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Coatings for Use on Wooden Bicycle Frames – Applicability, Test Methods and Artificial Weathering Results

Premazi za drvene okvire bicikla – primjenjivost, metode ispitivanja i rezultati simuliranog izlaganja vremenskim utjecajima

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ABSTRACT • *Seven different coating systems were tested regarding their suitability for application on bicycle frames made of wood. Since bicycles are ridden throughout the year, the coating system has to withstand different outdoor climate conditions and, especially in winter, the salt brines from the roads. For this reason, an artificial weathering test with an additional freezing step was performed, followed by a specially developed salt brine spray test in ambient outdoor winter climate. Another focus was on the applicability of the coatings. For the tests, a range of coatings, originally developed for wooden front doors, floors and for boat building, was selected. These coatings were expected to meet the main requirements for UV radiation - permanence, weather resistance and saltwater firmness. The main constituents of the coatings were water-based polymer dispersions, two-component polyurethane systems or synthetic and natural oils. The layer thicknesses of the coatings, as well as colour and gloss data of the specimens, were recorded and rated. The adhesion capability was examined by carrying out a cross-cut-test. Surface damages were observed visually. It turned out that colour and gloss change served as good indicators for the decay of the coating. Three different coatings passed the accelerated weathering test. Salt spray had no significant effect on any of the coatings.*

Keywords: *wooden bicycle, wood coating, durability, artificial weathering, salt spray*

SAŽETAK • *U radu se prikazuju rezultati istraživanja prikladnosti sedam različitih premaznih sustava za drvene okvire bicikla. Budući da se bicikl vozi tijekom cijele godine, premazni sustav mora izdržati različite vremenske utjecaje te, posebice zimi, utjecaj slane vode s cesta. Stoga je provedeno ispitivanje premaza nakon simuliranog izlaganja vremenskim utjecajima s dodatnom fazom zamrzavanja, nakon čega je proveden posebno razvijeni test utjecaja otopine soli na premaz u vanjskim zimskim uvjetima. Drugi fokus bio je na načinu nanošenja premaza. Za istraživanje je odabran niz premaza, izvorno razvijenih za ulazna drvena vrata, podove i brodogradnju, za koje se pretpostavilo da će udovoljiti glavnim zahtjevima za UV zračenje – da će biti trajni, otporni na vremenske uvjete i*

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otporni na utjecaj slane vode. Glavni sastojci premaza bile su polimerne disperzije na bazi vode, dvokomponentni poliuretanski sustavi ili sintetička i prirodna ulja. Zabilježena je i ocijenjena debljina sloja premaza te podaci o boji i sjaju uzoraka. Adhezivnost je ispitana metodom zarezivanja mrežice na premazu. Oštećenja površine vizualno su opažana. Pokazalo se da promjena boje i sjaja može poslužiti kao dobar pokazatelj propadanja premaza. Tri različita premaza prošla su ispitivanje ubrzanog izlaganja vremenskim utjecajima. Slani sprej nije imao znatniji učinak ni na jedan od premaza.

Ključne riječi: *drveni okvir bicikla, premaz za drvo, izdržljivost, simulirano izlaganje vremenskim utjecajima, slani sprej*

1 INTRODUCTION
1. UVOD

Since the beginning of mobility, wheeled vehicles as well as ships and planes were manufactured from wood (Childe, 1951; Piggott, 1969). For vessels, the protection of wood against UV exposure and salt water has been an issue (Laidlaw, 1952). Even today car manufacturers, as the Morgan Motor Company, use ash wood for their car frames. However, the hygroscopicity and limited durability of wood causes difficulties if used outdoors. At Morgan, therefore, steel or aluminium coverings are used to protect the wooden frame against decay ("The Morgan Motor Company," n.d.). This procedure of wood protection, however, does not make sense on wooden bicycles as weight is an issue and the frame should be visible as a design element (Figure 1). Another way to protect wood is practiced by boat building companies: wooden boats are coated in order to protect them against influences of UV radiation and salt water.

As coatings for wooden bicycle frames also have to provide protection against moisture accumulation in order to prevent biological deterioration, against UV-radiation and against deterioration caused by salt brine-induced corrosion, the need has become obvious to apply the wood protection method used in boat building to the bicycle frame building. Furthermore, coatings for wooden bicycle frames have to be flexible but also to show decent bonding properties in order to allow movements of the frame. Baur *et al*. (2006) studied the weathering performance of different wood species by determining the timber-specific colour degradation. They suggested coating the specimen with clear coat and specific additives in order to strengthen the protection against sunlight degradation. Dawson *et al*. (2008) proposed to enhance the exterior performance of clear coatings through delignifying the surface cells of *Pinus radiata*.

Finally, the coating should be easy to apply and maintain. Consequently, coatings were chosen for the bicycle wood frame that met the described requirements. Beside the resistance to weathering of the cured coating, the applicability and maintenance of the coating was also important for its choice.

To prove the performance of coatings on wood, the testing method EN 927-6 (DIN EN 927-6, 2006), which describes the exposure of wood coating systems to artificial weathering using fluorescent UV lights and moisture, was chosen. This method is described as suitable to test the performance of coatings on wood and gives evidence of durability in natural weathering (Grüll *et al*., 2014).

The main goal of the present study was to find the best UV, weather and salt brine resistant and easiest to maintain coating for wooden frame bicycles.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Material
2.1. Materijal

European ash wood (*Fraxinus excelsior* L.) lamellae were bound with polyurethane resin and pressed in moulds for the bicycle frame (Figure 2). Specimen with the dimension of 150 x 75 x 6 mm³ were prepared from the lamellae and then coated. As there are no coatings available, exclusively developed for wooden bicycle frames, alternative coatings, developed for similar purposes, were investigated.

Besides coatings for front doors, which are directly exposed to weathering, coatings for wooden

Figure 1 Electrically powered wooden frame bicycle
Slika 1. Električni bicikl drvenog okvira

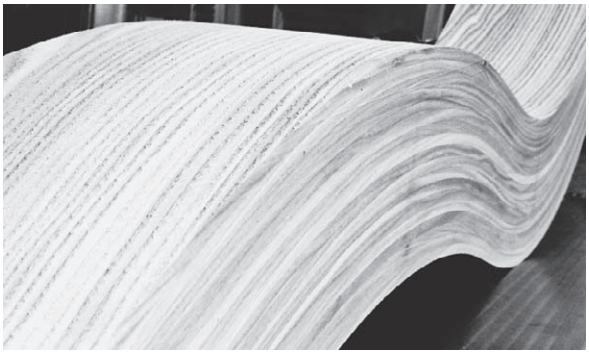

Figure 2 Wooden frame made of ash lamellae
Slika 2. Drveni okvir napravljen od jasenova lameliranog drva

Table 1 Selected coatings
Tablica 1. Odabrani premazi za drvo

Abbrev. *Kratica*	**Coating system / type** *Premazni sustav / vrsta*	**Area of application** *Područje primjene*	**Intended for indirect exposure to weather** *Namijenjen za neizravno izlaganje vremenskim utjecajima*	**Intended for direct exposure to weather** *Namijenjen za izravno izlaganje vremenskim utjecajima*	**Intended for seawater contact** *Namijenjen za kontakt sa slanom vodom*
WD	Water-based polymer dispersion *polimerna disperzija na bazi vode*	Exterior doors *vanjska vrata*		x	
PU	Two-component polyurethane system *dvokomponentni poliuretanski sustav*	Furniture and boat interior *namještaj i interijer broda*	x		
HW	Hard wax oil *ulje od voska*	Wooden floors *drveni podovi*	x		
O1	Linseed and tung oil *laneno i tung ulje*	boat building *brodogradnja*			x
O2	Oil based on alkyd / wood oil / phenolic resin *ulje na bazi alkida / ulje za drvo / fenolna smola*	boat building *brodogradnja*			x
O3	Natural oils, fatty acids and resins *prirodna ulja, masne kiseline i smole*	boat building *brodogradnja*			x
O4	Hydrocarbons, alkanes, cyclic and aromatic compounds, not film building *ugljikovodici, alkani, ciklički i aromatski spojevi; ne stvaraju prevlaku*	boat building *brodogradnja*			x
R	Reference samples, untreated *referentni uzorci, netretirani*				

flooring and interior coatings, developed to resist abrasion and stain, were selected, as well as coatings for wooden boats, made to withstand weathering and seawater (Table 1).

2.2 Applicability
2.2. Nanošenje premaza

The coatings consisting of several layers were applied according to the manufacturer instructions. As the repair-friendliness of the coating was in the focus of the manufacturer of the wooden bike, the applicability and maintenance of the coating had to be taken into account as selection criteria. The WD and PU- coating systems could be applied using a low volume low pressure (LVLP) spray gun with 1.4 mm nozzle - at 150 kPa air pressure. The WD System consisted of five components: a primer, an intermediate coat and a finish coat, which also needed a hardener and a solvent. The PU system consisted of a filling primer, a hardener and a clear lacquer as finish. All other coatings could be easily applied using a brush, also according to the manufacturer specifications. The oils consisted only of one component. In total, 6 specimen of each coating were produced. Since no matting agents were used, the coatings appear glossy on WD, PU and O1 specimens and semi-glossy, as defined in EN 927-1 (EN 927-1, 2013), on HW and O3 after application.

The coatings were applied in a paint booth at ambient room temperature between 18 and 22 °C and a relative humidity between 40 and 60 % RH. All specimens had to dry for 24 h in the same conditions between successive coatings. The untreated wood was prepared with 150 grit abrasive paper and sanded with 240 grit abrasive paper between the coatings. The total number of layers for each coating is listed in Table 2.

For comparison, reference samples without coating were produced. The wood lamellae were conditioned in standardized conditions at 20 °C and 65 % relative humidity for 28 days. Also, coated samples which were not exposed to artificial weathering were produced for the salt spray test and as control samples for the cross cutting test.

For characterization of the several coatings studied herein, the layer thickness of each coating was determined using a microscope at 10x and 20x magnification.

Table 2 Coating: number of layers
Tablica 2. Premaz – broj slojeva

Sample ID / *Oznaka premaza*	WD	PU	HW	O1	O2	O3	O4
Number of layers / *Broj slojeva*	4	3	3	3	3	3	3

Table 3 Accelerated weathering cycle program
Tablica 3. Ciklički program simuliranog izlaganja vremenskim utjecajima

Step / *Korak*	**Function** / *Funkcija*	**Temperature** / *Temperatura*	**Duration** / *Trajanje*	**Condition** / *Uvjet*
1	Condensation / *kondenzacija*	(45 ± 3) °C	24 h	
2	Subcycle / *podciklus*: 32 cycles of step 3 and 4 *32 ciklusa koraka 3. i 4.*		96 h	
3	UV- exposure *izlaganje UV zračenju*	(60 ± 3) °C	2.5 h	Irradiance set point 0.89 W/m² at 340 nm
4	Spray / *raspršivač*		0.5 h	6 l/min to 7 l/min, UV off
5	Freezing / *zamrzavanje*	(-25 ± 1) °C	48 h	

2.3 Artificial weathering
2.3. Simulirano izlaganje vremenskim utjecajima

Three days after completing the preparation of the samples, different coatings were tested following the EN 927-6 (DIN EN 927-6, 2006), which describes the exposure of wood coating systems to artificial weathering using fluorescent UV lights and moisture. As weathering tester, a Q-LAB QUV accelerated weathering testing machine was used. The machine simulates the effects of sunlight, dew and rain with UV- exposure, condensing humidity and water spray in alternating cycles.

As cold winter conditions also had to be simulated, a freezing step was inserted into the standard cycle, and the duration of the UV- exposure and spray subcycle was shortened from 48 to 32 (Table 3). For freezing, the samples were alternately removed from UV and from the spraying step at the end of each cycle. The samples were frozen in a laboratory freezer at a controlled temperature of -25 °C. In order to intensify the climatic stress, 14 cycles were performed instead of 12.

2.4 Measurement of colour and gloss changes
2.4. Mjerenje promjene boje i sjaja

Before each weathering cycle, the coating surface of each specimen was inspected by human eye for colour change, yellowing, fading, cracks and flaking following DIN EN ISO 4628-4 and 5 (DIN EN 4628-4, 2004, DIN EN ISO4628-5, 2004). For an evaluation of colour differences with the naked eye, scales as shown in Table 4 are often used. Additionally, at six individual spots on each specimen, the colour, lightness and gloss data were measured and recorded at the beginning of each weathering cycle with a BYK-Gardner spectro-guide 45/0 gloss spectrophotometer. The colour and lightness were determined in the CIE system (Commission Internationale de l'eclairage), according to DIN EN ISO 11664-4 (DIN EN ISO 11664-4, 2012), where the $L^*a^*b^*$ colour space is described as a tree-dimensional space, where L^* stands for lightness, a^* is a green to red coordinate and b^* is a blue to yellow coordinate.

The ΔE^*_{ab} (Equation 1) indicates the colour and lightness differences of the tested wood coatings and colour change during test procedure.

$$\Delta E^*_{ab} = ((L^*_2 - L^*_1)^2 + (a^*_2 - a^*_1)^2 + (b^*_2 - b^*_1)^2)^{1/2} \quad (1)$$

The mean values of colour and lightness differences were measured at the beginning of each testing cycle and mapped in a diagram (Figures 5 and 6). The intensity of the reflected light was measured as Gloss units (GU) together with colour and lightness at the beginning of each cycle.

2.5 Cross cutting test
2.5. Određivanje adhezije premaza metodom zarezivanja mrežice

DIN EN 927-6 requires a cross-cut test for the evaluation of adhesion capability of varnish on wooden surface. Two weeks after having passed the accelerated weathering cycle, a right angle lattice pattern was manually cut into the coating with a blade according to EN ISO 2409 (ISO 2409, 2013).

An average distance of 2 mm from each cutting line is required for soft substrates and layer thicknesses up to 60 µm. After cutting, the adhesion resistance of coatings to separation from the wood surface is tested using an adhesion tape applied over the grid. Five minutes after application, the tape is removed at an angle of 60°. The test results were classified according to EN ISO 2409 from 0 (no visible changes) to 5 (the worst adhesion), As only the WD, O1 and O2 series samples withstood the weathering cycle with an unscathed surface, these were rated and the mean value of each sample series was calculated. For comparison purposes, unexposed samples were also subjected to the cross-cut test.

Table 4 Rating scale for colour differences (Buchelt and Pfriem, 2010)
Tablica 4. Ljestvica ocjena promjene boje (Buchelt and Pfriem, 2010.)

Δ*E*	**Rating** / *Ocjena*
0.0 … 0.5	no difference or almost no difference / *uopće nema ili gotovo nema razlike u boji*
0.5 … 1.0	difference may be noticeable to the trained eye / *promjena je primjetna samo obučenom promatraču*
1.0 … 2.0	imperceptible colour difference / *neprimjetna razlika u boji*
2.0 … 4.0	perceived colour difference / *percipirana razlika u boji*
4.0 … 5.0	significant difference in colour, which is rarely tolerated / *znatna razlika boje koja se rijetko tolerira*
above 5.0	the difference is judged to be other colour / *razlika boje je takva da se procjenjuje kao druga boja*

For a more detailed evaluation, the samples were classified using a microscope with 10x and 20x magnification.

2.6 Salt-spray- test
2.6. Test raspršivanja slane otopine

To test the suitability of the bike frame coating for use in winter, two months after the accelerated weathering cycles, a salt-spray- test was performed in addition to the weathering test. Most corrosion tests for (coated) metal are based on a salt spray test, in which metal sample coupons are exposed to the salt spray. Such test methods are described in international standards such as ASTM B117 „Standard Practice for Operating Salt Spray (Fog) Apparatus“ (ASTM B117, 2011), ISO 9227 (ISO 9227, 2012) „Corrosion Tests in Artificial Atmospheres - Salt Spray Tests“ or EN 60068-2-11 „Basic Environmental Testing Procedures, Part 2: Test KA: Salt Mist“ (DIN EN 60068-2-11, 2000) and EN 60068-2-52 „Environmental Testing - Part 2: Test. Test KB. Salt Mist, Cyclic (Sodium Chloride Solution)” (EN 60068-2-52, 1996).

In standards for the automotive industry other test methods are also described, in which the parts are not exposed to a continuous salt spray, but are directly sprayed with salt brine. An example for this is the GMW 14872 Cyclic Corrosion Laboratory Test procedure (GMW14872, 2006), which provides an accelerated corrosion test for parts and components under laboratory conditions. The test method provides a combination of cyclic load by moisture, drying and salt spray to accelerate corrosion. The DIN EN ISO 15710 (2006) is intended primarily to test the protective effect of coatings on aluminium and aluminium alloys against corrosion and is vastly used in the aerospace industry. In this test method, a coated sample plate, whose coating is scratched, is alternately immersed in a dilute salt solution and removed from it.

Various testing methods indicate that there are different approaches to examine the influence of corrosion on materials and surface coatings. For the present

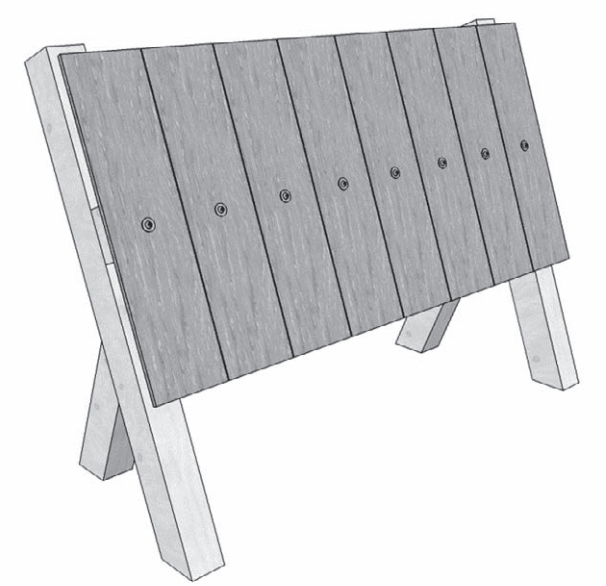

Figure 3 Rig for the salt spray test with mounted specimens
Slika 3. Sustav za ispitivanje utjecaja raspršene slane otopine na drvne premaze

application, the resistance of a wooden bicycle frame against pre-wetted salt, used by winter services in Germany, was of particular interest. Based on test methods for metallic components, a test method was developed to examine direct contact of coated wood with salt and brine. The specimens with a size of 75 mm x 300 mm were mounted on a frame in a 20° inclination (Figure 3) in southern direction and exposed to a natural outdoor climate for eight weeks. Temperature and relative humidity were continuously recorded (Figure 4).

German winter services mostly use up to 40 g/m² of the so-called wet salts to defrost snow or ice covered roads. Wet salts consist of dry salts moistened with saline. Accordingly, saturated brine, consisting of 22 % sodium chloride and 78 % water was prepared. Through a period of 8 weeks 60 g/m² of the salt solution was sprayed on the samples twice a day.

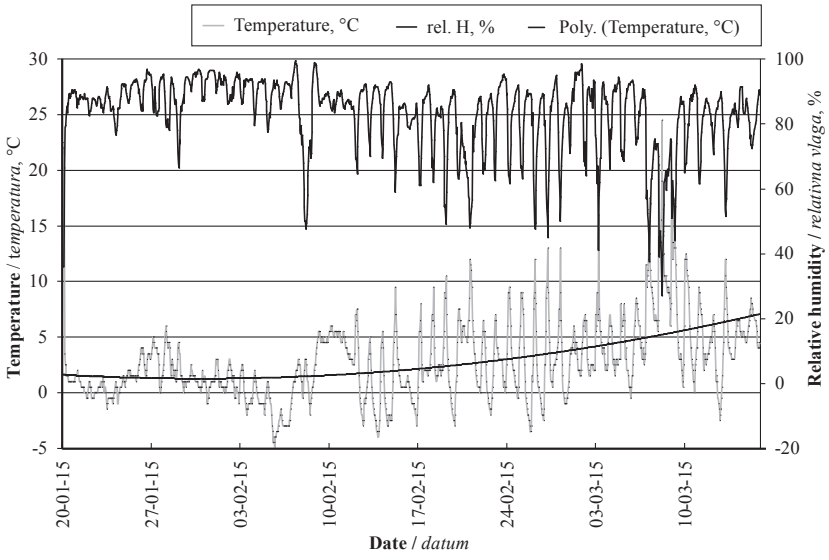

Figure 4 Recorded temperature and relative humidity, polynomic regression of temperature during salt spray test
Slika 4. Registrirana temperatura i relativna vlažnost zraka, polinomska regresija temperature tijekom ispitivanja raspršivanjem slane otopine

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1 Applicability
3.1. Nanošenje premaza

It can be noted that, regardless of the method of application, layer thicknesses ranging between 35 and 50 µm were obtained (Table 5). With an average layer thickness of 18.0 µm, the O4 product had the lowest layer thickness - due to the fluidity and method of application (wood had to be «saturated» with the oil at least one day) - Furthermore, the thickest layer of 51.8 µm was measured for the O1 product.

Both methods of application have advantages and disadvantages over the other method. The coating applied using a spraying gun produces a thinner and more uniform film. If repairs are necessary, preference must be given to the oils, because of the simpler application. Repairs of a multi-layered coating system can only be carried out by a qualified workshop.

3.2 Colour and gloss change
3.2. Promjena boje i sjaja

Form the beginning of weathering, a colour change and darkening of all specimens could be noticed. As shown in the average ΔE^*_{ab} change diagram (Figure 5), the colour of all samples changed after the first cycle. All coated samples showed the tendency to become darker (Figure 6) at as long as the surfaces were not damaged. A washout of the coating generally leads to flaking and, therefore, to a loss of protection against bleaching by UV irradiation. After the end of the fourth cycle, colour changes on PU and O4 samples could be measured. Only one week later, the discolouration could be seen by the naked eye.

The beginning of bleaching of the coating of HW samples could be measured after the fifth week by ΔE^*_{ab} data acquisition. On O3 samples, a visible fading could first be detected four weeks later. As the coating was largely destroyed having passed the eleventh cycle, the PU (quantity five, crack width parameter 3 according to DIN EN ISO 4628-4), O4 and HW (severe fading) coatings were removed from the artificial weathering cycle.

For all other samples, up to the 13th cycle, no flaking was detected. However, after the last cycle, incipient fading was observed also with the naked eye on the O3- samples.

The coated specimens became glossier after the first cycle. During the following test cycles, the gloss decreased in all samples. At the end of the tenth cycle, a significantly stronger decreasing of gloss of the O1, O2 and PU samples was detected (Figure 7).

