldrich) and deionized water were used for chemical pretreatment of juniper wood. Acetone (>97%, Sigma-Aldrich) and sulfuric acid (>95-98%, Sigma-Aldrich) were used for methods of chemical characterization.

Sample preparation. Manually debarked juniper logs 300 mm in length and 50-100 mm in diameter were air-dried for 1 month (Fig. 2 a). Logs were cut into the specimens with a size of 90 mm × 15 mm × 15 mm (longitudinal × tangential × radial). The initial average moisture content of samples was 7.62%.

Figure 1 schematically illustrates the research methodology of juniper wood densification and characterization.

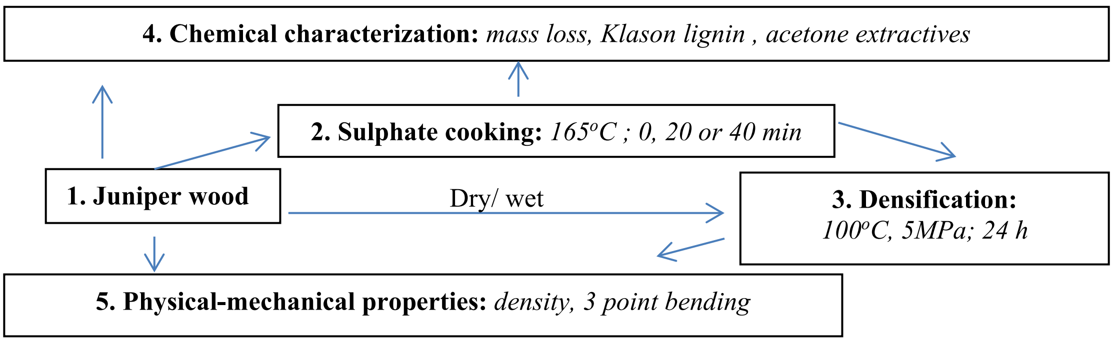

Figure 1. Schematic illustration of the research.

Chemical pretreatment. Typical Kraft cooking aqueous solution was prepared from 1.25M NaOH and 0.25M (calculated to anhydrous substance) Na_2S, what is widely used in the pulping industry [12]. Juniper wood specimens where immersed in a 100 ml autoclaves (one sample per autoclave) and fulfilled by the cooking solution for 24 hours. Then autoclaves with specimens were heated up to 165°C in a glycerin bath. The first specimen was removed immediately after reaching 165°C (K0) and other samples where cooked at 165°C for 20 minutes (K20) and 40 minutes (K40). After, the cooked specimens were washed several times with deionized water until stopped coloring and then kept in water.

Densification. The chemically pretreated juniper wood specimens were hot-pressed on a radial/tangential direction in a specially designed mold (Fig. 2 b) by a single-stage press JOOS (Type LAP 40, Germany) under a pressure of 5 MPa at 100°C for 24 hours followed by the interrupted heating for another 12 hours. To evaluate the impact of chemical pretreatment, control samples of dry (Control-D) and wet (Control-W) juniper wood were hot-pressed by the same method. The control wet specimens were prepared by immersing in a hot (90ºC) deionized water for several times until its sunk followed by the hot-pressing. Three specimens per each sample type were produced.

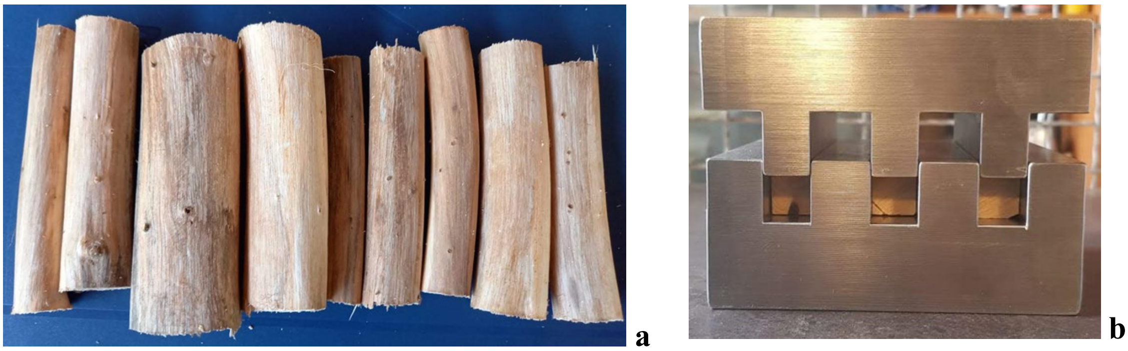

Figure 2. Sample preparation: a) debarked juniper logs; b) cut specimens in hot-pressing mold.