3.3 Cross Cutting Test
3.3. Određivanje adhezije premaza metodom zarezivanja mrežice

For comparison, specimens of all coated but not weathered control samples were cross cut. It can be stated that all control samples had intact surfaces, so all of these samples could be categorized as „0“ according to DIN EN ISO 2409. A cross cut of an intact HW surface with classification “0” is shown in Figure 8. From the samples exposed to weathering, only the samples that withstood the 14 cycles weathering test with an obviously intact surface were tested by cross-cut. The cross-cut samples of O1 and O2 series could be classified as 0-1 (Figure 9) after weathering. In case of the WD series, a cross-cut area between 5 % and 15 % showed flaking (Figure 10) (Table 6).

Table 5 Average layer thicknesses of the coating (µm) and standard deviation
Tablica 5. Prosječna debljina sloja premaza (µm) i standardna devijacija

Sample ID / *Oznaka premaza*	**WD**	**PU**	**HW**	**O1**	**O2**	**O3**	**O4**
Average layer thickness, µm	48.1	34.8	38.6	51.8	40.6	35.4	18.0
Prosječna debljina sloja, µm	(5.82)	(2.15)	(7.23)	(7.19)	(5.00)	(4.55)	(4.67)

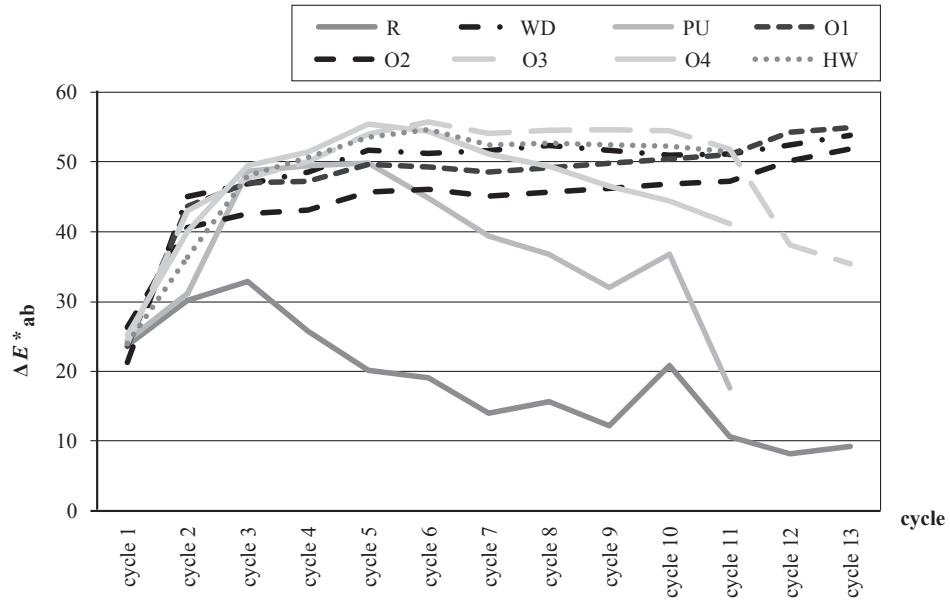

Figure 5 Average ΔE^*_{ab} change of wood coatings
Slika 5. Prosječna promjena boje ΔE^*_{ab} drvnog premaza

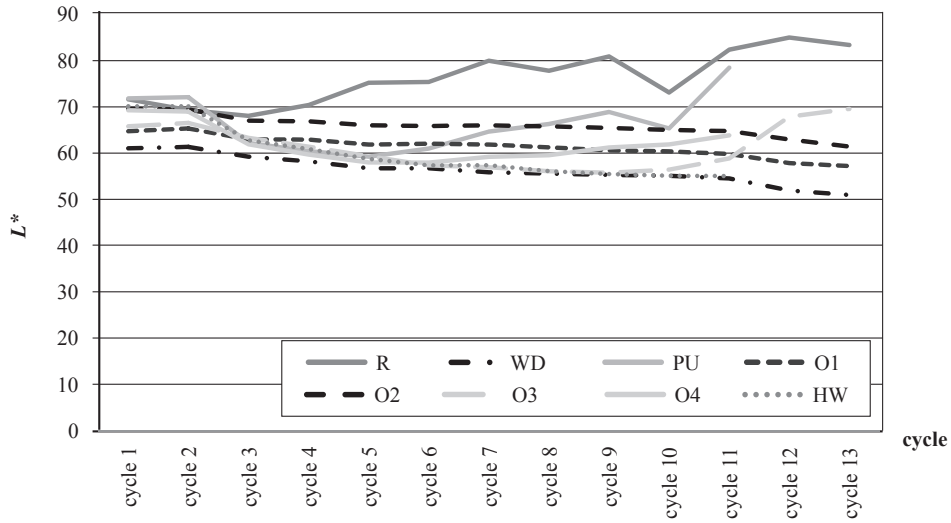

Figure 6 Average *L** change of wood coatings
Slika 6. Prosječna promjena svjetline *L** drvnog premaza

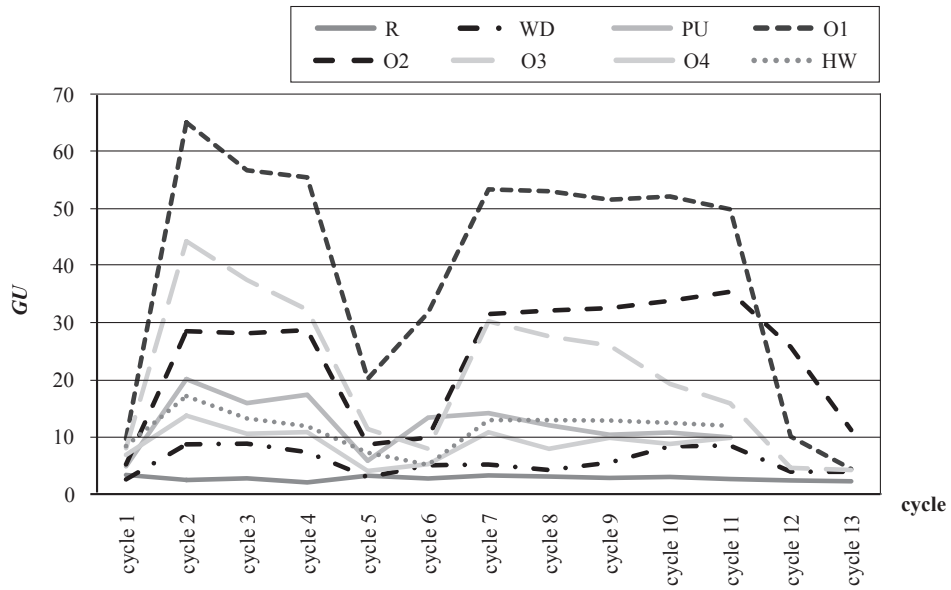

Figure 7 Average gloss unit change of wood coatings
Slika 7. Prosječna promjena sjaja drvnog premaza

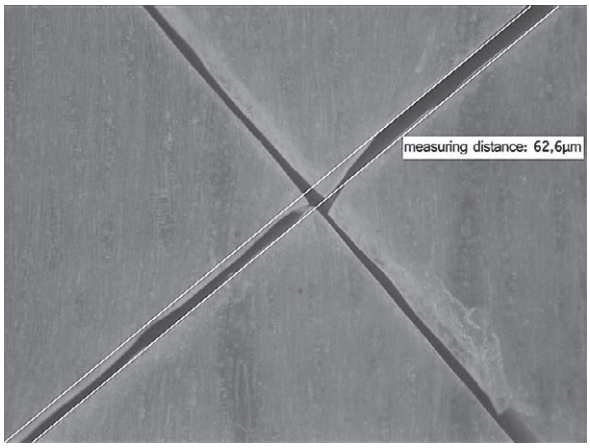

Figure 8 Microscopic image (10x magnification) of a cross-cut of an HW sample with intact coating on its surface. The edges of the cut are smooth and without detachments. 0 % of the cut area is affected by flaking
Slika 8. Mikroskopska slika (uvećanje 10 puta) zarezane mrežice HW uzorka s nepropusnim premazom na površini; rubovi rezanja glatki su i bez odvajanja; ljuštenja površine zazrezivanja nije bilo

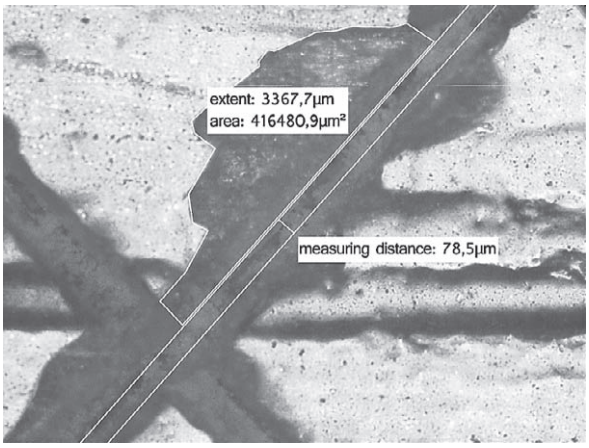

Figure 9 Cross-cut of the weathered O2 coating, view through microscope at 20x magnification. Maximum 5 % of the cut area shows small flakes of the coating at the intersections of the cuts
Slika 9. Zarezana mrežica premaza O2 nakon izlaganja vremenskim utjecajima; pogled mikroskopom uz povećanje 20 puta; maksimalno 5 % površine zarezivanja pokazuje malo ljuštenje premaza na sjecištima rezova

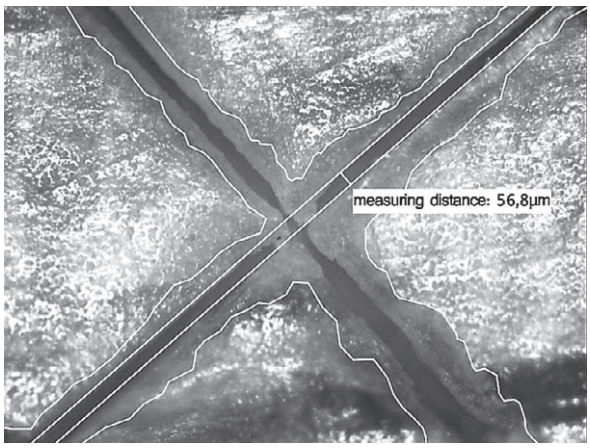

Figure 10 Cross-cut on weathered coating of WD sample, view through microscope at 10x magnification, example for classification 2. The coating has flaked along the edges and at the intersections of the cuts. A cross-cut area greater than 5 % is affected.
Slika 10. Zarezana mrežica premaza WD nakon izlaganja vremenskim utjecajima; pogled mikroskopom pri uvećanju 10 puta; primjer za klasifikaciju 2; premaz je oljušten duž rubova i na križanju rezova; promjene su zabilježene na površini zarezivanja većoj od 5 %

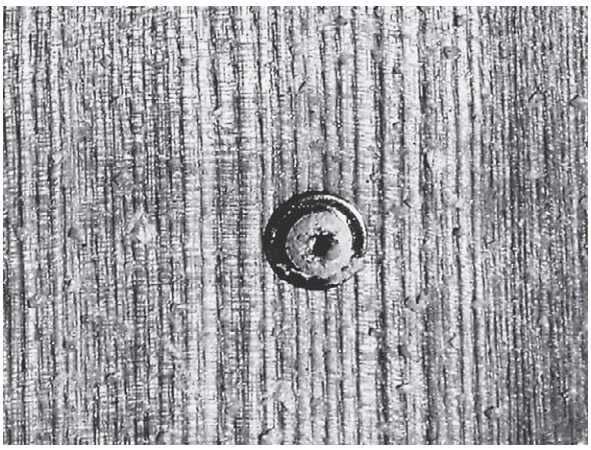

Figure 11 Specimen after eight weeks of salt spray test: corrosion appearances on stainless steel screws and salt crystals on the specimen.
Slika 11. Uzorak nakon osam tjedana testiranja slanom otopinom; pojava korozije na vijcima od nehrđajućeg čelika i kristali soli na uzorku

Table 6 Results of cross-cut test for samples after 14 cycles weathering test
Tablica 6. Rezultati ispitivanja adhezije premaza metodom zarezivanja mrežice nakon 14 ciklusa izlaganja vremenskih utjecajima

Sample series / *Serija uzoraka*	**WD series** / *Serija WD*	**O1 series** /*Serija O1*	**O2 series** / *Serija O2*
Average classification *Prosječna klasifikacija*	1-2	0-1	0-1

3.4 Salt-spray- test
3.4. Test raspršivanja slane otopine

The self-developed salt-spray-test follows the conditions that prevail on wintry German roads, and no generally valid conclusions can be drawn on its basis. For this purpose, a standardized test would have to be developed, that would also take into consideration colour and gloss measurements. This salt-spray test showed that, at the end of twelve weeks in ambient moderate winter climate, all test specimens survived the test unscathed. In periods of rising temperatures, the brine formed salt crystals on the surface of the specimen. These could be easily washed off. The surfaces had no visible cracks or flaking; neither the crystals nor the brine itself had an effect on the varnish. Corrosion appeared only on the stainless steel screw fasteners and washers (Figure 11). Table 5 shows the results of the single tests in a brief summary.

4 CONCLUSIONS
4. ZAKLJUČAK

Although recommended, the two-component PU coating system is not suitable for the intended use, as

Table 7 Summary table of final results
Tablica 7. Tablica konačnih rezultata

Sample ID *Oznaka premaza*	**Applicability** *Nanošenje premaza*	**Colour and gloss change** *Promjena boje i sjaja*	**Cross Cutting Test** *Test zarezivanja mrežice*	**Salt Spray Test** *Test slanim sprejom*
WD	Spray gun necessary *obvezno štrcanjem*	passed / *prošao*	1-2	passed / *prošao*
PU	Spray gun necessary *obvezno štrcanjem*	failed / *nije prošao*	No analysis possible *nije moguća analiza*	passed / *prošao*
HW	manually / *ručno*	failed / *nije prošao*	No analysis possible *nije moguća analiza*	passed / *prošao*
O1	manually / *ručno*	passed / *prošao*	0-1	passed / *prošao*
O2	manually / *ručno*	passed / *prošao*	0-1	passed / *prošao*
O3	manually / *ručno*	failed / *nije prošao*	No analysis possible *nije moguća analiza*	passed / *prošao*
O4	manually / *ručno*	failed / *nije prošao*	No analysis possible *nije moguća analiza*	passed / *prošao*

only after finishing the fifth cycle, flaking of the coating could be noticed. The hard wax oil, which is intended for the use on wooden floors, bleached at the beginning of the 8th week. Also, two boat building oils failed. Flaking appeared on the O4 specimen after only six cycles, due to leaching. The O3 oil faded at the end of the weathering cycle. The multi-component water-based coating for exterior doors (WD) and two oil-based coatings from manufacturers of yacht coatings (O1 and O2) can be recommended for the year round use as a good protection for wooden bicycle frames.

Considering the results of the colour change and gloss measurements, it can be concluded that the tested coatings, exposed to accelerated weathering, have shown significant differences in resistance to UV radiation and extreme climate conditions. It turned out that the measurement of colour changes in artificial weathering tests is - together with the cross cut test - an effective way to determine suitable coating products for wooden frames. The salt brine spray test showed no further degradation on the coating surface.

Taking into account the results from the colour and gloss measurements, the use of a multi-component water based coating, as well as some of the oil based paints for boat building, can be recommended for the intended application.

In order to create a stress scenario on wooden bikes that is closer to a real daily use, in future tests, the coated wooden lamellae could be exposed to mechanical forces before weathering. Additionally, the resistance of coatings against crushed stones from the road surface and their ability to withstand abrasion in daily use could be part of future testing.

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Evaluation of Linter Cellulose as an Alternative Raw Material for Tissue Paper Production

Procjena linter celuloze kao alternativne sirovine za proizvodnju upijajućeg papira

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ABSTRACT • *The study was carried out to evaluate Linter Cellulose (LC) as an alternative raw material for tissue paper production. Since LC is generally dark brown in color, it must be bleached before being used in tissue paper production. Bleaching process was applied to LC after impurities and oils were removed. LC was bleached in 9 different conditions with sodium hypochlorite (NaClO). The optical and physical properties of LC were measured in accordance with relevance standards in order to determine optimum bleaching condition. The best results in the optical properties were obtained by bleaching with 12 % NaClO. The whiteness, brightness, and yellowness values were found as 67.54, 64.39, and 6.20, respectively. The physical properties of bleached LC were not suitable for tissue paper production. For this reason, LC and wood fibers (WF) were mixed at certain rates to produce tissue paper. The physical and optical properties of the paper obtained from the mixtures were analyzed to determine the optimum mixing ratio. The results showed that 40 % LC and 60 % WF mixtures can be used in tissue paper products. The important physical properties for tissue paper were Water Retention Value(WRV) and Water Absorption Time (WAT) and these values were found as 293.6 g·m^{-2} and 1.67 s. WRV and WAT of LC were found to be better than those of WF (267 g·m^{-2} and 2.62 s). As a result, when considering the shortage of pulp and paper raw material, the use of LC in tissue paper production would contribute significantly to procuring the raw material and providing economic production.*

Keywords: *Linter cellulose, bleaching, sodium hypochlorite, tissue paper.*

SAŽETAK • *Istraživanje je provedeno radi procjene linter celuloze (LC) kao alternativne sirovine za proizvodnju upijajućeg papira. Budući da je LC tamnosmeđe boje, prije uporabe za proizvodnju upijajućeg papira potrebno ga je izbijeliti. Procesi izbjeljivanja LC-a primijenjeni su nakon uklanjanja nečistoća i ulja. LC je izbijeljen natrijevim hipokloridom (NaClO) pri devet različitih uvjeta. Izmjerena su optička i fizikalna svojstva LC-a u skladu s odgovarajućim standardima kako bi se odredili optimalni uvjeti izbjeljivanja. Najbolji rezultati optičkih svojstava dobiveni su izbjeljivanjem 12-postotnim NaClO. Vrijednost bjeline iznosila je 67,54 %, sjajnosti 64,39 % i žutila 6,20 %. Fizikalna svojstva izbijeljenog LC-a nisu prikladna za proizvodnju upijajućeg papira. Stoga je LC pomiješan s drvnim vlakancima (WF) u određenom omjeru kako bi se dobila sirovina prikladna za proizvodnju upijajućeg papira. Fizikalna i optička svojstva papira proizvedenoga od pripremljene smjese analizirana su radi određivanja optimalnog omjera miješanja LC-a i WF-a. Rezultati su pokazali da je smjesa od 40 % LC-a i 60 %*

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WF-a može upotrebljavati za izradu proizvoda od upijajućeg papira. Važna fizikalna svojstva upijajućeg papira jesu sposobnost zadržavanja vode (WRV) i vrijeme upijanja vode (WAT). Za proizvedeni upijajući papir izmjerena je vrijednost WRV-a od 293,6 g·m^{-2} i WAT-a od 1,67 s. Utvrđeno je da su vrijednosti WRV-a i WAT-a za LC bolje nego vrijednosti za WF (267 g·m^{-2} i 2,62 s). Kada se uzme u obzir nedostatak sirovine za proizvodnju celuloze i papira, može se reći da bi upotreba LC-a za proizvodnju upijajućeg papira mogla znatno pridonijeti lakšoj nabavi sirovina i ekonomičnosti proizvodnje.

Ključne riječi: *linter celuloza, izbjeljivanje, natrijev hipoklorit, upijajući papir*

1 INTRODUCTION
1. UVOD

Cellulose, the raw material of the paper, is obtained from wood and non-wood plants. Due to the use of wood raw materials in different industries (particleboard, plywood, furniture etc.), it has become an expensive raw material. In addition to this, since the process of obtaining wood takes a very long period of time, cellulose production from annual plants has become more attractive (Erdem, 2010). Cotton, one of these annual plants, is primarily grown as textile raw material. Linter is obtained as a by-product from the cotton seed. When compared with wood, cellulose can be more easily obtained from linter. Besides, it is also easier to bleach linter than wood pulps.

The decrease in the availability of raw materials for pulp and paper production has led papermakers to search for new raw material resources. Several studies have been carried out to discover these resources (Chandra, 1998; Tutus and Cicekler, 2016; Comlekcioglu *et al.,* 2016). As an alternative to wood-based raw materials, linter cellulose is an important raw material resource for pulp and paper production. Linter is an important by-product of the textile industry. Cotton linter is the short fiber that cannot be used in the textile process. In order to be used in oil production, cotton seed must be separated from its seed by special cutting methods. After special cutting methods, first and second cut linters are obtained from separated fibers. Cellulose content, color, fiber dimension, and contaminants are important to determine the quality of linter cellulose (LC). Linter has an excess of 80 % of holocellulose, and more than 75 % of it is alpha-cellulose (Dogmaz, 1994; Sczostak, 2009; Morais *et al.,* 2013). LC was first applied in regenerated cellulose production. Also, LC is used in the production of cellulose esters such as nitro cellulose and cellulose acetate (Ward *et al.,* 1965).

The type raw material is one of the most important factors affecting paper quality. Chemical components and fiber properties of wood differ from species to species. For this reason, the characteristics of the pulps produced in certain pulping conditions depend on the wood species (Perez and Funchon, 2003; Shackford, 2003). Softwood pulps are used to produce stronger paper. These pulps are often used as reinforcing pulp in paper production. On the other hand, hardwood pulps are preferred for producing smooth and high-quality writing paper (Chauhan *et al*., 2011; Gulsoy and Tufek, 2013).

Bleaching is a chemical process applied to enhance the brightness of cellulosic materials. It is possible to increase the service and usage area of the paper with the bleaching process (Reeve, 1996). The main purpose of the bleaching process is to modify and/or remove the lignin and lignin degradation products, extractive substances, metal ions, non-cellulosic carbohydrate components and any coloring materials in the paper poultry by using appropriate chemical substances and systems (Singh, 1978). Sodium hypochlorite (NaClO) is stable above pH 10 (Cardamone and Marmer, 1995). It is a very cheap oxidizer, with higher redox potential than hydrogen peroxide, and bleaches rapidly at room temperature (Karmakar, 1999; Ibrahim *et al.,* 2010).

Tissue paper is produced by a paper machine that has a single large steam heated drying cylinder (yankee dryer) fitted with a hot air hood. The raw material is paper pulp. The Yankee cylinder is sprayed with adhesives to make the paper stick. Creping is done by the Yankee's doctor blade that is scraping the dry paper off the cylinder surface. The crinkle (crêping) is controlled by the strength of the adhesive, geometry of the doctor blade, speed difference between the Yankee and final section of the paper machine and paper pulp characteristics (Paulapuro, 2000).

Generally, LC has been burned for energy production in the world. However, there is little to no information on the application of this resource for tissue paper production. The objective of this study was to evaluate LC for tissue paper production in the mixture with wood fibers.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Materials
2.1. Materijali

This study was performed at the Kahramanmaras Sutcu Imam University Faculty of Forestry, Pulp, and Paper Production Laboratory. LC was taken from Pakmil Oil and Cotton Industry Enterprises Inc., in Adana-Turkey and its fiber length and viscosity values are 2.95-3.00 mm and 1300-1350 cp, respectively. The bleached wood pulps, containing 70 % of short fibers (hardwood) and 30 % of long fibers (softwood), were supplied from Kombassan Paper Mill. Chemicals were supplied by Merck (Darmstadt, Germany). Raw material was prepared and physical and optical properties of tissue paper were determined according to the relevant standard methods.