Chemical characterization.

Mass loss (ML) of cooked samples was calculated according to Equation (1):

$$ML\ (\%) = \frac{M1 - Mo}{Mo} x100 \quad (1)$$

where *Mo, M1* – absolutely dry specimen mass before and after chemical pretreatment, respectively.

Extractives. The wood samples before and after chemical pretreatment were grounded (M20, IKA-WERKE, Germany) and then Soxhlet-extracted with acetone for 8 h to quantify the extractable components gravimetrically (ES 225SM-DR, Precisa, Switzerland) after rotary vacuum-evaporation (PC3001 VARIO, Green Vac, Germany) and expressed as a percentage of the initial wood sample mass (Eq. 2):

$$Extractives\ (\%) = \frac{M2 - M1}{M} x100 \quad (2)$$

where *M* – absolutely dry specimen mass, *M1* – mass of absolutely dry round flask, *M2* – mass of absolutely dry round flask with specimen extractives.

Klason lignin of the samples was obtained according to TAPPI 222om-98.

Physical-mechanical properties.

Density of all densified samples was measured after the conditioning and calculated according to Equation 3:

$$Density = \frac{M}{l \times w \times t} \quad (3)$$

where *M*, *l, w, t* – mass, length, width and thickness of conditioned (25ºC; relative humidity 50%) specimen, respectively.

Three point bending. The densified juniper samples were evaluated by the modulus of elasticity (MOE) and the modulus of rupture (MOR) in the three-point bending test on a ZWICK/Z100 (Ulm, Germany) universal machine for testing the mechanical resistance of materials. Three specimens per each sample type were determined in the test to calculate the average value property.

Results and Discussion

Visual summary of all obtained juniper wood samples is shown in Figure 3. The wood appearance and color were changed slightly for wet-densified (WD) control specimens (Fig. 3c), while after the chemical treatments the densified specimens contain even surface damages with split fibers (Fig. 3d-f). These changes are associated to the Kraft cooking process where lignin and hemicelluloses degrade in the wood cell walls and dissolve extractives [13;14]. The reason of chemically pretreated and densified juniper wood color changes could be explained by the chemical degradation of hemicelluloses and lignin that makes new chromophoric groups, as well as termochromatism of the chemicals on the wood surface [9].

The thickness of control samples, which were dry- and wet-densified, decreased by 12% and 47%, while for chemically pretreated and densified samples – in range of 62-73%.