2.2 Preparation of LC pulps
2.2. Priprema LC pulpe

Firstly, LCs was cleaned from rough and non-fibrous contamination. Then, it was kept into cold water

(24 h) and hot water (4 h) in order to remove impurities and oils. Alkali extraction removed a large part of the hemicellulose from linter fibers and decreased the content of the charged groups (Lund *et al.,* 2012). Before bleaching of linter cellulose, alkali extraction was applied at three different rates 8 %, 10 %, and 12 %. After alkali extraction, LC was beaten in a hollander beater to 40±5 °SR freeness, according to TAPPI standard T200 sp-96. All LC pulps were screened on a 0.15 mm slotted screen to remove non-fibrous matters. Test papers were produced from these LC pulps in order to determine optimum alkali extraction condition. According to the results, 10 % alkali extraction gave the best result in terms of the yield and optical properties. These pulps were subjected to NaClO bleaching processes.

2.3 Bleaching of LC pulps
2.3. Izbjeljivanje LC pulpe

LC pulps were bleached with NaClO in 9 different conditions given in Table 1. Time and temperature were kept constant, while NaClO rate and consistency were changed during bleaching processes.

After preparing the bleaching liquors given in Table 1, the pulps were placed in polyethylene bags. Then, the mixtures were put in a water bath, where the temperature was controlled by a thermostat. Fig. 1 presents the stages of the bleaching process. At the end of bleaching, the pulps were pressed up to 20-25 % dryness. The values of whiteness, brightness, and yellowness of the pulps were measured by a color-measuring instrument Datacolor Elrepho in accordance with applicable standards.

After bleaching, the LC pulps were taken out from the water bath and washed with hot and cold water until chemicals were completely removed from the pulp.

Table 1 NaClO bleaching conditions of Linter Cellulose
Tablica 1. Uvjeti izbjeljivanja linter celuloze uz pomoć NaClO

Bleaching Number *Redni broj izbjeljivanja*	**NaClO Charge** *Udjel NaClO* %	**Consistency** *Konzistencija* %	**Temperature** *Temperatura* °C	**Time** *Vrijeme* min
1	8	8	60	60
2	8	12	60	60
3	8	16	60	60
1	12	8	60	60
2	12	12	60	60
3	12	16	60	60
1	16	8	60	60
2	16	12	60	60
3	16	16	60	60

2.4 Tissue paper production with bleached linter cellulose and wood fiber
2.4. Proizvodnja upijajućeg papira od izbijeljene linter celuloze i drvnih vlakanaca

Test papers were produced from bleached LC and the optical properties of these papers were analyzed. Bleached LC pulps with 12 % NaClO at 8 % consistency gave the best results in the optical properties among 9 different bleaching levels. The physical properties of bleached LC were not suitable for tissue paper production. For this reason, LC and wood fibers (WF) were mixed at certain rates to produce tissue paper given in Table 2. As shown in the table, tissue paper was made using 11 different mixture rates. Ten handsheets per tested sequence, with the grammage of 30±5 ($g \cdot m^{-2}$), were prepared using a British Sheet Former according to TAPPI T 205 sp-02.

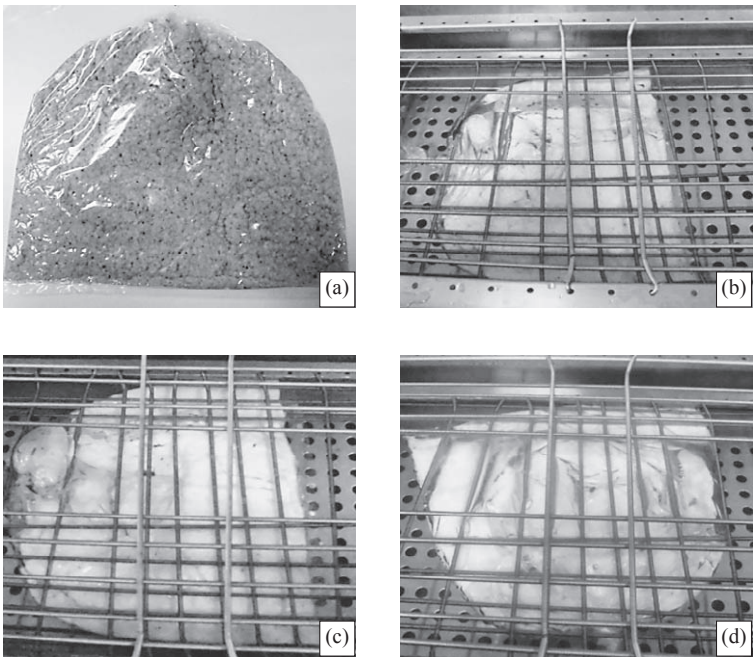

Figure 1 Bleaching stages: before (a), after 15 min (b), after 30 min (c), after 60 min (d)
Slika 1. Prikaz faza izbjeljivanja: a) prije izbjeljivanja, b) 15 minuta nakon izbjeljivanja, c) 30 minuta nakon izbjeljivanja, d) 60 minuta nakon izbjeljivanja

Table 2 Mixing rates of LC and wood fiber
Tablica 2. Omjeri miješanja linter celuloze i drvnih vlakanaca

Mixture No / *Broj smjese*	**Linter cellulose** / *Linter celuloza* %	**Wood fiber** / *Drvna vlakanca* %
1	0	100
2	10	90
3	20	80
4	30	70
5	40	60
6	50	50
7	60	40
8	70	30
9	80	20
10	90	10
11	100	0

Table 3 Tests applied on tissue paper and applicable standards
Tablica 3. Provedeno ispitivanje upijajućeg papira i primijenjeni standardi

Physical and optical properties *Fizikalna i optička svojstva*	**Napkin** *Ubrus*	**Paper towel** *Papirnati ručnik*	**Toilet paper** *Toaletni papir*
Grammages / *gramaža*, g·m^{-2}	ISO 12625	ISO 12625	ISO 12625
Moisture content / *sadržaj vode*, %	ISO 12625	ISO 12625	ISO 12625
Whiteness / *bjelina* (ISO)	ISO 11476	ISO 11476	ISO 11476
Brightness / *sjajnost* (ISO)	ISO 2470	ISO 2470	ISO 2470
Yellowness / *žutilo* (ISO)	ISO 5631	ISO 5631	ISO 5631
Thickness / *debljina*, µm	ISO 12625	ISO 12625	ISO 12625
Bulkiness / *obujmnost*, cm^{-3}·g	ISO 287	ISO 2470	ISO 12625
Density / *gustoća*, g·cm^{-3}	ISO 287	ISO 2470	ISO 12625
Breaking length / *duljina lomljenja*, m	ISO 1924/2	ISO 1924/2	ISO 12625
Water absorption time / *vrijeme upijanja vode*, s	ISO 12625	ISO 12625	ISO 12625
Water retention value / *vrijednost zadržavanja vode*, g·m^{-2}	ISO 12625	ISO 12625	ISO 12625

Wood fibers used in this study consist of hardwood (70 %) and softwood (30 %) fibers. They were also beaten in a Hollander beater to 40±5 °SR before being mixed with bleached LC pulps.

2.5 Determining physical and optical properties of tissue paper
2.5. Određivanje fizikalnih i optičkih svojstava upijajućeg papira

The test papers were conditioned at 23±1 °C and 65 % relative humidity in the conditioning room in accordance with TAPPI T 402 om-88 standard. Then, they were prepared for physical and optical tests. Tests were performed according to the standards given in Table 3.

Regression analysis was performed to determine the effect of LC on physical and optical test results of the paper obtained from WF and LC mixtures, and R^2 values were calculated and plotted in the figures bellow.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

The optical properties and yields of LC pulps subjected to alkali extraction are presented in Table 4.

According to Table 4, as the alkali charge increased, the optical properties of the LC pulps increased at first, then decreased. Alkali extraction removes a large amount of hemicellulose and causes the yield loss. For this reason, the yields decreased with increasing lkali charge. As 10 % NaOH charge resulted in the best optical properties, these pulps were subjected to NaClO bleaching process.

Table 4 Optical properties and yields of LC pulps after alkali extraction
Tablica 4. Optička svojstva i prinos pulpe LC-a nakon ekstrakcije lužinom

NaOH charge / *Udjel NaOH*, %	8 %	10 %	12 %
Whiteness / *Bjelina* (ISO)	37.09	41.10	40.22
Brightness / *Sjajnost* (ISO)	29.63	33.66	33.37
Yellowness / *Žutilo* (ISO)	29.25	25.85	27.35
Yield / *Prinos*, %	93.81	89.99	88.62

Bleached LC handsheets, with the grammage of 70±5 (g m^{-2}), were prepared to determine optical properties in order to better understand the bleaching efficiency. The yields and optical properties of LC pulps bleached with NaClO are given in Table 5.

As can be seen in Table 5, the best optical properties were obtained from LC pulps bleached with 12 % NaClO. In the same table, pulps bleached at 8 % consistency resulted in the best optical properties. According to these results, pulps bleached with 12 % NaClO at 8 % consistency were used for tissue paper produc-

Table 5 Optical properties and yields of LC pulps bleached with NaClO
Tablica 5. Optička svojstva i prinos pulpe LC-a izbijeljene uz pomoć NaClO

NaClO Charge *Udjel NaClO*, %	8 %			12 %			16 %		
Pulp properties *Svojstva pulpe*	**Consistency, %** *Konzistentnost, %*			**Consistency, %** *Konzistentnost, %*			**Consistency, %** *Konzistentnost, %*		
	8%	12%	16%	8%	12%	16%	8%	12%	16%
pH	10.4	10.2	10.1	10.5	10.3	10.2	10.6	10.8	11.0
Viscosity / *viskoznost*, $cm^2 \cdot gr^{-1}$	1013	1086	1105	983	997	1001	956	977	981
Fiber length / *duljina vlakanaca*, mm	2.60	2.63	2.66	2.48	2.48	2.50	2.32	2.33	2.40
Whiteness / *bjelina* (ISO)	76.87	75.91	76.88	76.57	76.25	76.26	75.97	73.06	73.13
Brightness / *sjajnost* (ISO)	71.38	70.67	71.47	73.47	72.34	72.22	72.23	68.87	68.78
Yellowness / *žutilo* (ISO)	9.34	9.02	9.20	5.54	6.64	6.92	6.34	7.40	7.79
Yield / *prinos*, %	85.40	91.60	88.75	85.80	82.80	83.64	81.96	79.96	82.88

Table 6 Optical properties of tissue paper obtained with mixed pulps
Tablica 6. Optička svojstva upijajućeg papira proizvedenoga od različitih smjesa pulpe

Mixture rates, % *Omjer smjese,* %	**Whiteness (ISO)** *Bjelina (ISO)*	**Brightness (ISO)** *Sjajnost (ISO)*	**Yellowness (ISO)** *Žutilo (ISO)*
100 WF	70.99	69.07	3.60
90 WF+10 LC	70.21	68.18	3.85
80 WF+20 LC	69.76	67.58	4.15
70 WF+30 LC	69.24	67.00	4.30
60 WF+40 LC	69.21	66.94	4.32
50 WF+50 LC	68.78	66.33	4.77
40 WF+60 LC	68.73	66.19	4.84
30 WF+70 LC	68.38	65.68	5.26
20 WF+80 LC	68.19	65.39	5.46
10 WF+90 LC	67.59	64.67	5.74
100 LC	67.54	64.39	6.20

tion with WF. As NaClO charge increases, the bleaching yield decreases due to degradation of other carbohydrates, such as cellulose and hemicellulose. The oxidation of cellulose with hypochlorite is non-specific and degradation proceeds most rapidly near a neutral pH (Lewin and Epstein, 1962).

Mixed LC and WF handsheets, with the grammage of 30±5 ($g \cdot m^{-2}$), were produced and optical properties of these handsheets are presented in Table 6.

In Table 6, it can be clearly seen that as LC ratio increased, the whiteness and brightness values decreased and the yellowness value increased. The optical properties of the LC pulps bleached by the above methods were lower than those of WF. Therefore, the brightness and whiteness values of the mixed pulp decreased.

The physical properties of the paper manufactured with mixed pulps are given in Table 7. This table indicates that increased LC ratio in the mixture significantly reduced the breaking length of the paper. This may be due to the fact that WF has longer fibers than LC as mentioned in the introduction. Several researchers found that the fiber length directly affects the physical properties of the paper. This finding led to the conclusion that long fibers are stronger than short fibers (Diaz *et al*. 2007; Beg and Pickering, 2008; Thumn and Dickson, 2013; Tutus and Cicekler, 2016).

In European and international trade, both water absorption time and water retention value represent important parameters for comparison of the tissue product (Anon., 2011; Tutus *et al.,* 2016). When compared with WF, the water retention value increased

Table 7 Physical properties of tissue paper obtained with mixed pulps
Tablica 7. Fizikalna svojstva upijajućeg papira proizvedenoga od različitih smjesa pulpe

Mixture rates, % *Omjer smjese,* %	**Thickness** *Debljina*, µm	**Density** *Gustoća*, $g \cdot cm^{-3}$	**Bulkiness** *Obujmnost* $cm^{-3} \cdot g$	**Breaking length** *Duljina lomljenja* m	**Water absorption time** *Vrijeme upijanja vode* s	**Water retention value** *Vrijednost zadržavanja vode* $g \cdot m^{-2}$
100 WF	103	0.30	3.34	1319.94	2.62	267.50
90 WF+10 LC	104	0.30	3.31	1159.34	2.21	271.80
80 WF+20 LC	106	0.28	3.52	1030.99	1.99	279.70
70 WF+30 LC	108	0.29	3.40	919.23	1.74	288.20
60 WF+40 LC	112	0.29	3.48	750.52	1.67	293.60
50 WF+50 LC	117	0.26	3.90	803.30	1.43	295.30
40 WF+60 LC	124	0.25	3.94	753.18	1.26	301.20
30 WF+70 LC	128	0.25	4.01	377.67	1.07	307.00
20 WF+80 LC	131	0.25	4.08	352.61	0.98	312.50
10 WF+90 LC	131	0.25	3.92	242.20	0.85	316.00
100 LC	135	0.25	3.93	218.68	0.76	320.40

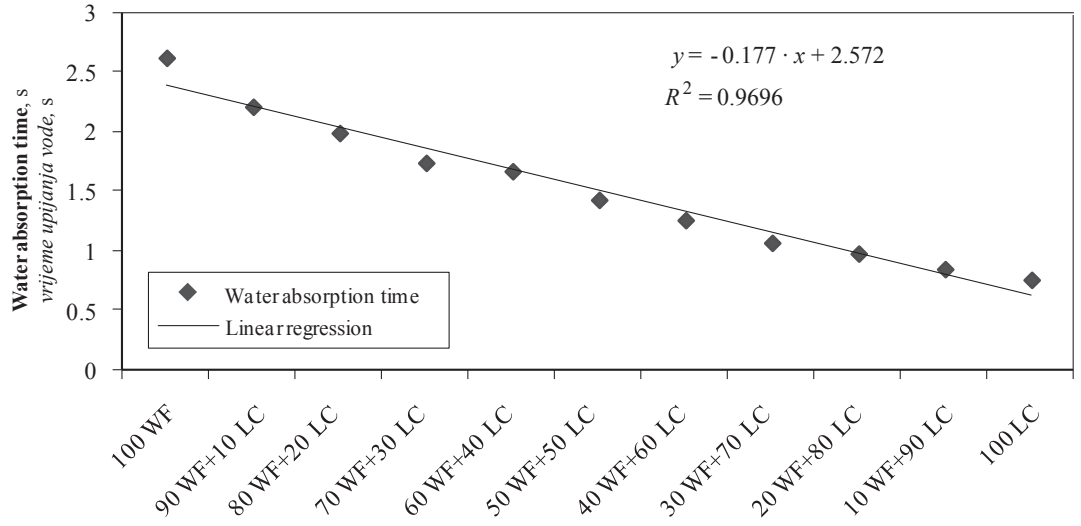

Figure 2 Water absorption times of tissue papers
Slika 2. Vrijeme upijanja vode upijajućih papira proizvedenih od različitih smjesa pulpe

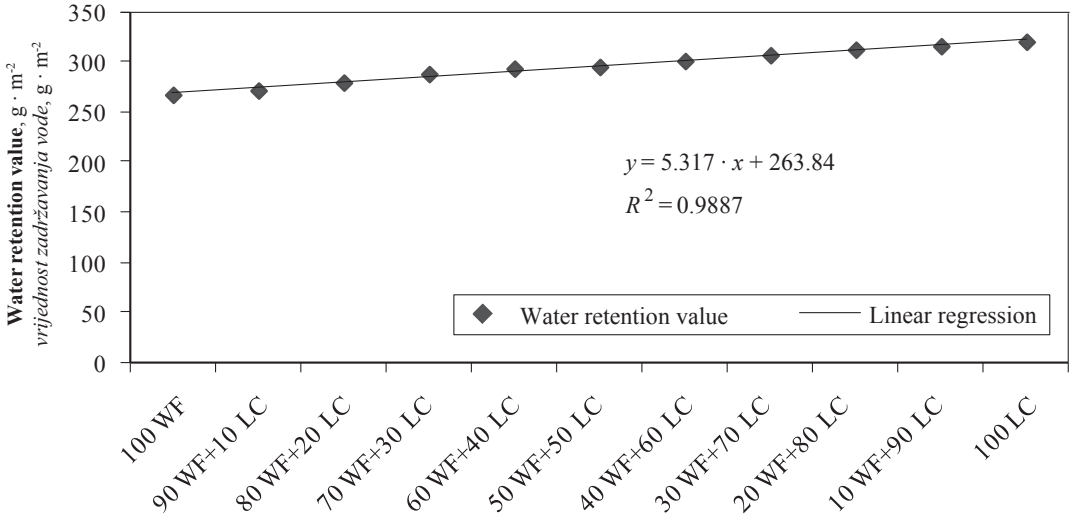

Figure 3 Water retention values of tissue papers
Slika 3. Vrijednosti zadržavanja vode upijajućih papira proizvedenih od različitih smjesa pulpe

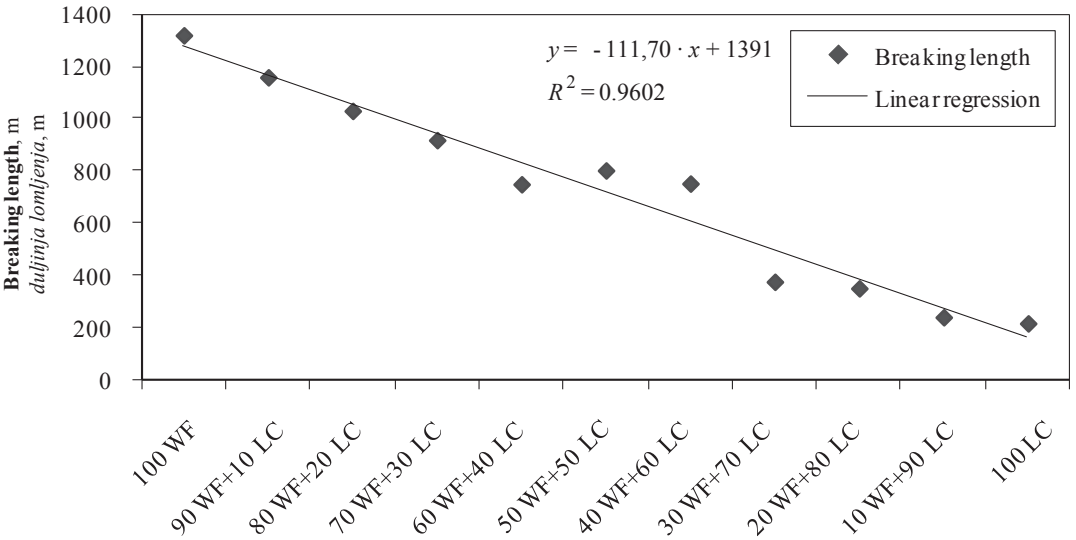

Figure 4 Breaking length values of tissue papers
Slika 4. Duljina lomljenja upijajućih papira proizvedenih od različitih smjesa pulpe

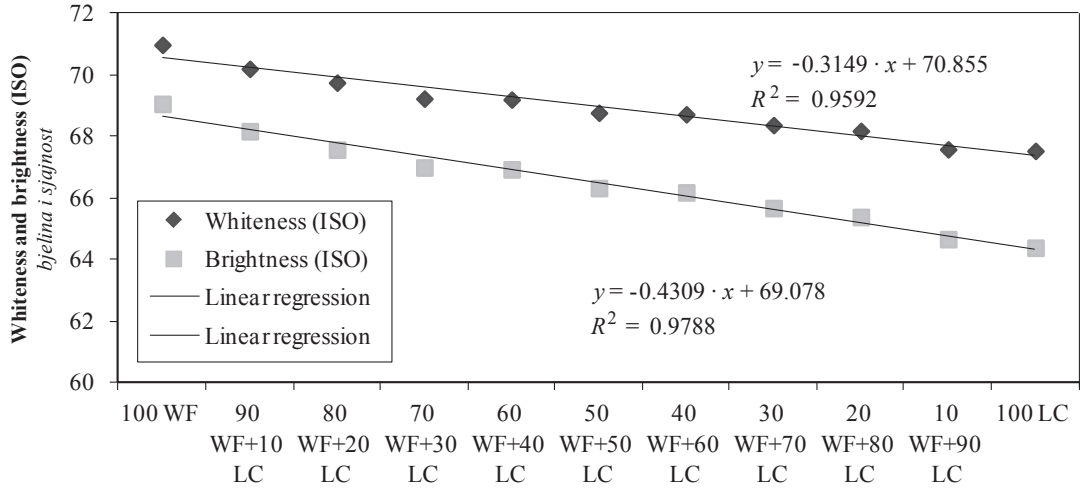

Figure 5 Whiteness and brightness values of tissue papers
Slika 5. Bjelina i sjajnost upijajućih papira proizvedenih od različitih smjesa pulpe

about 120 % and the water absorption time of the tissue paper decreased about 344 % with increasing LC pulp ratio (Table 7). These values have an important role in determining the quality of the tissue paper. On the contrary, the breaking length of the tissue paper reduced with increasing LC pulp ratio.

Fig. 2, 3, 4, and 5 present water absorption time, water retention value, breaking length, whiteness and brightness values of the tissue paper in order to determine the relationship between LC ratios.

Linear correlations with regression coefficients R^2 = 0.97, 0.99, 0.96, and 0.96 were found for water absorption time, water retention value, breaking length, whiteness and brightness, respectively. It can be obviously seen that there is strong correlation between LC ratios and these values.

4 CONCLUSION
4. ZAKLJUČAK

1. It was determined that the optimal bleaching conditions for LC pulps were 12 % NaClO at 8 % consistency. Using bleached LC pulps, these conditions are suitable for tissue papermaking. These pulps can be used mixed with bleached wood pulps in tissue paper production.

2. LC pulps bleached with NaClO have lower optical properties than bleached WF. The optical properties can be further improved, but the bleaching was performed in mild conditions due to loss yield and degradation of other carbohydrates. On the other hand, some important properties for tissue paper, such as water absorption time and water retention value, were better than those of WF.

3. Some physical and optical properties showed a strong logarithmical correlation with LC pulps ratio. The breaking length, whiteness, brightness and water absorption time decreased with increasing LC pulp ratio, while on the contrary, the water retention values increased.

4. When examining the optical and physical properties of the tissue paper produced with LC and WF mixture, it was determined that tissue paper can be manufactured with 40 % LC and 60 % WF mixture.

5. Evaluation of linter could increase the availability of fibers in countries such as Turkey, where wood resources are limited. The use of linter cellulose in the paper production would be a great contribution to the economy.

6. Turkey has an important potential in the production of linter cellulose. The assessment of this potential will have positive effects on both Turkey's development and its economy.

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Surface Wettability of Wood Species from Tropical and Temperate Zones by Polar and Dispersive Liquids

Kvašenje površine drva iz tropskih i umjerenih zona polarnim i disperzivnim tekućinama

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ABSTRACT • *Wood species from Africa, South America and Europe, primarily used as a flooring and construction material, were acquired for the study. Wettability was determined using the measurement of the contact angle of wood with the reference liquids (water, diiodomethane) based on the sessile drop method. Surface free energy of wood on tangential sections within first 60 s after applying a drop was determined. Among the species from the tropical zone, the greatest hydrophobicity, similar to oak wood, was characteristic for courbaril wood. After 60 s, the value of the surface free energy for the heartwood of the studied species was between 60 and 70 mJ·m^{-2}, while for the sapwood of pine and birch, it was about 80 mJ·m^{-2}. The biggest changes in the work of adhesion, within 60 s after the application of a drop of water on the surface of the wood, was stated for pine sapwood, and the smallest one for tauari and courbaril wood.*

Keywords: *contact angle, diiodomethane, surface free energy, water, wettability*

SAŽETAK • *Istraživanje je provedeno na vrstama drva rasprostranjenima u Africi, Južnoj Americi i Europi, ponajprije na onima koje se upotrebljavaju kao materijal za podove i za gradnju. Kvašenje drva određeno je mjerenjem kontaktnog kuta drva s referentnim tekućinama (vodom, dijodometanom) postupkom kapanja. Utvrđena je površinska slobodna energija na tangencijalnom presjeku drva unutar prvih 60 s nakon nanošenja kapi. Među vrstama drva iz tropske zone najveću je hidrofobnost, sličnu onoj koju ima hrastovo drvo, pokazalo drvo jatobe. Vrijednost slobodne površinske energije za srževinu ispitivanih vrsta drva nakon 60 s bila je između 60 i 70 mJ·m^{-2}, dok je za borovinu i brezovinu bila oko 80 mJ·m^{-2}. Najveće promjene zbog djelovanja adhezije unutar 60 s od nanošenja kapljice vode na površinu drva zabilježene su za borovinu, a najmanje za drvo brazilskog hrasta i drvo jatobe.*

Ključne riječi: *kontaktni kut, dijodometan, slobodna površinska energija, voda, kvašenje*

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1 INTRODUCTION
1. UVOD

Wood, as an organic material, is built of carbohydrates (ca. 70 %), i.e. cellulose and hemicelluloses, which are compounds with a relatively large quantity of polar hydroxyl groups -OH in their structure (Požgaj *et al*., 1993; Gindl *et al*., 2004). For that reason, wood shows high affinity for water. This property of wood is described by a number of parameters including adsorption, desorption, swelling, water absorption, wettability expressed by the measurement of the contact angle (Mantanis *et al*., 1994; Wolkenhauer *et al*., 2009; Buyuksari *et al*., 2011; Dündar *et al*., 2012; Hill *et al*., 2012).

An important variable that allows the determination of the ability of wood to interact with liquids is the measurement of the wettability expressed through the contact angles for different types of reference liquids (De Meijer *et al.*, 2000; Gindl *et al*., 2001; Wolkenhauer *et al*., 2009). The difficulties associated with it result from the fact that wood, as porous material, varies in terms of morphological and chemical structure, having different properties within and between species. Studies carried out so far (Zhang *et al*., 1997; Kúdela, 2014; Rolleri *et al*., 2016) show that the wettability of wood shows a significant differentiation depending on the chemical composition, roughness, polarity of the wetting liquid, processing method and air parameters. Wood wettability is also significantly affected by thermal treatment (Gérardin *et al*., 2007; Kocaefe *et al*., 2008) or fungicide protection, among others (Fuczek *et al*., 2010).

Liptáková and Kúdela (1994) and Kúdela (2014) determined the contact angle after the separation of a drop of liquid from the needle (t = 0 s) and in the equilibrium state at the phase boundary wood-liquid. Huang *et al.* (2012) varied the time of determining the contact angle of jack pine wood (*Pinus banksiana* Lamb.) depending on the type of the reference liquid. Authors studied the contact angle of wood with water for 50 s, with ethylene glycol for 10 s and with formamide for 1 s, while maintaining the appropriate intervals between the measurements. Santoni and Pizzo (2011) studied the contact angle of Mediterranean wood species with water at intervals of 0.3 s for 150 s. Kocaefe *et al*. (2008) marked the contact angle of white ash (*Fraxinus americana*) and soft maple (*Acer rubrum*) before and after heat treatment within 30 s. Due to the dynamics of changes, the more rational solution is to define the contact angle of wood with water for a specified period of time. This makes it possible to determine more complete wettability characteristics of wood. Wettability of wood is described by a number of parameters, of which the most studied and analysed are contact angle and surface free energy. Only a few authors examine wetting energy, spreading coefficient of reference liquid, work of adhesion for the phase boundary wood-liquid, surface tension of the liquid (Zhang *et al*., 1997; Kocaefe *et al*., 2008; Wolkenhauer *et al*., 2009; Gonzalez de Cademartori *et al*., 2015).

The aim of this study was to determine the wettability of wood species from Africa, South America and Europe used mainly as flooring and construction materials. Important aspect of the study was to determine the dynamics of changes in parameters describing the phenomenon of wood wettability.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

Wood species selected for the study are used to manufacture flooring materials and construction elements according to EN 1912:2012+AC (2013). Table 1 summarizes the basic information about the studied species of wood. Surfaces of wood samples were finished by planing. After conditioning the samples to an air-dry condition in accordance with the recommendations of ISO 13061-1 (2014), wood density was determined using a stereometric method in accordance with the requirements of ISO 13061-2 (2014). Wood moisture content was determined according to ISO 13061-1 (2014).

Contact angles of wood with reference liquids were studied in a goniometer Phoenix 300 of Surface

Table 1 Investigated species of wood
Tablica 1. Istraživane vrste drva

Latin name *Latinski naziv*	**Trade name of wood (and code) according to EN-13556 (2003)** *Trgovački naziv (i kôd) prema EN-13556 (2003)*	**Occurrence** *Podrijetlo vrste*	**Structure of wood** *Građa drva*
Afzelia africana Smith ex. Pers.	afzelia (AFXX) / *afzelija*	Africa / *Afrika*	deciduous *listača* diffuse-porous *difuzno porozno drvo*
Betula pendula Roth	European birch (BTXX) *obična breza*	Europe / *Europa*	
Couratati multiflora (J.E. Smith) Eyma	tauari (CIXX) / *brazilski hrast*	South America *Južna Amerika*	
Hymenea courbaril L.	courbaril (HYCB) / *jatoba*	South America *Južna Amerika*	
Khaya ivorensis A. Chev.	African mahogany (KHXX) *afrički mahagonij*	Africa / *Afrika*	
Pinus sylvestris L.	Scots pine (PNSY) / *obični bor*	Europe / *Europa*	coniferous / *četinjača* Sapwood / *bjeljika*
Quercus robur L.	European oak (QCXE) *hrast lužnjak*	Europe / *Europa*	deciduous / *listača* ring-porous *prstenasto porozno drvo*

Table 2 Surface tension components of reference liquids (Gindl *et al.*, 2001)
Tablica 2. Komponente površinske napetosti referentnih tekućina (Gindl *et al*., 2001.)

Liquid *Tekućina*	**Property** / *Svojstvo*		
	Surface tension / *Površinska napetost* mJ·m^{-2}	Dispersive / *Disperzivnost* mJ·m^{-2}	Polar / *Polarnost* mJ·m^{-2}
water (H_2O) / *voda*	72.80	21.90	51.00
diiodomethane (CH_2I_2) *dijodometan*	50.80	50.80	0.00

Electro Optics company (Suwon City, Korea), based on a "sessile" drop method. The volume of the drop applied to the surface of wood (tangential section) was 3 µl. Two reference liquids were used for the study: water and diiodomethane (Table 2).

Based on the conducted studies, work of adhesion for the phase boundary wood-water was determined. Surface free energy of wood species selected for the study was determined using the Owens-Wendt method (Owens and Wendt, 1969) based on Young's equation:

$$\sigma_S = \gamma_{SL} + \sigma_L \cdot \cos\theta \quad (1)$$

where: σ_S is the total surface free energy of the solid (mJ·m^{-2}), γ_{SL} is the interfacial tension between solid and liquid, σ_L is the surface tension of the liquid, and θ is the contact angle (°).

The total surface energy (σ_S) is divided into a dispersive part (σ^D) and a polar part (σ^P) according to the equation:

$$\sigma_S = \sigma^D + \sigma^P \quad (2)$$

The interfacial tension between solid and liquid is described by the equation:

$$\gamma_{SL} = \sigma_S + \sigma_L - 2 \cdot \left(\sqrt{\sigma_S^D \cdot \sigma_L^D} + \sqrt{\sigma_S^P \cdot \sigma_L^P} \right) \quad (3)$$

where: σ_S^D and σ_L^D are dispersive and polar parts of liquid, respectively; σ_S^D and σ_S^P are dispersive and polar parts of solid, respectively.

The work of adhesion (W_{SL}) is determined by the equation:

$$W_{SL} = \sigma_S + \sigma_L - \gamma_{SL} \quad (4)$$

In order to obtain an optimal adhesion, the work of adhesion must achieve the maximum value. This occurs when the interfacial tension (γ_{SL}) is 0. Good adhesion is obtained if the dispersive and polar parts of the solid and liquid phases are in the right ratio, because only dispersive - dispersive and polar - polar interactions occur (Wolkenhauer *et al*., 2009). Therefore, the work of adhesion can be divided into a dispersive and a polar part according to the equation:

$$W_{SL} = W_{SL}^D + W_{SL}^P \quad (5)$$

where:

$$W_{SL}^D = 2\sqrt{\sigma_L^D \cdot \sigma_S^D} \quad (6)$$

$$W_{SL}^P = 2\sqrt{\sigma_L^P \cdot \sigma_S^P} \quad (7)$$

Values of the contact angle were determined 1, 2, 3, 10, 20, 30, 40, 50 and 60 s after the application of a liquid drop on the surface of the wood and by extrapolating within 0 s. Surface free energy of investigated wood species and components of the surface free energy - polar, dispersive, work of adhesion were determined after 60 s. Studies were performed after 24 h from the sample preparation. Statistical analysis was performed using STATISTICA version-12 software of StatSoft, Inc. Statistical analysis of the test results was carried out at the significance level of 0.050. For other studied parameters, trend lines were determined, and the parameters for the equation of the curve (y) and the coefficients of determination R^2 were provided.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

According to ISO 13061-2 (2014), the density of wood from the tropical zone was as follows: African mahogany 562 kg·m^{-3} (±24), afzelia 717 kg·m^{-3} (±21), courbaril 847 kg·m^{-3} (±5), tauari 844 kg·m^{-3} (±16), and the density of wood from the temperate zone was as follows: European birch 635 kg·m^{-3} (±21), Scots pine (sapwood) 495 kg·m^{-3} (±9), European oak (heartwood) 758 kg·m^{-3} (±84). The wood moisture content ranged from 6.53 % (±0.12) to 6.82 % (±0.25) in case of all tested wood species. The density of the tested wood species was typical, showing at the same time the typical variability of the property. For example, according to the study of Sekhar and Negi (1960), carried out on 250 logs from 50 different wood species, density variation coefficient within a single species of wood in an air-dry condition averaged to about 6 %. In the standard ISO 3129 (1979), an average value of 10 % was assumed for a typical variation coefficient of wood density.

A statistically significant correlation was established between density and contact angle for wood-water relations and between density and contact angle for wood-diiodomethane relations ($p = 0.00001$). However, if we tried to describe these relationships by the linear regression model, the values of the coefficient of determination would be low. The R^2 value for the relationship between density and contact angle for wood-water was 0.517, and for the relationship between density and contact angle for wood-diiodomethane, it was 0.394 (Figure 1).

The difference between the wettability of softwood (Scots pine) and hardwood (African mahogany, afzelia, birch, courbaril, European oak, tauari) species was demonstrated. This difference was statistically significant (Table 3). The variability of contact angle is most likely the result of different anatomical structure and chemical composition (non-structural compounds

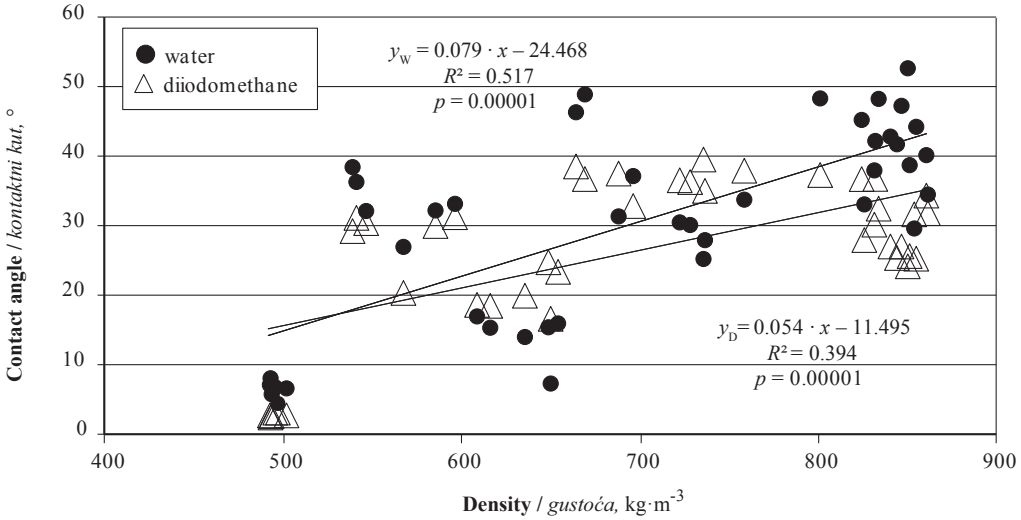

Figure 1 Relationship between density and contact angle determined 60 s after application of a liquid drop on wood surface
Slika 1. Odnos između gustoće i kontaktnoga kuta određen 60 s nakon nanošenja kapi tekućine na površinu drva

Table 3 Results of statistical analysis (t - test) for contact angle and surface free energy determined 60 s after application of a liquid drop on wood surface
Tablica 3. Rezultati statističke analize (*t*-test) za kontaktni kut i slobodnu površinsku energiju utvrđeni 60 s nakon nanošenja kapi tekućine na površinu drva

Wood species *Vrsta drva*	**Contact angle** / *Kontaktni kut*				**Surface free energy** *Slobodna površinska energija*	
	wood - water *Drvo - voda*		wood - diiodomethane *Drvo - dijodometan*			
	Statistical measures					
	t	*p*	*t*	*p*	*t*	*p*
softwood vs. hardwood *drvo četinjača vs. drvo listača*	-4.384760	0.000097	-10.099300	0.000000	3.634960	0.008343
Wood area / *dio drva*						
sapwood vs. heartwood *bjeljika vs. srževina*	-11.825300	0.000000	-9.151830	0.000000	7.778898	0.000109

content), different surface structure and thus different roughness of particular wood species (Liptáková *et al*., 1995; Wolkenhauer *et al*., 2009). The value of the contact angle depends primarily on whether it takes place through the heartwood (African mahogany, afzelia, courbaril, European oak, tauari) or sapwood (birch and pine) (Table 3). This was due to the fact that sapwood has an open structure for conducting water. In the cell walls of sapwood, the pits are open. Furthermore, the increased wettability of this area is determined by the presence of living unlignified parenchyma cells of wood and wood rays. The results obtained for pine sapwood and heartwood of hardwood species were confirmed in previous research. Santoni and Pizzo (2011),

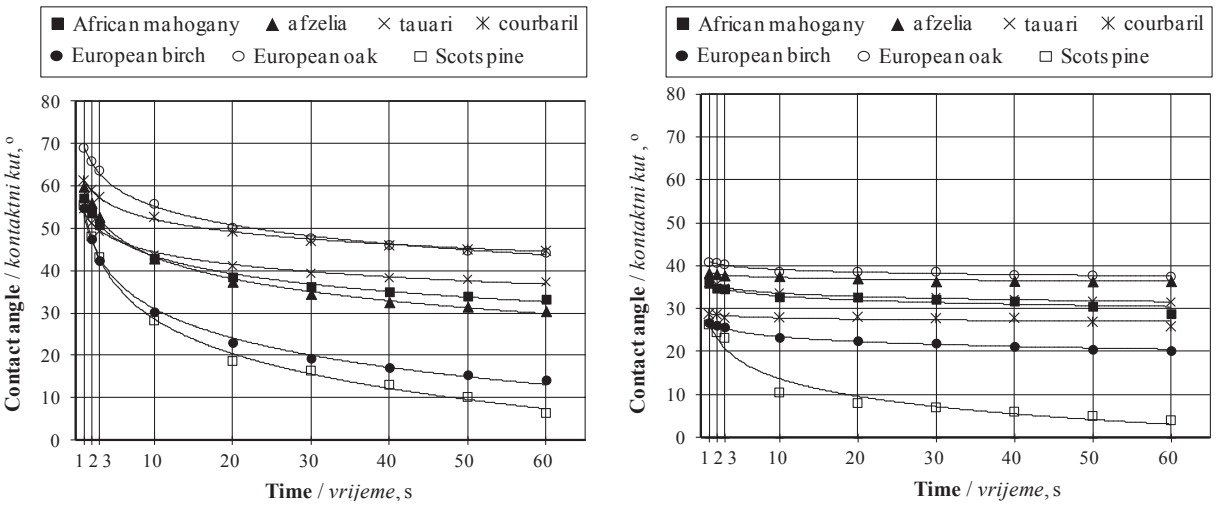

Figure 2 Contact angles at phase boundary wood-water (a), wood-diiodomethane (b)
Slika 2. Kontaktni kutovi na granici drva i vode (a), drva i dijodometana (b)

Table 4 Parameters of curve equation $y = a \cdot \ln(t) + (b)$ describing the changes of contact angle for phase boundary wood-water, wood-diiodomethane (a - direction coefficient, b - free term, r^2 - coefficient of determination, t - time)
Tablica 4. Parametri jednadžbe krivulje $y = a \cdot \ln(t) + (b)$ koja opisuje promjene kontaktnog kuta na granici drva i vode te drva i dijodometana (a – koeficijent smjera, b – odsječak na osi y, r^2 – koeficijent determinacije, t – vrijeme)

Wood species *Vrsta drva*	**Parameters of curve equation $y = a \cdot \ln(t) + b$** *Parametri jednadžbe krivulje $y = a \cdot \ln(t) + b$*					
	Contact angle wood-water *Kontaktni kut drvo - voda*			Contact angle wood-diiodomethane *Kontaktni kut drvo - dijodometan*		
	a	*b*	R^2	*a*	*b*	R^2
African mahogany / *afrički mahagonij*	-6.04	57.34	0.997	-1.36	36.05	0.883
Afzelia / *afzelija*	-7.48	60.48	0.998	-0.50	38.40	0.944
Tauari / *brazilski hrast*	-4.24	54.16	0.996	-1.10	36.13	0.990
Courbaril / *jatoba*	-4.24	61.86	0.997	-0.45	28.86	0.590
European birch / *obična breza*	-10.01	54.08	0.997	-1.62	27.17	0.987
European oak / *hrast lužnjak*	-6.40	69.93	0.996	-0.84	41.02	0.955
Scots pine / *obični bor*	-11.84	55.86	0.998	-5.93	27.34	0.966

who examined the Mediterranean species of wood, stated that in general softwoods showed higher contact angles than hardwoods due to different anatomy and presence of resins and terpenes in addition to fatty acids and phenolic components, also presents in hardwoods.

The surface of pine sapwood was the most hydrophilic among all studied wood species. Comparable changes of the contact angle of wood with water were reported for birch wood (Figure 2a). Within the conducted studies, the contact angle of pine and birch, 3 s after the application of a drop of water on the wood surface, was 46.25° (±6.22) and 42.44° (±3.58), respectively, and after 60 s, 6.45° (±1.83) and 14.29° (±3.91), respectively. The presented data show that, over time, the hydrophobicity of pine sapwood decreased significantly and was lower than in case of birch wood. Pine sapwood was characterized by considerably lower density, i.e. higher porosity (67 %) than other wood species under research (from 44 to 62 %). The process of water and diiodomethane penetration into the porous structure of pine sapwood was quicker than into other wood species tested. This resulted in the biggest changes in contact angle in time. Bekhta *et al*. (2015) stated that pine wood was the most hydrophobic among the studied wood species (pine, alder, beech, birch). The authors state that the contact angle of the pine and birch wood, 5 s after applying a drop of water on the wood surface, was 54.19° and 45.34°, respectively. These differences may be due to, among others, the type of the studied wood (pine sapwood or heartwood) and the resin content in the wood, which is a component significantly affecting wood hydrophobicity (Fengel and Wegener, 1989). Kúdela (2014) stated that the contact angle for the phase boundary beech-water at the beginning of the wetting process (t = 0 s) was 63.9°, while the contact angle at the time necessary to reach the equilibrium state at the phase boundary wood-water (at the moment when the drop started to contract) was 20.8°.

The surface of oak wood was the most hydrophobic one. The contact angle of oak wood, 60 s after the application of a drop of water on the wood surface, was 44.28° (±5.63). It is worth noting that the contact angle of European oak with the ring-porous structure was higher than the contact angle of tropical species i.e. afzelia, tauari, courbaril with diffuse-porous structure. Among the species from the tropical zone, the greatest hydrophobicity, similar to oak wood, was characteristic for courbaril wood. These interdependencies are mainly due to the fact that, generally, the species from the tropical zone have a much larger diameter of vessels compared to species of the temperate zone (Wagenführ, 2007).