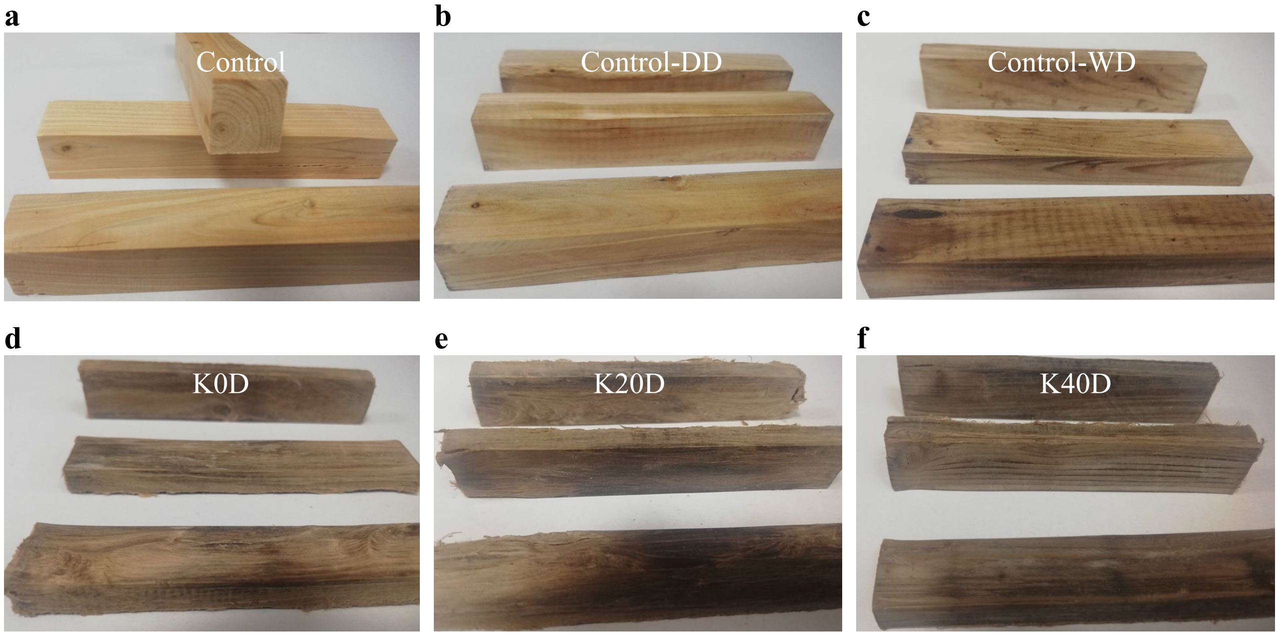

Figure 3. Visual characteristics of juniper wood samples.
Untreated control specimens: a) without densification, b) dry-densified (DD), c) wet-densified (WD); densified specimens after the Kraft cooking: d) removed immediately after reaching 165°C (K0D), e) cooked 20 minutes (K20D) and f) cooked 40 minutes (K40D).

The impact of Kraft cooking on juniper wood's mass loss and contents of lignin and extractives is shown in Table 1. Partial degradation and thermal modification of lignin was performed during Kraft cooking pretreatment and relative content of lignin decreased by 16-23%.

Table 1. Chemical characterization of juniper wood before and after chemical treatment.

	Mass loss, %	Lignin, %	Extracts, %
Control	0	34	4.8
K0	24	28.5	3.3
K20	27	29.5	3.2
K40	32	26	3.9

The significant increase of mass loss after the Kraft cooking could be more explained by the fact of hemicelluloses destruction [13;14] and then by reduction in lignin. Lignin content (34%) in the juniper wood is higher than in other popular softwood [15-16], as example in pine 24-29% [13] and spruce 26-28% [17]. Table 1 shows that the detected lignin content of chemically pretreated juniper wood is equivalent to that of pine or spruce and it is good since thermal modified lignin can act as an adhesive in the following densification step by hot-pressing [18].

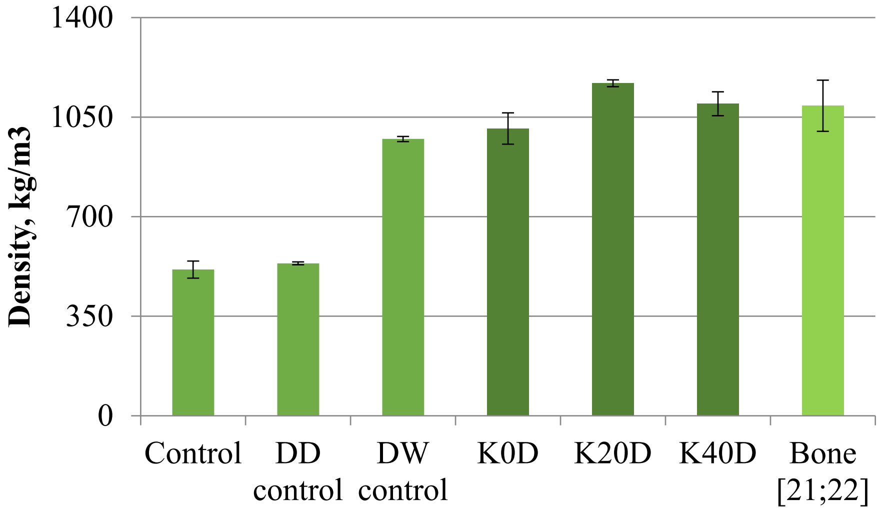

Figure 4. Density of juniper wood depending on pretreatment and densification vs bone.

The density of all densified juniper wood increased by 96-127% reaching the value over than 1000 kg/m^3 (Fig. 4) which is equivalent to that obtained by other authors [6-7;9-10;19]. The higher density appeared in the densified juniper wood after 20 minutes of Kraft cooking pretreatment. The resulting densified juniper wood density is similar to bone density, which is one of the most important properties for the material to be used in bone implants [20].

The detected bending properties of juniper wood samples are summarized in Fig. 5. Densification of dry control sample was insufficient, while wet-densification resulted to significant increase of both MOE and MOR. Densification of chemically pretreated juniper wood increased even more both MOR and MOE. The highest increase in MOR and MOE was achieved by densified juniper wood after 20 minutes of Kraft cooking pretreatment. Compared to untreated juniper wood, MOE increase is 620% reaching the average value of 12500 MPa while MOR increase is up to 85% reaching the value of 174 MPa.