Contact angles with a polar liquid (water) significantly changed over time. The dynamics of changes of the contact angle was significantly greater in the case of wetting wood with water than with diiodomethane (Figure 2 a, b). Contact angles of wood with water were the highest at the time of the drop application (at 0 s time of 70°), and then within 60 s decreased logarithmically (curve equations presented in Table 4). In case of heartwood, the dynamics of changes was lower and the terminal value of the angle (60 s after applying a drop) ranged from 35 to 40°. In case of sapwood, the terminal values of contact angle were only about 10°. In case of a nonpolar liquid (diiodomethane), the angles changed to a lesser extent. The initial values of contact angles of the tested wood species were in the range from about 30° to 40°. The biggest changes of the contact angle were noted for pine sapwood, for which the contact angle with diiodomethane, 60 s after applying a drop, was only about 5° (change at the level of 85 %). In case of European birch and African mahogany, the changes of the contact angle within 60 s were about 20 %. For the remaining species of wood, comparable changes of the contact angle with diiodomethane were observed. Within 60 s after applying a drop of liquid on the surface of the wood, the contact angle decreased by about 10 %. Gérardin *et al*. (2007), who studied the contact wetting angle based on the Wilhelmy method (based on the procedure indicated in Gardner *et al*., 1991; Wålinder and Johansson, 2001; Wålinder and Ström, 2001; Pétrissans *et al*., 2003), obtained the contact angle for water-pine sapwood at 55.4°, and for the diiodomethane-pine sapwood at 27.1°. The studies carried out by the authors, despite the implementation of different testing method for determining the contact angle of wood, confirm the dif-

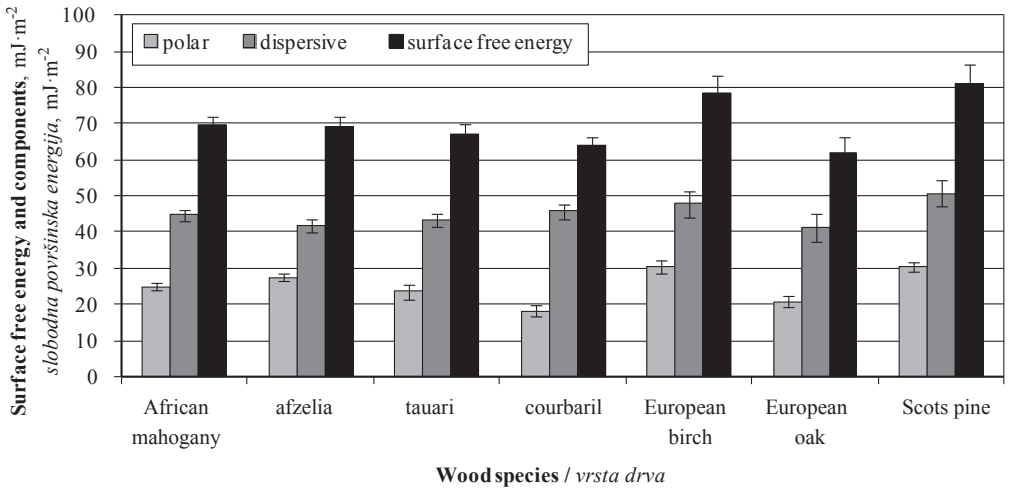

Figure 3 Surface free energy of investigated wood species and components of surface free energy – polar, dispersive
Slika 3. Slobodna površinska energija istraživanih vrsta drva i komponente slobodne površinske energije – polarna i disperzivna

ferences in the wettability of pine wood with polar and dispersive liquids, obtained in this work.

Surface free energy of wood was also dependent on wood species and, above all, on whether it was sapwood or heartwood (Table 3). After 60 s, the value of surface free energy for heartwood of the studied species was in the range of 60 to 70 mJ·m^{-2}, while for pine and birch sapwood, it was about 80 mJ·m^{-2} (Figure 3). The dispersive component was the dominant component of the surface free energy. This is a typical feature characteristic for polymers of which the wood is composed (Mohan *et al*., 2011; Shen *et al*., 1998). According to Li *et al*. (2014), the high value of the dispersive component is the result of high interaction ability of the dispersive part of available carbon-oxygen and carbon-carbon bonds within the wood. On the other hand, the polar component refers to the interaction between hydroxyl groups of wood and functional groups of adhesive by forming the hydrogen bond. The research carried out in the field of surface free energy is confirmed by literature data. Kúdela (2014) stated that the surface free energy of beech wood, determined based on the study of the contact angles of wood wetted with water and α-bromonaphthalene, was 84.7 mJ·m^{-2}. Gérardin *et al*. (2007) stated that the total surface free energy (calculated based on the examination of the contact angle of wood with three reference liquids i.e. water, diiodomethane, formamide) obtained for untreated pine sapwood and beech was relatively close. The authors stated that the surface free energy of pine sapwood and beech was 58.6 mJ·m^{-2} and 54.8 mJ·m^{-2}, respectively.

Statistically significant differences were identified in the work of adhesion for wood-water and wood-diiodomethane phase boundaries (Table 5). Exceptions were African mahogany, tauari and pine wood ($p > 0.05$). The average work of adhesion values for wood-water phase boundaries for tropical zone wood species ranged from 124 to 135 mN·m^{-1} (Figure 4). The work of adhesion value observed for oak wood was similar (125 mN·m^{-1}), whereas the average work of adhesion value for birch and pine wood amounted to 143 and 145 mN·m^{-1}, respectively. Similar dependencies were noted in investigating the work of adhesion for wood-diiodomethane phase boundaries. In this case, the work of adhesion values, observed for oak wood, was likewise comparable to those of the tropical zone wood species. Li *et al*. (2014) stated that low values of the work of adhesion may be attributed to the air trapped in the rough and porous structure of the wood surface, which can decrease the wood-liquid contact area. Investigated wood species from tropical zone have large vessels, with average diameter above 150 μm, but without thyloses (Richter and Dallwitz, 2000). Oak wood has large diameter vessels as well (average diameter 160 μm), but only in earlywood, and they are filled with thyloses (Wagenführ, 2007), which mechanically block the penetration of water.

Investigated hygroscopic properties of wood largely depend on changes due to chemical and mechanical processes occurring in the wood structure in the process of creating heartwood. Mechanical closing of pits, presence of thyloses and over saturation with non-structural compounds affect the reduction of sur-

Table 5 Results of statistical analysis (*t*-test) for work of adhesion determined 60 s after application of a liquid drop on wood surface
Tablica 5. Rezultati statističke analize (*t*-test) za adhezijski rad određen 60 s nakon nanošenja kapi tekućine na površinu drva

Wood species *Vrsta drva*	**Work of adhesion** *Adhezijski rad*	
	Statistical measures *Statističke mjere*	
	t	*p*
African mahogany *afrički mahagonij*	-2.0059	0.072670
Afzelia / *afzelija*	2.9958	0.013439
Tauari / *brazilski hrast*	-2.0194	0.071049
Courbaril / *jatoba*	-7.5945	0.000019
European birch / *obična breza*	2.8456	0.019226
European oak / *hrast lužnjak*	-3.0288	0.012703
Scots pine / *obični bor*	1.9063	0.098288

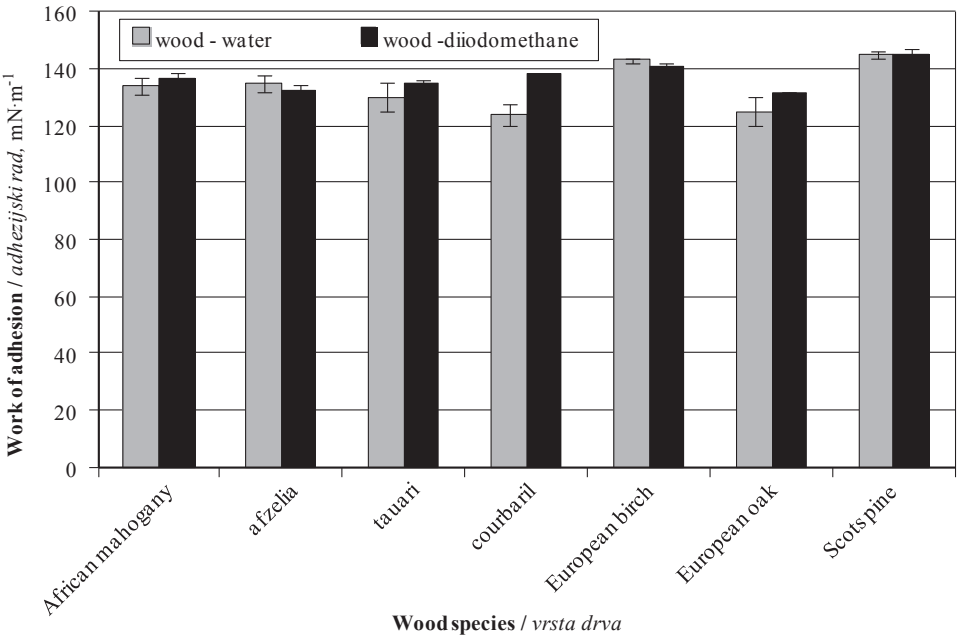

Figure 4 Work of adhesion for phase boundary wood-water and wood-diiodomethane
Slika 4. Adhezijski rad za granicu drvo – voda i drvo – dijodometan

face wettability and wood absorptivity. The result of this was the high value of contact angles for European oak and courbaril, and a low one for the sapwood of pine and birch. The essential relationship between wood wettability and surface chemical composition as well as surface morphology was noticed by, among others, Shen *et al*. (1998) and Li *et al*. (2014). The results of the research have shown that, among the tested wood species, oak wood was characterized by the lowest susceptibility to wetting with polar and dispersive liquids, expressed by the highest contact angle values. Among the wood species from tropical zones, courbaril wood showed the lowest polar liquid wetting susceptibility, whereas afzelia wood had the lowest dispersive liquid wetting susceptibility. In view of the above, these wood species ought to be regarded as particularly suitable for use as flooring material.

4 CONCLUSIONS
4. ZAKLJUČAK

The biggest changes of contact angles in the case of polar liquid (water) were recorded for pine and birch sapwood (changes at the level of 24 - 84 % during 60 s). In the case of dispersive liquid (diiodomethane) for the first 60 s after applying a drop, the angles changed in a much smaller range (changes at the level of 3 - 10 %). Wettability of oak wood with ring-porous structure was lower than wettability of tropical wood species with diffuse-porous structure. Surface free energy of wood depended on the wood species and, above all, on whether it was heartwood or sapwood. After 60 s, the value of the surface free energy for the heartwood of tested species was in the range of 60 to 70 $mJ \cdot m^{-2}$, while for the sapwood of pine and birch, it was about 80 $mJ \cdot m^{-2}$. The biggest changes of the work of adhesion, within 60 s after applying a drop of water on the wood surface, was recorded for pine sapwood (increase of 28 %) and the smallest one (increase of 15 %) for tauari and courbaril wood.

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Influence of Temperature on Composition of Wood Pyrolysis Products

Utjecaj temperature na sastav proizvoda pirolize drva

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ABSTRACT • *Experiments on birch wood chips of a size < 20 mm have been conducted in a laboratory scale batch pyrolysis reactor to study the effect of temperature on the pyrolysis product yields and the balance of elements in the products. The investigated variable was the pyrolysis temperature, which was equal to 300, 400 and 500°C in consecutive pyrolysis runs. Products were separated into five fractions: gases, tar, water, char, and a low-boiling liquid fraction. The paper presents the mass share of each fraction as a function of temperature. The content of carbon, hydrogen and nitrogen was analysed in each fraction. The paper summarizes the weights of different fractions and the distribution of elements in each fraction. The gas fraction was analysed with the use of a gas chromatograph with thermal conductivity detector, while the liquid fraction was analysed in a gas chromatograph with mass detector. To analyse the content of C, H and N in tar and charcoal, an elemental analyser was used. The preformed study has revealed that the increase of the pyrolysis temperature leads to the increase of the amount of char and to the decrease of the amount of tars (heavy tars and low boiling tars). The amount of water in the pyrolysis products does not change as significantly as the amount of tars, which is the result of constant amount of water obtained in the pyrolysis process. The amount of pyrogenic water increases with the increasing temperature of the process.*

Keywords: *Pyrolysis, thermal decomposition, Thermogravimetric Analysis (TGA), Biomass, Bio-oil*

SAŽETAK • *Radi proučavanja utjecaja temperature na prinose produkata pirolize i ravnoteže elemenata u proizvodima pirolize, u laboratorijskom su reaktoru za pirolizu provedeni eksperimenti s česticama drva breze manjima od 20 mm. Promjenjiva varijabla u eksperimentu bila je temperatura pirolize, koja je u uzastopnim ciklusima pirolize iznosila 300, 400 i 500 °C. Proizvodi pirolize razdvojeni su u pet frakcija: plinove, katran, vodu, ugljen i tekuću frakciju niskog vrelišta. U radu je prikazan maseni udio svake frakcije kao funkcije temperature. U svakoj je frakciji analiziran sadržaj ugljika, vodika i dušika. U radu su prikazani udjeli pojedinih frakcija i raspodjela elemenata u svakoj od njih. Frakcija plina analizirana je upotrebom plinskog kromatografa s detektorom toplinske vodljivosti, dok je tekuća frakcija analizirana u plinskom kromatografu s detektorom mase. Za analizu sadržaja C, H i N u katranu i drvenom ugljenu upotrijebljen je elementarni analizator. Provedena je studija pokazala da povećanje temperature pirolize dovodi do povećanja količine ugljena i smanjenja količine katrana (teških katrana i katrana niskog vrelišta). Količina vode u proizvodima pirolize ne mijenja se značajno s promjenom temperature, što je rezultat stalne količine vode u uzorcima, koja u procesu pirolize ispari. Količina pirogene vode povećava se s porastom temperature procesa pirolize.*

Ključne riječi: *piroliza, termička dekompozicija, termogravimetrijska analiza (TGA), biomasa, bioulje*

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1 INTRODUCTION
1. UVOD

Pyrolysis is an endothermic thermochemical process used to receive a variety of chemicals or fuels. As a result of the pyrolysis of wood, liquid, gaseous and solid products are obtained (Kardaś, 2014). The relative amount of each pyrolysis product (gas, char, liquid) can be modified by adjusting parameters of the operating process. The major operating parameters are: temperature, sweep gas flow rate, heating rate, and pressure (Akhtar, 2012). Numerous studies exhibit dramatic influence of the pyrolysis temperature on product distribution. During the pyrolysis in a solar reactor (Zeng, 2015), the gas yield increased by more than three times when the temperature increased from 600 °C to 2000 °C. The maximum gas yields of 50.9 % (mainly CO and a little of CH4) were achieved for beech wood pyrolysis at 2000 °C and 50 °C/s heating rate with 6 Ndm^3/min argon flow rate. The highest temperature gives the highest gas yields. The most important gas yield increases (15.3 % to 37.1 %) and liquid yield decreases (70.7 % to 51.6 %) were found between 600 and 1000 °C (Zeng, 2015). The char yield is approximately constant above 600 °C and depends on the heating rate. This is roughly between 10-30 % for slow-pyrolysis and 5-20 % for fast pyrolysis (Blasi, 2009). The temperature also affects the liquid yield. Numerous works on biomass pyrolysis showed yield increase with temperature in the range 400-550 °C, with further yield decrease (Bridgwater, 1999). The liquid product was composed of aqueous and bio-oil phases. The former phase, including all the water-soluble organic compounds, consists of water coming from both the moisture in the wood and the dehydration reactions taking place during the pyrolysis process (Antonakou, 2006). The main constituent of the aqueous phase was water (~90 wt%). The water-soluble organic compounds were mainly acetic and formic acid, and they contained low molecular-weight oxygenated organic compounds such as aldehydes, ketones, alcohols, phenols and others (Wei, 2006; Mohan, 2006). All the water-soluble organic compounds could be recovered as useful chemicals (Zhang, 2005). Yorgun (2015) presents the results of pyrolysis of paulownia wood and shows how the pyrolytic aqueous chase fraction increases with temperature. At the temperature of 623 K, the aqueous fraction amounted to 19.9 % of the product mass, while at 873 K, it increased to 21.1 %. There is a large number of works addressing various process conditions and influence of these parameters on the obtained products (Wang, 2010; Septien, 2012; Yorgun, 2015). In the present paper, due to a very large number of variables influencing the pyrolysis, only one parameter was chosen for examination - temperature. Different amounts of individual pyrolysis products at different temperatures are due to the degree of thermal conversion of biomass and the reactions occurring at a given temperature.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Birch wood samples
2.1. Uzorci drva breze

Chips of birch of a grain size <20 mm were used as fuel in the experiment. The wood was analysed for its technical and elemental characteristics. The measured parameters included humidity, heat of combustion, elemental composition, ash and volatiles. The characteristics of the used fuel were important for interpretation of the obtained results. The results of the performed analysis are shown in Tab. 1.

Table 1 Technical and elemental analysis
Tablica 1. Tehnička i elementarna analiza

Parameter / *Veličina*	**Value** / *Vrijednost*
Combustion heat *toplina izgaranja*, MJ / kg	17.37
Carbon / *ugljik*, %	48.81
Hydrogen / *vodik*, %	5.85
Nitrogen / *dušik*, %	0.43
Oxygen / *kisik*, %	42.6
Ash / *pepeo*, %	2.3

2.2 Experimental setup and procedures
2.2. Provedba eksperimenta

Pyrolysis experiments were carried out in a high-temperature pyrolysis reactor ŚMIGŁY (Fig. 1.). The reactor has the shape of a cylindrical vessel with an internal diameter of 98 mm. The active part of the reactor chamber, located in the central section, is wrapped with induction heating and thermal insulation. The upper part is a chamber with a valve spacer loading the reactor. The bottom of the active part of the reactor chamber is provided with valve spacer revision. The reactor is designed for pyrolysis at temperatures up to 950 °C. The system is equipped with bleed air coolers to cool the gases discharged from the reactor. The stream of the pyrolysis gas formed in the reactor passes through the system of five scrubbers. During the experiment, the first washer worked at room temperature and was filled with isopropanol. The next four muds

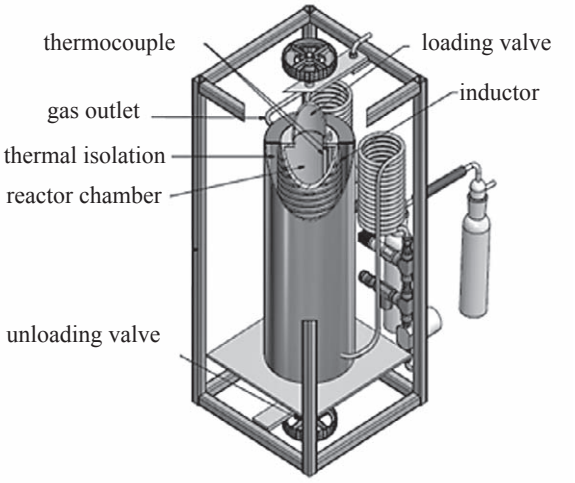

Figure 1 Pyrolysis reactor Smigly
Slika 1. Reaktor za pirolizu *Smigly*

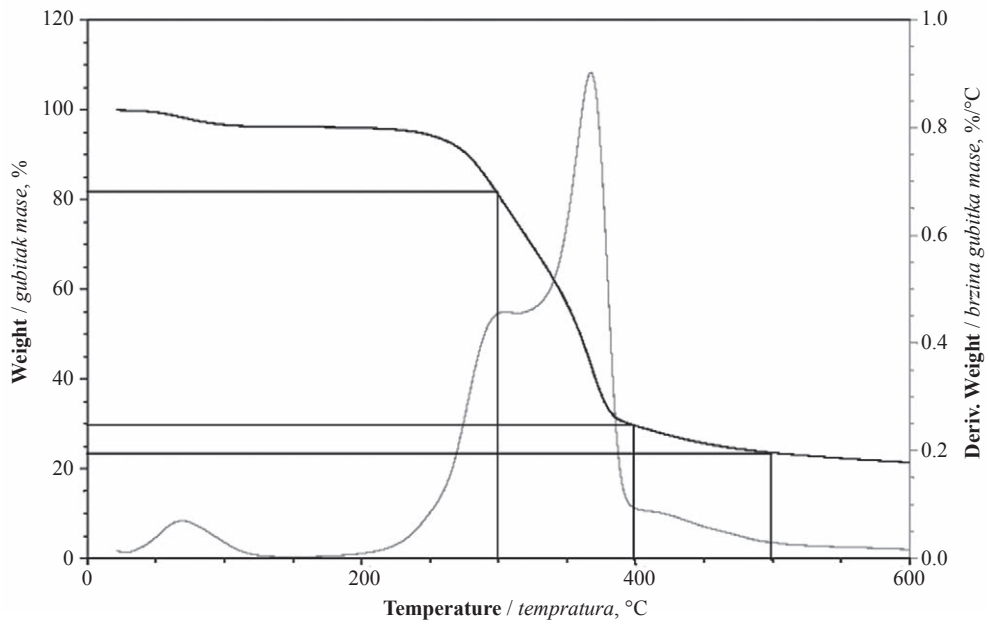

Figure 2 Thermogravimetric pyrolysis of birch wood
Slika 2. Termogravimetrijska analiza brezovine

were placed in a cryostat at -20 °C, two of which were filled with isopropanol, while the next two were blank. The pyrolysis gas was analysed by GC-ECD. The contents of CO, CO_2, H_2 and CH_4 were considered in the gas analysis. Low temperatures, at which the scrubbers were kept, supported the condensation of the liquid fraction with low volatility components and protected against evaporation of the isopropanol scrubbers.

After the experiment, the contents of all fluids were pooled in a flask, the flushing was washed in isopropanol, and the washings were poured into the flask. Then the flask was refilled with fresh isopropanol to give a total volume of 0.5 dm^3. This procedure was used in all experiments. Next, a liquid sample was analysed for water content using a Carl-Fischer titrator. Another sample of the liquid was placed in a tarred glass evaporator, reweighed and left under the hood until the isopropanol, water and low-boiling fractions evaporated. The remaining fraction, here denoted as heavy tar, was weighed and then analysed in terms of combustion heat, and the contents of H, N and C. Once the reactor had cooled, another solid fraction - char, was unloaded. This fraction was also weighed and examined in terms of heat content. The gaseous fraction was determined by chromatography, and its calorific value was calculated from the composition of the pyrolysis gas.