The Kraft cooking after 40 minutes resulted to decrease in bending properties of densified juniper wood meaning that the optimal cooking time was reached after 20 minutes. Therefore, the chemical pretreatment longer than 20 minutes under the given conditions is unreasonable. The MOR and MOE obtained in this study by absolute values are lower than those reported by other authors, however, the percentage increase is comparable [7;9;19]. As shown in the Fig. 5 the MOE and MOR of densified juniper wood samples are equivalent to the bone properties [21-22].

It is known that the wood cell wall is formed of cellulose, hemicelluloses and lignin, and the hemicelluloses and lignin cross-linking cellulose microfibrils. Cellulose chain microfibrils with cross-linked lignin and hemicelluloses function as a skeleton. In the lignocellulosic materials hemicelluloses provides shape stabilization and lignin is responsible for the quasi-elastic recovery mechanism (shape memory effect). Lignin content in the wood has negative correlation with wood elasticity [9-10]. The high lignin content in the juniper wood (Table 1) explains the low MOE value in untreated (control) juniper wood sample [15-16].

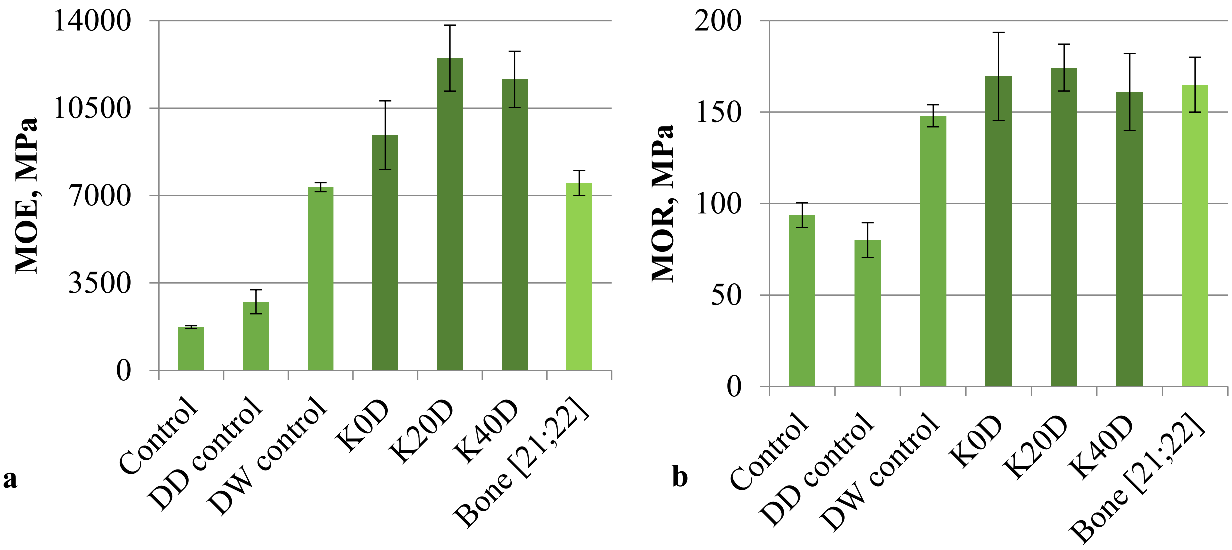

Figure 5. Bending properties of juniper wood depending on pretreatment and densification vs bone.

However, this is highly related to the wood moisture content. This effect could be compared observing the dry-densified sample which MOE increase is not sufficient, however, wet-densified sample demonstrate significant MOE increase. So, the increase in moisture content helps to form hydrogen bonds during pressing and allows improved densification process by leading to increase in density and simultaneously increase in bending properties. In turn the chemical pretreatment of juniper wood has partially destroyed lignin and hemicelluloses and new covalent bonds are formed what leads to even higher increase of all detected properties suggesting it as an effective remedy for wood improvement comparable to bone properties.

In this study, partial degradation and modification of lignin and hemicelluloses of solid juniper wood samples was performed by Kraft cooking pretreatment in combination with the change in the structure of wood cell walls during hot-pressing, provided an increase in density and corresponding increase in MOR and MOE.

Summary

It is possible to obtain densified juniper wood with similar density and bending properties as bone by Kraft cooking pretreatment and following hot-pressing. Density of pretreated and densified juniper wood increase up to 2.5 times, while MOE and MOR increase up to 7 and 2 times, respectively. The study showed that the detected physical-mechanical properties of densified juniper wood are comparable to the bone suggesting to continue the research on densified wood for bone implants.

Acknowledgements

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