2.3 Results of thermogravimetric analysis
2.3. Rezultati termogravimetrijske analize

In order to plan the experiment in the pyrolysis reactor, preliminary experiments were performed in a thermogravimetric analyser. Figure 2 presents a graph of thermogravimetric pyrolysis of birch wood. The graph shows the weight change with temperature. The most intense degassing can be noticed for the temperature of 370 °C. The figure also presents the derivative weight of the temperature. In the graph, points correspond to the discharge of solid residue at the temperature at which the experiments were conducted in the pyrolysis reactor. For the temperatures of 300, 400 and 500 °C, the solid residue was 82, 29 and 23 % of the initial mass, respectively. The most intensive degassing was 0.9 % of weight/°C and applied to the temperature of 370 °C. The TGA studies are the introduction to the experimental research. They provide the information on the temperature at which the pyrolysis of wood starts and on pyrolysis residues at specific temperatures. However, these studies do not answer the question what products are obtained during the pyrolysis.

3 RESULTS
3. REZULTATI

3.1 Pyrolysis runs to 300 °C
3.1. Piroliza pri 300 °C

Products of the pyrolysis of birch chips at 300 °C were divided into five fractions, which were in three states of matter: solid - char, gas - pyrolysis gas, and liquid - water, heavy tars, and low-boiling liquids. The percentage of each fraction is presented in Fig. 3. The

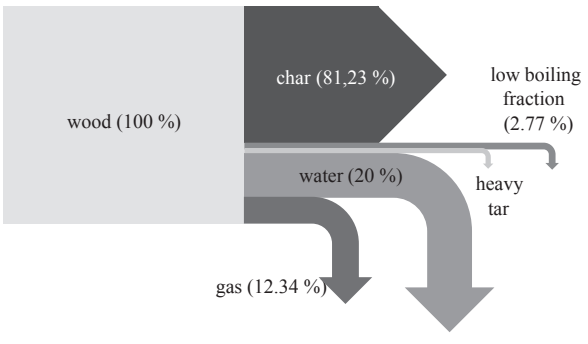

Figure 3 Share of each fraction obtained below 300 °C, presented as the Sankey diagram
Slika 3. Udjeli pojedinih frakcija dobivenih pri temperaturi pirolize nižoj od 300 °C prikazani kao Senkijev dijagram

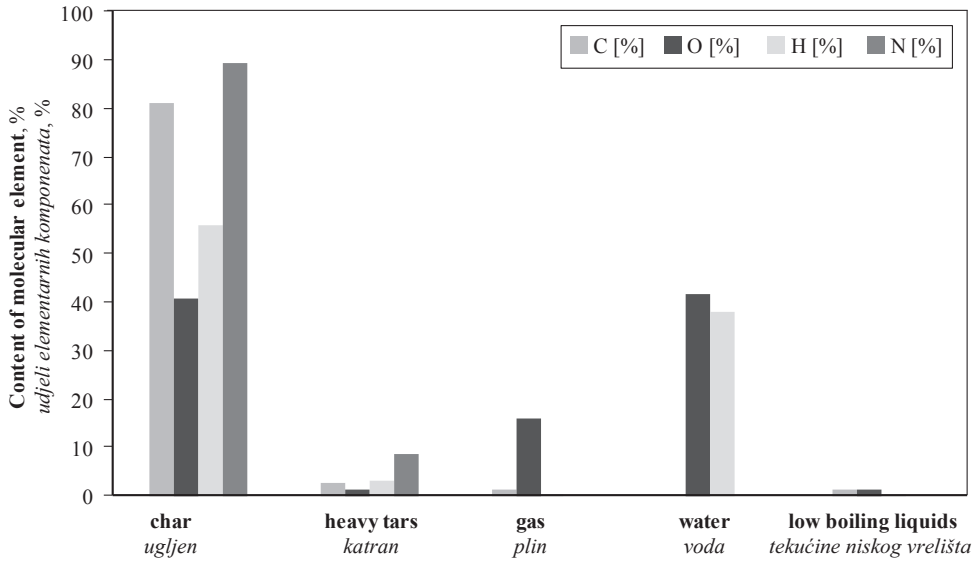

Figure 4 Contributions of individual elementary components (C, O, H, N) in the products of pyrolysis at 300 °C
Slika 4. Udjeli pojedinih elementarnih komponenata (C, O, H, N) u proizvodima pirolize pri 300 °C

main product obtained was char, representing 62.86 % of weight, with 63.07 % carbon content. The char contained more than 81 % elemental carbon in the wood before the trial. The solid fraction contained the greater part of nitrogen in the wood (89 %) and 55 % of hydrogen. The remaining nitrogen was mostly contained in heavy tars (8.58 %). A large part of hydrogen in the timber constituted water hydrogen, present as the moisture condensed out with the liquid fraction (38 %). The obtained fraction was characterized by the combustion heat slightly greater than that of the wood used for the experiments (17.37 MJ/kg) and amounting to 18.84 MJ/kg. The determination of the water content in the products showed the increase of 20 grams of water per 100 grams of timber sample. The amount of tar obtained in the experiment was low and amounted to low-boiling liquids and heavy tars, with 2 and 3 % contents, respectively. Figure 4 presents the contributions of individual elementary components (C, O, H, N) in the products of pyrolysis.

The main combustible components in the pyrolysis gas are hydrogen, carbon monoxide and methane. In the experiments carried out at the temperature of 300 ° C, low content of combustible gases was recorded. The average calorific value of the pyrolysis gas was 1.57 MJ/Nm^3.

3.2 Pyrolysis runs to 400 °C
3.2. Piroliza pri 400 °C

In a series of experiments at 400 °C, the share of char decreased in relation to the lower temperature and accounted for 34 % of the products. However, the content of carbon in the char increased to 78 %. The solids were up to 54 % of the biomass carbon. To a lesser extent, elemental carbon was stored in heavy tars (16.3 %) and in pyrolysis gas (10 %). At the expense of smaller amount of solid residue, the share of other fractions increased. Half of the hydrogen (49.3 %) contained in the fuel becomes water. The hydrogen in the char and heavy tars spread out evenly and amounted to 17.8 % and 17.3 %. Nitrogen, similarly to the experiment at 300 °C, was mainly concentrated in the char, in which 78.4 % of the nitrogen from the fuel was recorded. Mass shares of individual fractions of the pyrolysis products are presented in Fig. 5, while the distributions of carbon, oxygen, hydrogen and nitrogen in the products of pyrolysis are shown in Fig. 6. In the studies of pyrolysis at 400 °C, more than 30 % of flammable gases were recorded. The main combustible gas was carbon monoxide. The average calorific value of the gas mixture was 4.23 MJ/Nm^3.

3.2 Pyrolysis runs to 500 °C
3.2. Piroliza pri 500 °C

The pyrolysis carried out at 500 °C resulted in a small amount of solid fraction (28 %) with high carbon content, and a large amount of liquid fraction. The solid fraction mainly consisted of carbon, constituting 85 % of its weight, and contained 48.95 % of the biomass carbon. Carbon substantially ended as heavy tar (35 %) and, to a lesser extent, as the pyrolysis gas and low boiling liquid fraction (about 5 %). The total yield of liquid products was 62 % of the substrate mass. The main components of the liquid

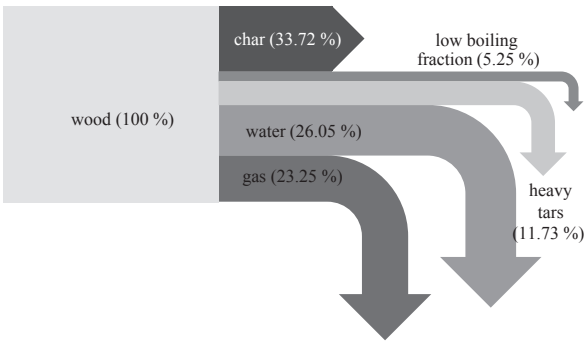

Figure 5 Share of each fraction obtained below 400 °C, presented as the Senkey diagram
Slika 5. Udjeli pojedinih frakcija dobivenih pri temperature pirolize nižoj od 400 °C prikazani kao Senkijev dijagram

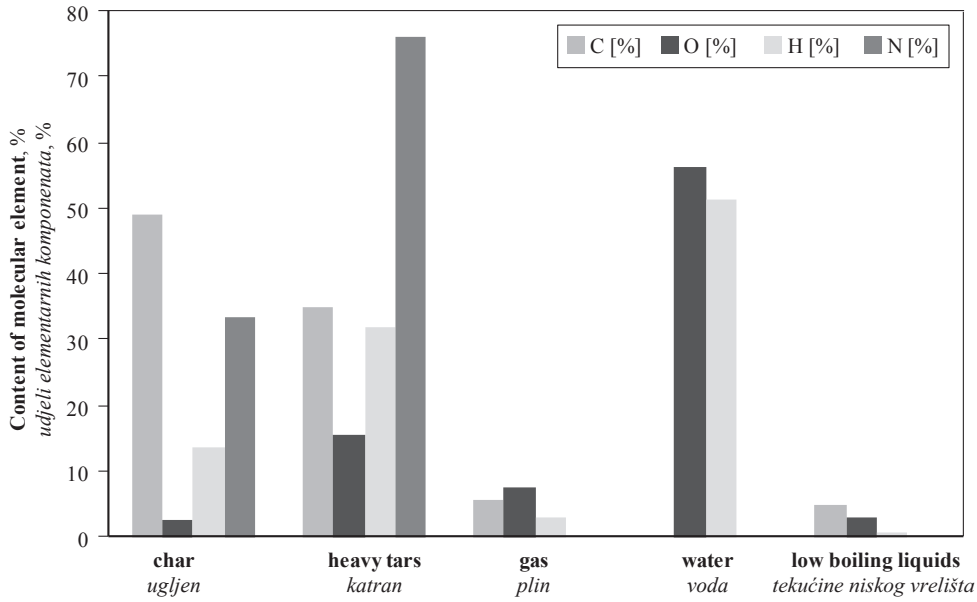

Figure 6 Contributions of individual elementary components (C, O, H, N) in the products of pyrolysis at 400 °C
Slika 6. Udjeli pojedinih elementarnih komponenata (C, O, H, N) u proizvodima pirolize pri 400 °C

fraction were: water (27 %), heavy tar (26 %), and low boiling liquid (9 %). 50 % of the biomass hydrogen was in the water after the process, as in the experiment at 400 °C. Additional 32 % of the hydrogen from the fuel was in heavy tars. The char contained only 13 % of the hydrogen from the fuel. Most of the biomass nitrogen was in heavy tars (76 %). The remaining nitrogen was in the char. Mass shares of individual fractions of pyrolysis products are presented in Fig. 7, while the distributions of carbon, oxygen, hydrogen and nitrogen in the products of pyrolysis are shown in Fig. 8.

The experiments carried out at 500 °C were characterized by large amounts of hydrogen in the pyrolysis gas. Its average calorific value was 5.26 MJ/Nm^3.

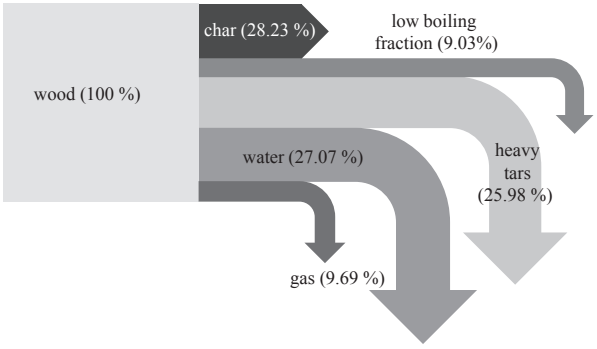

Figure 7 Share of each fraction obtained below 500 °C, presented as the Senkey diagram
Slika 7. Udjeli pojedinih frakcija dobivenih pri temperaturi pirolize nižoj od 500 °C prikazani kao Senkijev dijagram

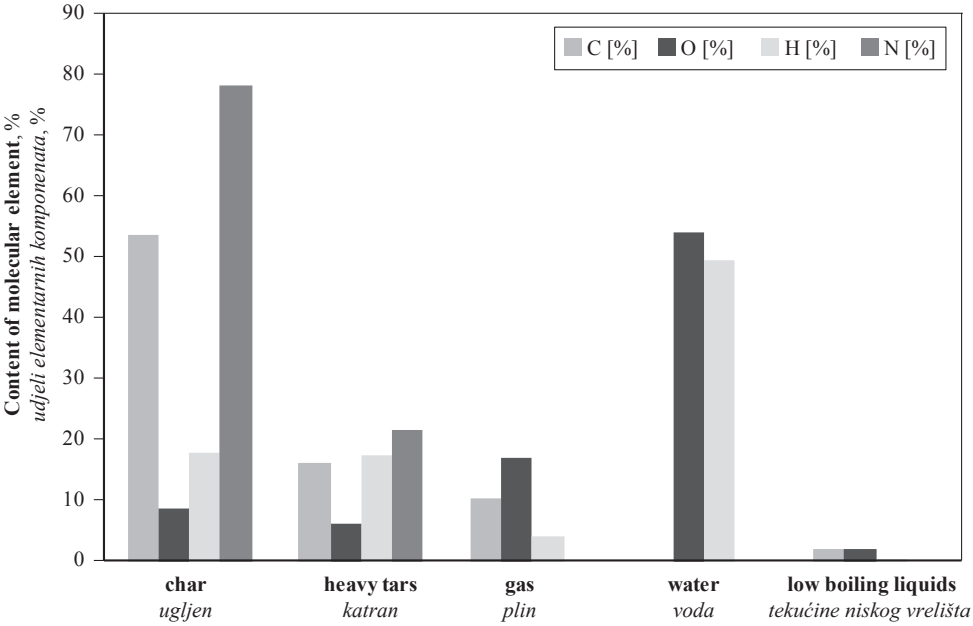

Figure 8 Contributions of individual elementary components (C, O, H, N) in the products of pyrolysis at 500 °C
Slika 8. Udjeli pojedinih elementarnih komponenata (C, O, H, N) u proizvodima pirolize pri 500 °C

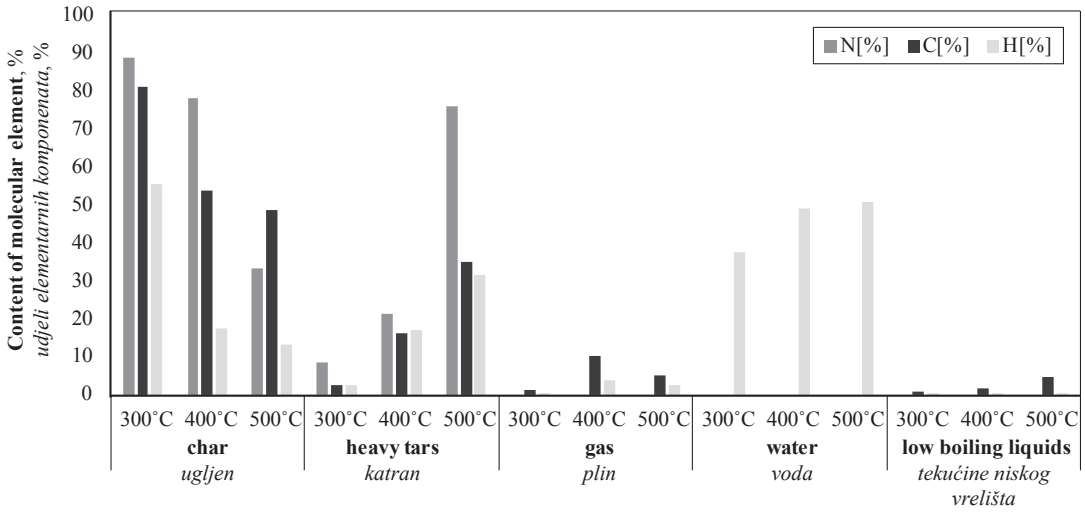

Figure 9 Contributions of individual elementary components (C, H, N) in the products of pyrolysis at 300, 400 and 500 °C
Slika 9. Udjeli pojedinih elementarnih komponenata (C, O, H, N) u proizvodima pirolize pri 300, 400 i 500 °C

The content of combustible components in the pyrolysis gas is shown in Tab. 3.

4 CONCLUSIONS
4. ZAKLJUČAK

The contributions of individual fractions of the products obtained during the pyrolysis of wood biomass vary with temperature. The tendency to produce more liquid fraction and smaller amounts of char with the increasing temperature is clearly visible. Changes are also visible in the elemental composition of the pyrolysis products.

The diagram in Fig. 9 compares the percentages of pyrolysis products obtained for three temperatures of the process.

The char obtained at the highest temperature had higher carbon content and lower content of hydrogen. The calorific value of the pyrolysis gas increased with temperature, as well as the contents of hydrogen and methane in the gas mixture. At lower temperatures, most of the carbon in the timber was concentrated in the char; however, at higher temperatures, the share of carbon changed. As the temperature increased, more carbon entered into heavy tars, gases and low-boiling liquid fraction. With the increasing temperature, the concentration of nitrogen decreased in the char, increasingly going to the heavy tar. A large part of hydrogen, independently of the temperature, was in the water (from 38 % at 300 °C to 51 % at 500 °C). The remaining hydrogen was initially mainly concentrated in the char. As the temperature increased, the total mass of hydrogen in the char decreased, while the hydrogen mass contained in heavy tars increased.

The aim of the research is to better understand the process in order to better design industrial installations. Pyrolysis is one of the stages occurring during gasification. The major problem of gasification is the formation of liquid pyrolysis products. Gas generator must be cleaned for further use. Good understanding of the process and knowledge of its pyrolysis products can help with gas purification and provide better design of process parameters.

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The Effect of Heat Modification and Densification on Physical Properties of Poplar Wood

Utjecaj toplinske modifikacije i ugušćivanja na fizikalna svojstva topolovine

Original scientific paper • Izvorni znanstveni rad
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ABSTRACT • *In this study, density, volumetric swelling, mass loss, volume weight, fiber saturation point and water absorption of the poplar wood (Populus usbekistanica) were investigated with the effect of heat modification (HM) and heat-modified densification (HMD). Poplar samples were modified with steam at 120 °C, 160 °C and 200 °C for 1 and 3 h. After heat modification, the samples were compressed in hot press at a temperature of 120 °C, press pressure of 5 MPa and press time of 30 minutes for densification. Physical properties of the samples were determined according to Turkish standards. The results showed that heat modification affected densification and increased density. Densification had a positive effect on oven dry density (D_0), oven dry density after soaking (D_{0S}), volume weight (R) and fiber saturation point (FSP), except for volumetric swelling. Similarly, the densification process had an increasing effect on the water absorption, excluding 360 hours.*

Keywords: *poplar wood, densification, heat modification, physical properties*

SAŽETAK • *U ovoj je studiji istražen utjecaj toplinske modifikacije (HM) i ugušćivanja (HMD) na gustoću, volumno bubrenje, gubitak mase, volumnu težinu, točku zasićenosti vlakanaca i upijanje vode drva topole (Populus usbekistanica). Uzorci topolovine modificirani su parom pri 120, 160 i 200 °C tijekom jednoga i tri sata. Nakon toplinske modifikacije uzorci su radi ugušćivanja stlačeni u vrućoj preši, pri temperaturi 120 °C, tlaku prešanja 5 MPa i vremenu prešanja 30 minuta. Fizikalna svojstva uzoraka utvrđena su prema Turskim standardima. Rezultati su pokazali da je toplinska modifikacija utjecala na proces ugušćivanja i pridonijela povećanju gustoće. Ugušćivanje je imalo pozitivan učinak na gustoću topolovine u apsolutno suhom stanju (D_0), na njezinu gustoću u apsolutno suhom stanju nakon natapanja (D_{0S}), na volumnu težinu (R) i na točku zasićenosti vlakanaca (FSP), ali ne i na volumno bubrenje. Također, ugušćivanje je znatnije utjecalo na sposobnost upijanja veće količine vode, osim za vrijeme od 360 sati.*

Ključne riječi: *topolovina, ugušćivanje, toplinska modifikacija, fizikalna svojstva*

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1 INTRODUCTION
1. UVOD

There have been many studies on heat modification recently, due to its many advantages such as improving the dimensional stability and durability of wood, without using chemicals (Tjeerdsma *et al*.; 1998; Weiland *et al*.; 2003; Garcia *et al*., 2012). This technology was applied to wood at a temperature of about 200°C for several hours at low oxygen level, a non-inflammable gas like oil or nitrogen. The main aim of this technique is to convert the chemical composition of wood using heat, which results in a change of physical properties. The process of thermal modification is based on high temperatures, which cause the decomposition of basic wood component like hemicelluloses and celluloses (Tjeerdsma and Militz, 2005; Rowell *et al*., 2009). Schneider (1973) noted that treatment, at temperatures above 200 ºC and of longer duration, decreased swelling and shrinkage up to 50 %. Besides, he stated that sorption and desorption characteristics also changed in heat modified wood.

In 1980s, densified wood products were produced from low density wood species, especially for utilization of some fast growing trees (Wang *et al*., 2000). The utilization of hardwood species for flooring and furniture reduced their supply all over the world. Various efforts have been made to modify the surface of low-quality softwood and planted fast-growing species. The surface densification technology has been developed and several researches have studied this technology (Rautkari *et al*., 2008; Gong and Lamason, 2007; Diouf *et al*., 2011). The thermal compression process might affect the drying duration, dimensional stability, surface quality, hygroscopicity, durability, and mechanical properties (Welzbacher *et al*., 2008).

The aim of this research is to determine the interactive effect of heat modification and post-heat densification on the poplar wood. The specific objective of the study was to analyze volumetric swelling and other chosen properties of heat threated and densified samples compared with samples densified without heat modification. These properties are: density, mass loss, volume weight, fiber saturation point and water uptake.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

Populus trees were obtained from Kahramanmaraş province in Turkey. Wood samples used in the study were prepared in dimensions 20×20×30 mm. For each group of modification, 27 samples were prepared from logs. Before testing, each sample was conditioned at 20 °C temperature and at 65 % relative humidity until reaching a moisture content of 12 %.

The samples were first heat modified by using laboratory drying oven at a temperature of 120 °C, 160 °C and 200 °C and modification time of either 60 or 180 min (Table 1). During heat modification, 100 ml water vapor was heated up to 100 °C degrees in the oven, and then the vapor was removed and kept still until the desired temperatures reached 120 °C, 160 °C and 200 °C. After the heat modification, samples were hot pressed by using a laboratory hot press at 120 °C temperature and 5 MPa press pressure for 30 minutes (Table 1).

The obtained results were statistically analyzed by using one-way ANOVA and Duncan's mean separa-

Table 1 Parameters used in tests of samples - undensified and densified
Tablica 1. Parametri obrade toplinski modificiranih uzoraka, neugušćenih i ugušćenih

Treatment *Obrada*	**Heat temperature** *Temperatura zagrijavanja* °C	**Heat time** *Vrijeme zagrijavanja* min	**Pressure** *Tlak* MPa	**Pressure temperature** *Temperatura prešanja* °C	**Pressure time** *Vrijeme prešanja* min
Undensified / *Neugušćeni uzorci*					
Control / *kontrolni uzorak*	-	-	-	-	-
Heat modified (HM) *Toplinski modificirani uzorci*					
HM11	120	60	-	-	-
HM13	120	180	-	-	-
HM21	160	60	-	-	-
HM23	160	180	-	-	-
HM31	200	60	-	-	-
HM33	200	180	-	-	-
Densified / *Ugušćeni uzorci*					
Control / *kontrolni uzorak*	-	-	5	120	30
Heat modified (HM) *Toplinski modificirani uzorci*					
HM11	120	60	5	120	30
HM13	120	180	5	120	30
HM21	160	60	5	120	30
HM23	160	180	5	120	30
HM31	200	60	5	120	30
HM33	200	180	5	120	30

tion test to populate homogeneity groups that showed significant differences at the 95 % confidence level.

Oven dry density (D_0): This term expresses the amount of substance in the full dry unit volume and it is calculated according to TS 2472.

Volume weight value (R): This value describes the amount of substance in the full wet unit volume and it is determined according to TS 2472.

Fiber saturation point (FSP) was calculated according to Turkish standards TS 2371 and Equation 1 given below:

$$FSP = \frac{V_S}{D_0} \cdot 100 \quad (1)$$

where V_S is volumetric swelling (%).

Oven dry density after soaking (D_{0S}): After soaking for 15 days in water, samples were dried to 0 % moisture content and oven dry densities were determined according to TS 2472. Mass loss (ML), volumetric swelling (%) and water absorption (W_A) were calculated by equations (2), (3) and (4), respectively,

$$ML = \left(\frac{M_0 - M}{M_0}\right) \cdot 100 \quad (2)$$

ML – mass loss (%), M_o – mass of oven-dry sample before heat modification (gr), M – mass of the sample after heat modification (gr).

$$V_S(\%) = \left(\frac{L - L_0}{L_0}\right) \cdot 100 \quad (3)$$

V_S – volumetric swelling (radial, tangential and longitudinal), L – wet dimension after immersion in water (mm), L_o – oven-dry dimension (mm),

$$W_A(\%) = \left(\frac{W - W_0}{W_0}\right) \cdot 100 \quad (4)$$

W_A – water absorption, W – weight after immersion in water (gr), W_o – oven-dry weight before immersion in water (gr).

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

Average oven density values of densified and undensified poplar wood samples with and without heat modification are shown in Table 2.

The effect of heat modification on density is given in Table 2. According to this Table, it can be seen that oven dry density of densified samples differs from that of undensified samples. Heat modification has not shown significant effect on undensified poplar and has caused 1 % decrease in density. The highest decrease in density among undensified poplar was observed at 200 ºC heat modification (HT31 and HT33). Means of samples densified with heat modification (897 kg/m^3) were compared to density of densified control samples (668 kg/m^3), and the results clearly showed that heat modification increased density by 34 %. The density of samples densified with and without heat modification was increased by 102 % and 174 % on average, respectively. Gong *et al*. (2010) studied the effect of heat treatment on density between undensified and densified poplar (*Populus tremuloides*) and concluded that wood density in densified poplar decreased to 11 % during the heat treatment, while density decreased to 2 % in undensified poplar wood. In another words, they concluded that the heat treatment of densified poplar increased density. Wang and Cooper (2005) found that the density of densified wood was affected by compress temperature, press duration time, press closing time and humidity of samples before compressing

The average volumetric swelling is given in Figure 1 for undensified and densified poplar samples with and without heat modification. The undensified volumetric swelling values at 120 and 160 ºC are higher than those of control samples but at 200 ºC they are lower. These differences are insignificant (p<0.062). Besides, the duration of heat modification did not indicate significant differences in all parameters, except for control samples. On the other hand, in densified samples, all temperatures and durations had a significant effect (p<0.001) on respective values. Moreover, as the duration of heat modification rose, volumetric swelling decreased. The mean volumetric swelling of undensified and modified samples (10.1 %) decreased by 3.7 % in comparison with the undensified control group (10.49 %). The value of modified and densified samples (180.35 %) increased by 85.68 % compared to their control samples (97.13 %).

Table 2 Average oven density (kg/m^3) values of undensified and densified poplar wood; control and heat modified
Tablica 2. Srednja vrijednost gustoće neugušćenih i ugušćenih uzoraka topolovine u apsolutno suhom stanju; vrijednosti kontrolnih i toplinski modificiranih uzoraka

Treatment *Obrada*	**Densified** / *Ugušćeni*	**Undensified** / *Neugušćeni*	**Increase** / *Povećanje* **%**
Control / *kontrolni uzorak*	668	331	102
Heat modified / *Toplinski modificirani uzorci*			
HM11	950	334	184
HM13	859	335	156
HM21	944	331	185
HM23	884	330	168
HM31	878	310	183
HM33	869	321	171
Average / *prosječna vrijednost*	897	327	174

HM: Heat modified / *toplinski modificirani uzorci*

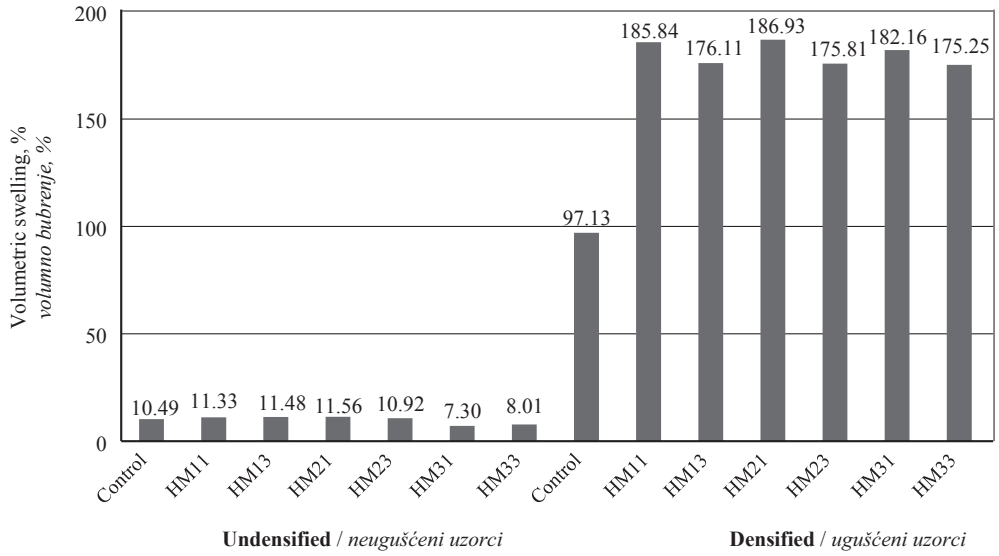

Figure 1 Average volumetric swelling of undensified and densified poplar wood with and without heat-modification
Slika 1. Prosječno volumno bubrenje neugušćenih i ugušćenih te nemodificiranih i toplinski modificiranih uzoraka topolovine

Comparable results were recorded in other studies. For instance, Gong et al. (2010) studied the effect of heat modification on densification and stated that heat modified wood is more resistant to swelling than densified wood. Also, Bal and Bektaş (2012) noted that heat treatment without steam decreased thickness swelling specially above 180 °C. In some studies, it was noted that the relationship between volumetric swelling and oven dried density was potently positive (Table 3) (Kord *et al*., 2010; Kurt, 2010). Candan *et al*. (2013) noted that all thermally compressed boards increased thickness swelling values. This result could be explained by springback behavior of wood due to densification (Abraham *et al*., 2010).

The results of physical properties of undensified and densified poplar samples without and with heat modification are given in Table 3.

Densification process with and without heat modification increased density values according to Table 3. The highest density for undensified poplar was observed for heat modification temperature of 120 °C compared to control group. Table 3 shows that the densities measured at 200 °C in undensified samples seem to be lower, but this decrease is not significant. As seen from statistical results in Table 3, while heat temperature duration had no effect on density in undensified samples, a significant increase in density was observed when the duration of heat modification decreased from

Table 3 Comparison of physical properties of undensified and densified poplar wood
Tablica 3. Usporedba fizikalnih svojstava neugušćenih i ugušćenih uzoraka topolovine

Treatment / *Obrada*	D_o, g/cm^3	D_{os}, g/cm^3	*ML*, %	*R*, g/cm^3	*FSP*, %
Undensified / *Neugušćeni uzorci*					
Control / *kontrolni uzorak*	0.331a(*)	0.328ab	__	0.299a	31.74a
Heat modified / *Toplinski modificirani uzorci*					
HM11	0.334a	0.333	0.30a	0.299a	33.92a
HM13	0.335a	0.324b	0.44a	0.299a	34.33a
HM21	0.331a	0.329ab	1.05ab	0.296a	34.89a
HM23	0.330a	0.328ab	1.82bc	0.297a	33.11a
HM31	0.310a	0.303a	8.40e	0.289a	23.41a
HM33	0.321a	0.316ab	6.61d	0.296a	24.99a
Densified / *Ugušćeni uzorci*					
Control / *kontrolni uzorak*	0.668b	0.376cd	__	0.320b	146.02b
Heat modified / *Toplinski modificirani uzorci*					
HM11	0.950d	0.425e	0.42a	0.335b	195.58c
HM13	0.859c	0.394d	0.66ab	0.323b	205.06c
HM21	0.944d	0.386cd	0.97ab	0.337b	197.98c
HM23	0.884c	0.366c	1.49abc	0.301a	223.36d
HM31	0.878c	0.396d	6.36d	0.322b	205.99c
HM33	0.869c	0.393cd	2.60c	0.327b	202.56c
ANOVA	p<0.001				

D_0 - Oven dry density / *gustoća u apsolutno suhom stanju*; D_{OS} - Oven dry density after soaking / *gustoća u apsolutno suhom stanju nakon natapanja*; *ML* - Mass loss / *gubitak mase*; *R* - Volume weight / *volumna težina*; FSP - Fiber saturation point / *točka zasićenosti vlakanaca*. *Means with the same small letter are not significantly different in Duncan's mean separation test. / *Srednje vrijednosti označene istim malim slovom nisu signifikantno različite prema Duncanovu testu.*

3 to 1h for densified poplar wood. As for densified samples, density decreased depending on the increase of the process duration (from 1 to 3h), except for the temperature of 200 °C. No significant difference was observed. This is in accordance with literature data. For example, Metsä-Kortelainen and Viitanen (2011) determined that 120 °C heat modification increased density compared to control samples, while 200 °C heat modification decreased density due to degradation of hemicellulose and cellulose. In another study, Cao and Huang (2012) noted that steam-heat-modification increased wood thermal conductivity and density.

Comparing the mean oven dry density after soaking (D_{0S}) with oven dry density (D_0), the density decreased 1 % in undensified samples and decreased 55 % in densified samples as seen in Table 3. This reduction occurred due to the permanent springback effect of the compressed wood. Densified and undensified poplar oven-dry densities after soaking (D_{os}) decreased compared to D_0. However, D_{0S} of densified poplar wood was still higher after soaking compared to undensified samples.

Values given in Table 3 demonstrate that densification process did not cause mass loss but heat modification increased mass loss with increased temperature. ML values of poplar at 200 °C were greater than at 120 and 160 °C. The average mass loss at 200, 160 and 120 °C was 6 %, 1.33 % and 0.45 %, respectively for all samples. A notably increased dimensional stability following thermal modification above 180 °C was noted in many studies (Welzbacher *et al*., 2008). This could be explained by the decreased hygroscopicity of components on wood cell walls (Fang *et al*., 2012). Decomposition of hemicelluloses and lignin at elevated temperatures and stress relaxation in samples caused a reduction in the hygroscopicity of wood (Cai *et al*., 2013). The value of volume weight of densified poplar (*R*) increased because density of densified poplar was higher than that of undensified poplar. The volume weight of densified wood increased by 9.31 %. The value of volume weight of undensified poplar (*R*) decreased at 200 °C with heat modification compared to other temperatures. Furthermore, *FSP* is directly related to volumetric swelling and oven dry density according to Equation (1) mentioned in the Method section. As is known, there is a linear relationship between *VS* and *FSP*. The *FSP* value of the control group (undensified and control) was 31.74 %. After the samples were heat modified at 200 °C (the mean of HT31 and HT33), the *FSP* values decreased to 23.75 % in poplar wood. Furthermore, the *FSP* values at 120 °C and 160 °C increased by 7.3 %. The *FSP* value of the control group (densified and control) was 146.02 %. After the densification, the *FSP* values increased to 40.47 %. Bal and Bektas (2012) noted that heat treatment at higher temperatures (180 °C) decreased values of *FSP*. Additionally, the volumetric swelling is very high due to the back-spring effect of wood. Abraham *et al*. (2010) also noted that the densified wood exhibited this behavior. For this reason, the high springback effect has caused the *FPS* value to increase up to 223 %.

Table 4 shows that the effect of heat modification on water absorption (%) differed between undensified and densified samples. It can be seen from Table 4 that, in the densified samples, the heat modification time had no statistically significant effect on water absorption at 120 ºC (HM11, HM13), whereas at 200 ºC (HM31, HM33) the respective effect was significant (p<0.000). As shown in Table 4, the modification temperature and duration have no statistically significant effect in the first 48 hours only in heat modified (not densified) wood. The water absorption values of heat modified samples decreased after 48 hours compared to control group. However, in 72 h and 96 h there was no statistically sig-

Table 4 Water absorption (%) of undensified and densified poplar wood without and with heat-modification
Tablica 4. Upijanje vode (%) ugušćenih i neugušćenih te nemodificiranih i toplinski modificiranih uzoraka topolovine

Treatment *Obrada*	1 h	2 h	3 h	24 h	48 h	72 h	96 h	360 h
Undensified *Neugušćeni uzorci*								
Control / *kontrolni uzorci*	7.64a(*)	13.77a	21.24a	51.49a	81.94bcd	92.05b	99.19b	129.62bcd
HM11	8.16a	13.48a	21.74a	48.26a	77.78bc	88.92b	95.13b	129.19bc
HM13	8.95a	15.75a	21.16a	51.67a	80.55bcd	91.00b	99.83b	130.42bcde
HM21	8.95a	15.04a	21.02a	49.43a	79.05bcd	90.78b	99.53b	131.44bcde
HM23	8.61a	14.42a	18.79a	45.03a	74.90bc	87.81b	94.32b	122.71bc
HM31	10.00a	17.57a	21.70a	50.57a	77.74bc	100.74b	112.24b	150.44def
HM33	6.25a	11.50a	17.39a	43.28a	68.51ab	87.52b	95.32b	131.78bcde
Densified / *Ugušćeni uzorci*								
Control / *kontrolni uzorci*	30.98cd	54.44b	56.96b	84.12b	96.54d	105.50b	108.78b	119.02b
HM11	31.21cd	49.44b	58.55b	112.48cd	126.23ef	132.82c	135.64cd	151.00ef
HM13	23.32bc	50.15b	62.84b	107.05c	122.02e	127.69c	130.33c	149.29cdef
HM21	36.20cde	59.74b	80.25c	126.09d	141.08f	156.15d	150.80d	167.31f
HM23	48.24e	62.70b	69.70bc	78.80b	90.08cd	94.59b	98.23b	111.81b
HM31	11.54ab	21.08a	25.60a	48.87a	58.09a	67.76a	68.01a	89.56a
HM33	41.33de	50.73b	58.65b	81.33b	91.55cd	98.68b	100.85b	118.49b
ANOVA	p<0.001							

HM – Heat-modified / *toplinski modificirani uzorci*. *Means with the same small letter are not significantly different in Duncan's mean separation test. / *Srednje vrijednosti označene istim malim slovom nisu signifikantno različite prema Duncanovu testu*.

nificant difference in water absorption compared to the control sample. As water absorption (%) changed with time, the lowest water absorption in undensified group was obtained in HT23 (122.71 %) after 360 hours. The lowest water absorption in the densified wood in the interval from 1 hour to 360 hours was determined in HT31 compared to the densified control. The water absorption in the first 24 hours in the densified wood continued to be water intake without heat treatment temperature and duration effective, and after 24 hours HT23, HT31 and HT33 showed lower water absortion than the densified control sample. When compared to the undensified control sample (129.62 %), the lowest water absorption percentage was determined in HM23 (122.71 %). Likewise, in densified samples, the lowest decrease in HM31 (89.56 %) was calculated according to control samples (119.02 %).Also, Cai *et al*. (2013) noted that the water absorption of densified wood with and without heat treatment was affected by compression temperature, compression ratio and pressure holding time. Similar findings were obtained by Unsal *et al*. (2009), and they indicated that the compressed pine decreased water absorption for 5MPa at 120 °C compared to uncompressed pine, while higher compression temperature and compression ratio increased water absorption.

4 CONCLUSIONS
4. ZAKLJUČAK

The main outputs of this study are summarized below:

1. Density of undensified poplar wood was minimally (1 %) affected by heat modification. However, density was influenced by heat modification before densification and it increased density by 34 %.
2. Volumetric swelling of undensified poplar wood decreased significantly only at 200 °C heat modification. Moreover, the densification increased the volumetric swelling due to the springback effect.
3. In comparison to oven dry density (D_0), the oven dry density after soaking (D_{0S}) decreased in undensified and densified samples at the rate of 1 % and 55 %, respectively. In addition, the mass loss increased with the increase of heat modification temperature in all samples, notwithstanding the densification process. Densification process increased the volume weight and fiber saturation point compared to heat modification.
4. No significant correlation was found between water absorption time and heat modification process for undensified samples. On the other hand, in densified samples, water absorption retention improved as the heat modification temperature and duration increased. Besides, the effect of the application time increased depending on temperature increase.
5. Poplar trees are fast growing and have low durability. However, poplar wood has become a material with high density and lower water absorption by heat modification and densification process. Thus, species with low durability can be converted to wood material of high density and extended service life by heat modification and densification process.
6. One of the remarkable characteristics of this study is that no chemicals have been used during the process and there have been no side effects that could adversely affect human and environmental health during and after the process.
7. In order to make the above physical properties meaningful and useful at the desired level, mechanical properties should also be researched in future as a part of this study.

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Influence of Some Boron Compounds on Kraft Pulping of European Black Pine and European Aspen

Utjecaj nekih spojeva bora na sulfatni postupak proizvodnje pulpe od drva europskoga crnog bora i europske jasike

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ABSTRACT • *This study investigated the effects of E-48 borax pentahydrate (A), E-67 agro boron (B), and Ground Colemanite (C) on properties of kraft pulp-paper obtained from European black pine and European aspen. The highest screened pulp yield values were determined by adding 8 % B during cooking of both species. The best pulp strength increases were determined by adding 8 % B during cooking of European aspen. Likewise, compared to control samples, the stability of Xylose, Mannose and 4-0-MeGlcA units was increased in European black pine kraft pulp after adding 8 % B. Furthermore, in producing the European aspen pulp, adding of 8 % A during cooking positively affected the total amount of hemicelluloses.*

Key words: *Boron, Kraft pulping, European black pine, European aspen, Paper strength, Hemicelluloses*

SAŽETAK • *U radu su ispitivani učinci E-48 boraks pentahidrata (A), E-67 agro bora (B) i kolemanita (C) na svojstva papira proizvedenoga od pulpe dobivene sulfatnim postupkom od drva europskoga crnog bora i europske jasike. Najveći prinos pulpe dobiven je dodavanjem 8 % agro bora tijekom kuhanja obiju vrsta drva. Najveća čvrstoća pulpe dobivena je dodavanjem 8 % agro bora tijekom kuhanja europske jasike. Jednako tako, stabilnost ksiloze, manoze i jedinica 4-0-MeGlcA u usporedbi s kontrolnim uzorcima povećana je u pulpi europskoga crnog bora nakon dodavanja 8 % agro bora. Također, dodavanje 8 % boraks pentahidrata tijekom kuhanja drva pri proizvodnji pulpe od drva europske jasike pozitivno je utjecalo na ukupnu količinu hemiceluloza.*

Ključne riječi: *bor, sulfatni postupak proizvodnje pulpe, europski crni bor, europska jasika, čvrstoća papira, hemiceluloze*

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1 INTRODUCTION
1. UVOD

Turkey has a total boron reserve of 955.3 million tons (72.8 % of the world boron reserves) on the basis of B_2O_3 content. Also, it is one of the biggest producers of boron compound in the world (47 % of boron market). The annual boron compound production of Turkey is 1.95 million tons. The important boron minerals in Turkey are tincal ($Na_2O \cdot 2B_2O_3 \cdot 10H_2O$), colemanite ($2CaO \cdot 3B_2O_3 \cdot 5H_2O$) and ulexite ($Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$) (Eti Mine, 2013).

Since the development of alkaline pulping in 1851, many researchers have tried to increase the pulp yield owing to delignification with a minimum carbohydrate loss. As known, polyoses (hemicelluloses) have some effect physical and mechanical properties of pulp and paper (Bai *et al.,* 2012; Hu *et al.,* 2013). The pulp yield losses can be prevented by reduction or oxidation of carbohydrate reducing end. For this purpose, cooking liquor additives such as sodium borohydride (Hartler, 1959; Aurell and Hartler, 1963; Diaconescu and Petrovan, 1976; Akgül *et al*., 2007; Istek and Ozkan, 2008; Tutus *et al.,* 2010; Gulsoy and Eroglu, 2011; Gumuskaya *et al.,* 2011) anthraquinone (Jakate *et al.,* 1981; Manji, 1996; Atik, 2002; Akgul and Tozluoglu, 2009; Kamyar *et al.,* 2014; Gulsoy *et al.,* 2015) and polysulfide (Pekkala, 1982; Jiang, 1994; MacLeod *et al.,* 2002; Paanenen and Sixta, 2015) were extensively studied. However, there are no published data related to effects of E-48 ($Na_2B_4O_7 \cdot 5H_2O$), E-67 ($Na_2B_8O_{13} \cdot 4H_2O$), and GCol ($CaB_3O_4(OH)_3$-$H_2O$) on pulp and paper properties.

In this scope, European black pine and European aspen, two wide spread species, are used with different ratios (4 % and 8 %) of A, B, and C to determine the effects of adding boron compounds on kraft pulp and paper properties, as well as on the composition of polyoses.

2 MATERIALI AND METHODS
2. MATERIJALI I METODE

2.1 Materials
2.1. Materijali

Freshly cut European black pine (*Pinus nigra* Arn.) and European aspen (*Populus tremula* L.) from the Bartin province of Turkey were debarked and chipped into 3.0-1.5-0.5 cm. Chips were air dried and stored with less than 15 % moisture content until used for the pulping process. Samples used for polyoses analysis were stored in a cold and dark place. A ($Na_2B_4O_7 \cdot 5H_2O$), B ($Na_2B_8O_{13} \cdot 4H_2O$), and C ($CaB_3O_4(OH)_3$-$H_2O$) used in this study were obtained from Eti Mine, Turkey. Boron oxide (B_2O_3) contents of A, B, and C were 48 %, 67 %, and 40 %, respectively.

2.2 Methods
2.2. Metode

The kraft cooking conditions of European black pine and European aspen are summarized in Table 1. For both species, the 4 % and 8 % (oven-dried wood) boron compounds in powder form were added to kraft cooking liquor. A and B were dissolved, while C was partially dissolved in the cooking liquor at room temperature. Under the same cooking conditions, the boron compound-free kraft cooking was also done as control. The air dried chips equivalent to 650 g oven dried for each cooking experiment were cooked in a 15 L electrically heated laboratory cylindrical type rotary digester. After cooking, pulps were washed with tap water to remove residual liquor. After washing, pulps were disintegrated and screened on 0.15 mm slot screen (TAPPI T 275). Pulps were then beaten to 25°SR in a Valley Beater (TAPPI T 200). Kappa number, screened yield, viscosity, and freeness of pulps were determined using TAPPI T 236, TAPPI T 210, SCAN-CM 15-62 and ISO 5267-1, respectively.

Table 1 Kraft cooking conditions of European black pine and European aspen
Tablica 1. Uvjeti kuhanja pri sulfatnom postupku proizvodnje pulpe od drva europskoga crnog bora i europske jasike

Conditions / *Uvjeti*	**European black pine** *Europski crni bor*			**European aspen** *Europska jasika*		
	A	**B**	**C**	**A**	**B**	**C**
Active alkali / *aktivna lužina*, %	20			16		
Sulfidity / *sulfidnost*, %	25			20		
A ratio / *udjel A*, %	4-8	-	-	4-8	-	-
B ratio / *udjel B*, %	-	4-8	-	-	4-8	-
C ratio / *udjel C*, %	-	-	4-8	-	-	4-8
Temperature / *temperatura*, **°C**	170					
Time to max. temperature, min *vrijeme do maks. temperature,* min	90					
Time at max. temperature, min *vrijeme na maks. temperaturi,* min	60					
Total cooking time, min *ukupno vrijeme kuhanja,* min	150					
Liquor/chip ratio *omjer otapala i sječke*	4/1					
A: E-48, **B**: E-67, **C**: GCol.						

75 g/m^2 handsheets made by Rapid-Kothen Sheet Former (ISO 5269-2) were conditioned (TAPPI T 402). Tensile properties (tensile index, stretch, and TEA), burst index tear index and brightness of the handsheets were measured according to TAPPI standards T 494, T 403, T 414, and T 525, respectively. The data of handsheet properties for each cooking were statistically analyzed using analyses of variance (ANOVAs) and Duncan test at a 95 % confidence level. The same lower case letter in Figure 5-9 denotes that the difference in the mean values of properties among the compared groups was not statistically significant (P>0.05).

The remaining polyoses (Hemicelluloses) after the pulping process were determined by acid methanolysis (Sunderberg *et al.,* 1998). Mean values are presented in Table 4.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

The kappa number of pulp indicates the degree of delignification in cooking. In the European black pine pulp samples, B additions caused the increase of the kappa number, while A and C additions led to the decrease of the kappa number compared to control pulp (Figure 1). The lowest and highest kappa numbers, 36.1 and 63.4, respectively, were observed when 4 % A and 8 % B were added to cooking. In the European aspen pulp samples, the kappa number decreased with the addition of A (Figure 1). However, the addition of B and C to the cooking liquor caused an increase in the kappa number. The lowest and highest kappa numbers, 14.6 and 37.9 respectively, were observed when 4 % A and 8 % C were added to the cooking. These results showed that the addition of A accelerates the delignification, while the addition of B has a negative effect on the kappa number of pulps. On the other hand, the addition of C seems not to affect delignification rate of European black pine, whereas it clearly decreases delignification rate of European aspen.

The pulp viscosity is an indicator of degree of polymerization (DP) of polysaccharides (especially cellulose). Therefore, the degradation of polysaccharides during cooking results in a decrease in pulp viscosity. In the European black pine pulp samples, the addition of A and C resulted in pulp viscosity losses. However, the addition of B caused an increase compared to control pulp. The lowest and highest pulp viscosity values of 907 cm^3/g and 1070 cm^3/g, respectively, were observed when 8 % A and 8 % B were added to the cooking. In the European aspen pulp samples, pulp viscosity increased with the addition of all boron compounds. The addition of B to the cooking liquor of both species led to the increase of viscosity. This result can be explained by higher kappa number and higher reject ratio of these pulps compared to control samples (Table 2 and Table 3). Also, higher polyoses retention during cooking causes higher pulp viscosity. With the exception of 4 % B in European black pine, as can be seen in Table 4, the addition of 8 % B to the cooking resulted in the highest viscosity values with the highest concentration of polyoses (119 mg/g).

The brightness of handsheets obtained from boron compounds-added pulps of European black pine was found to increase with the addition of A and C (Table 2). However, the addition of B to the cooking liquor caused the decrease in handsheet brightness. This results can be explained by lower kappa number of A and

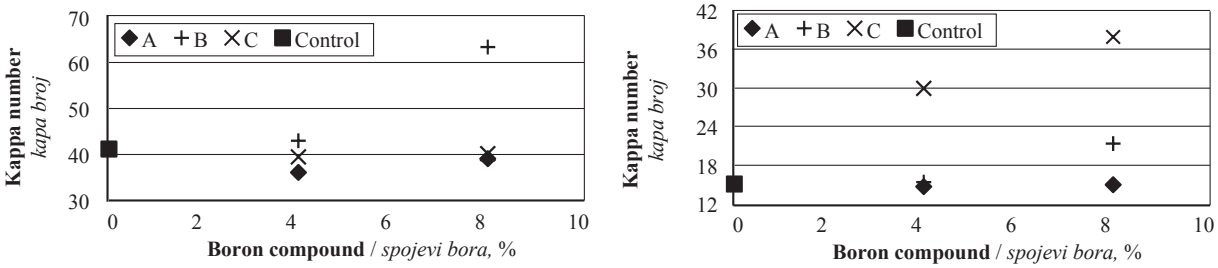

Figure 1 Effect of boron compounds on kappa number of pine (a) and aspen (b) pulps
Slika 1. Utjecaj spojeva bora na kapa broj pulpe proizvedene od drva (a) bora i (b) jasike

Table 2 Pulp properties of control and boron compound-added pulps of European black pine
Tablica 2. Svojstva pulpe proizvedene od drva europskoga crnog bora, kontrolnog uzorka pulpe i pulpe s dodatkom spojeva bora

Cooking *Kuhanje*	**Screened yield** *Prinos prosijavanja* %	**Reject** *Škart prosijavanja* %	**Total yield** *Ukupni prinos* %	**Kappa number** *Kapa broj*	**Viscosity** *Viskoznost* cm^3/g	**Brightness** *Sjajnost* %
Control / *kontrolni uzorak*	49.0	0.5	49.5	41.2	959	19.2
4 % A	49.9	0.5	50.4	36.1	952	19.6
8 % A	50.8	0.3	51.1	39.1	907	20.1
Control / *kontrolni uzorak*	49.0	0.5	49.5	41.2	959	19.2
4 % B	50.5	0.6	51.1	43.0	1002	18.9
8 % B	54.1	1.6	55.7	63.4	1070	17.5
Control / *kontrolni uzorak*	49.0	0.5	49.5	41.2	959	19.2
4 % C	50.3	0.6	50.9	39.5	936	20.2
8 % C	51.0	0.6	51.6	40.2	949	20.5

Table 3 Pulp properties of control and boron compound-added pulps of European aspen
Tablica 3. Svojstva pulpe proizvedene od drva europske jasike, kontrolnog uzorka pulpe i pulpe s dodatkom spojeva bora

Cooking *Kuhanje*	**Screened yield** *Prinos prosijavanja* %	**Reject** *Škart prosijavanja* %	**Total yield** *Ukupni prinos* %	**Kappa number** *Kapa broj*	**Viscosity** *Viskoznost* cm^3/g	**Brightness** *Sjajnost* %
Control / *kontrolni uzorak*	53.6	0.2	53.8	15.0	959	26.8
4 % A	55.6	0.3	55.9	14.6	1002	26.0
8 % A	56.2	0.5	56.7	14.9	1056	25.8
Control / *kontrolni uzorak*	53.6	0.2	53.8	15.0	959	26.8
4 % B	55.9	0.6	56.5	15.3	1012	25.4
8 % B	56.4	1.9	58.3	21.3	1092	23.2
Control / *kontrolni uzorak*	53.6	0.2	53.8	15.0	959	26.8
4 % C	52.9	3.9	56.8	29.9	959	20.0
8 % C	46.3	16.8	63.1	37.9	1134	16.1

C pulps and higher kappa number of B pulps than that of the control pulp. The highest brightness increase of 6.8 % was found in the pulp when 8 % C was added. In the European aspen samples, brightness of handsheets decreased with the addition of all boron compounds (Table 3). The highest brightness loss of 39.9 % was determined in the pulp when 8 % C was added. These results show that the effect of A and C on brightness of handsheets depends on tree species.

For many years, digester additives such as anthraquinone (Gulsoy *et al.,* 2015), polysulfur, and sodium borohydride (Gulsoy and Eroglu, 2011) have been used to increase relatively low pulp yield of kraft method as shown in many studies. The screened pulp yield of boron compound-added pulps in both species increased with the increase of the added boron compound ratio (Figure 2). The pulp yield increases can be explained by the prevention of degradation reactions, such as peeling and alkaline hydrolysis, when boron compound was added during cooking. The highest screened yield in European black pine and European aspen was 54.1 % and 56.4 %, respectively, when 8 % B was added to the pulp of both species. However, the screened pulp yield of European aspen decreased with the addition of C, because the defibration point has not been reached. On the other hand, the total yield of pulps increased with the addition of all boron compounds to both species. The highest total yield values of European black pine and European aspen samples were 55.7 % and 58.3 %, respectively, when 8 % B was added to the pulp of both species.

When comparing the screened yield vs kappa No, boron addition clearly results in increased yield at a given kappa number for softwood (Figure 3a). For hardwood, the yield increases when A and B are added. Addition of C decreases the yield (Figure 3b). However, this is because the defibration point has not been reached, and the reject content is much higher when cooking with C.

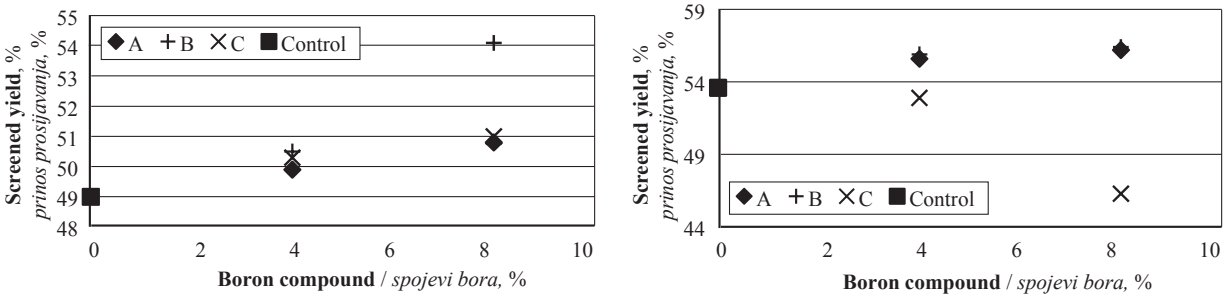

Figure 2 Effect of boron compounds on screened yield of pine (a) and aspen (b) pulps
Slika 2. Utjecaj spojeva bora na prinos prosijavanja pulpe od drva (a) bora i (b) jasike

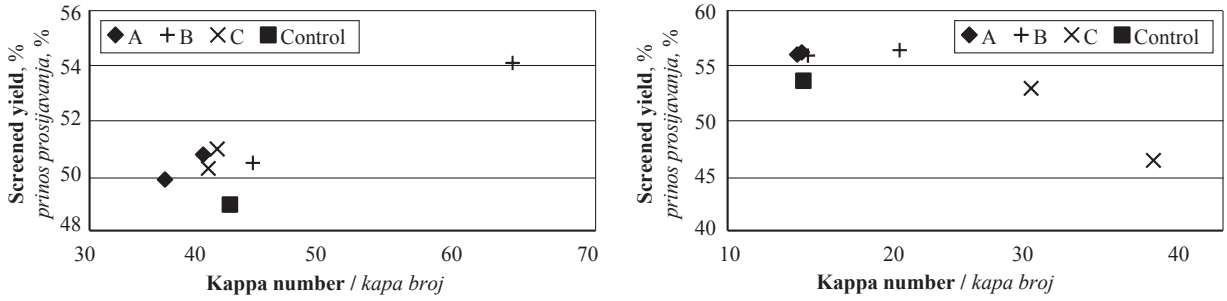

Figure 3 Relationship between screened yield and kappa number of pine (a) and aspen (b) pulps
Slika 3. Odnos između prinosa prosijavanja i kapa broja pulpe od drva (a) bora i (b) jasike

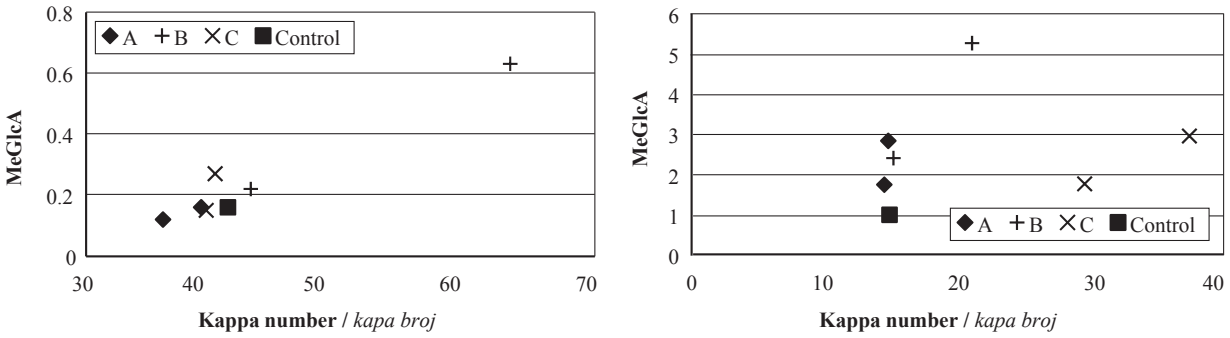

Figure 4 Relationship between MeGlcA and kappa number of pine (a) and aspen (b) pulps
Slika 4. Odnos između količine MeGlcA i kapa broja pulpe od drva (a) bora i b) jasike

The reject ratio of pulp provides information related to the pulping efficiency and penetration of the cooking liquor into wood chips. In the European black pine samples, the addition of A caused the decrease of reject ratio, while the addition of B and C resulted in the increase of reject ratio compared to control pulp. In the European aspen samples, the reject ratio of the pulp increased with the addition of all boron compounds. The highest reject ratios of European black pine and European aspen samples were 1.6 % and 16.8 % when 8 % B and 8 % C were added to the pulp, respectively. High reject ratio of 3.9 % was also determined when 4 % C was added to the pulp of European aspen. These results showed that the addition of C to the cooking liquor of European aspen samples slows the penetration of the cooking liquor into wood chips. In this case, longer cooking time is required to reach defibration point.

During the kraft pulping process, 40 % of European aspen and 50 % of European black pine polyoses were lost. Boron compounds, B (4-8 %) and A (8 %), slightly improved the stability of polyoses. As known, in softwoods Mannose are dominant units (20-25 %), and in hardwoods Xylose (15-30 %) are dominant units. This can also clearly be seen from Table 4. The effect of boron compounds on the stability of these units showed varieties. Except C and 4 % B, all boron compounds had a positive effect on the Mannose units in European black pine. The 8 % B showed a 15 % increase in the stability. Likewise, in the European aspen boron compounds, 4-8 % B and 8 % A enhance the Xylose stability. Hexuronic acids (Glucoronic and Galacturonic acids), except 4-0-MeGlcA, were totally destroyed during the pulping process. However, the addition of boron compounds increased the stability of 4-0-MeGlcA, especially in the aspen pulp, e.g. B increased acid by 28 % compared to the control sample.

When boron compounds are added to hardwood, higher amounts of MeGlcA groups are created, although xylan remains more or less the same. For softwood, the MeGlcA content seems to depend on the degree of delignification (Figure 4a), which is not the case for hardwood (Figure 4b).

All boron compounds added to kraft cooking liquor of European black pine chips led to the decrease in strength properties of the resulting pulp (Figure 5-9). The highest and lowest strength losses were determined when 8 % C and 4 % B were added to the pulp, respectively. The strength properties of boron compounds-added pulps of European aspen were determined to be higher than those of control pulp (Figure 5-9). The highest strength increases were determined in the pulp when 8 % B was added.

Tensile index of handsheets in European black pine samples decreased with the addition of boron compounds, while tensile index of handsheets in European aspen samples increased (Figure 5). In the European black pine samples, the highest tensile index loss of 13.8 % (from 102.6 N·m/g to 88.4 N·m/g) was determined when 8 % C was added to the pulp. On the other hand, tensile index losses caused by the addition of 4 % A to the pulp were not statistically significant (P>0.05). Furthermore, tensile index losses increased with increasing the addition of boron compound ratios. In the European aspen, the highest tensile index increase of 24.0 % (from 70.1 N·m/g to 86.9 N·m/g) was found when 8 % B was added to the pulp. Also, tensile index increases correlated positively with the increasing addition of boron compound ratios, excluding C additions (Figure 5). This result can be explained by the increase of the hemicellulose content of the pulp obtained when 8 % B was added to the cooking liquor. The strength improving effect of hemicellulose is attributed to its high hydrophilic properties. Due to the high affinity for water, hemicellulose improves swelling of the fiber. Thus, fiber flexibility increases with increasing the hemicellulose content (Shin and Stromberg, 2006; Danielsson, 2007). Flexible fibers enable larger contact areas with neighboring fibers. This results in stronger inter-fiber bonds (Forsström *et al.,* 2005), and higher tensile index (Santos *et al.,* 2008).

The stretch ratio of handsheets obtained from boron compounds-added pulps of European black pine was determined to be lower than that of the control pulp (P<0.05). The highest stretch loss of 7.5 % (from % 2.28 to % 2.11) was determined when 8 % C was added to the pulp. In the European aspen, stretch ratio of handsheets increased with the addition of boron compounds, except for pulps where C was added. The highest stretch increase of 6.3 % (from % 2.08 to % 2.21) was found in the pulp when 8 % B was added. However, stretch ratio of handsheets decreased by 9.1 % with the addition of 8 % C (Figure 6).

As can be seen in Figure 7, TEA of handsheets in European black pine samples decreased with the addi-

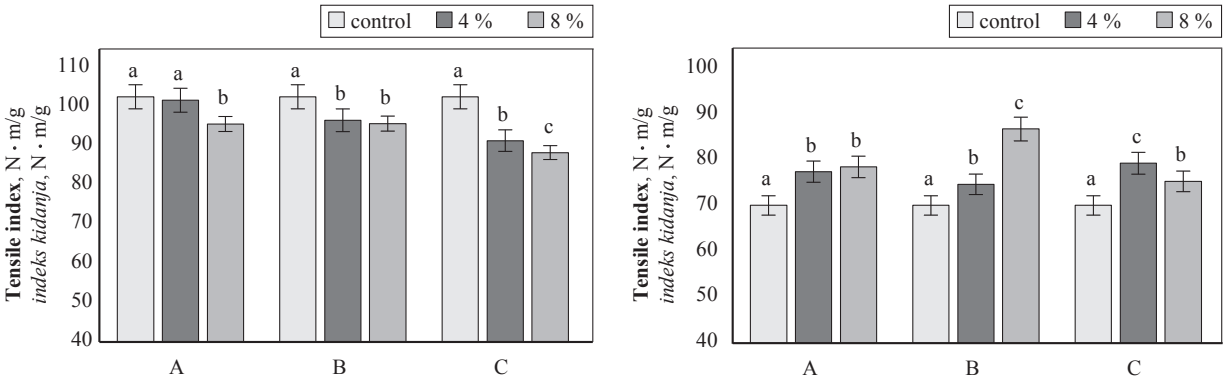

Figure 5 Effect of boron compounds on tensile index of pine (a) and aspen (b) handsheets
Slika 5. Utjecaj spojeva bora na indeks kidanja uzoraka papira od (a) bora i (b) jasike

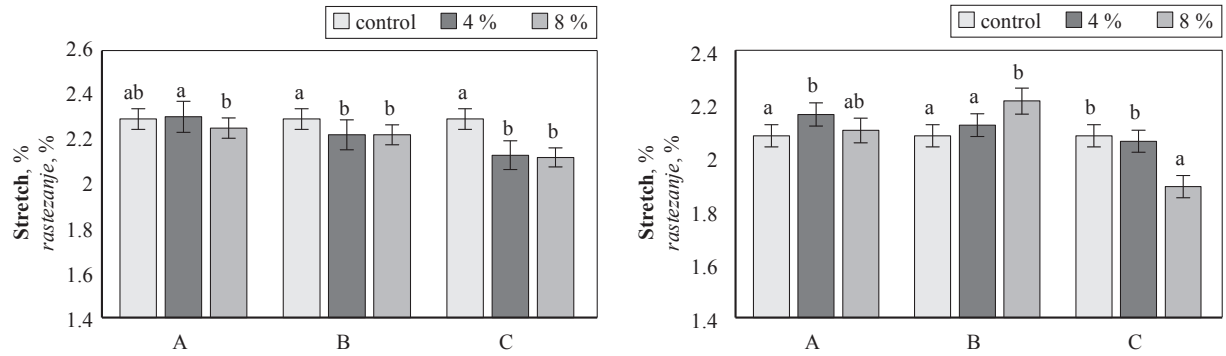

Figure 6 Effect of boron compounds on stretch of pine (a) and aspen (b) handsheets
Slika 6. Utjecaj spojeva bora na rastezanje uzoraka papira od (a) bora i (b) jasike

tion of boron compounds, while TEA of handsheets in European aspen samples increased, except when 8 % C was added to the pulp (6.5 % TEA loss). In the European black pine samples, the highest TEA loss of 18.6 % (from 119.3 J/m^2 to 97.1 J/m^2) was found when 8 % C was added to the pulp. On the other hand, TEA losses in the pulp when 4 % A was added were not statistically significant (P>0.05). In the European aspen, the highest TEA increase of 31.9 % (from 78.1 J/m^2 to 103.0 J/m^2) was found when 8 % B was added to the pulp.

The effects of boron compounds on tear index of handsheets are shown in Figure 8. It was observed that the tear index of handsheets of both species increased significantly (P<0.05) with the addition of boron compounds, except for the pulp of European black pine when C was added. In European black pine and European aspen, the highest tear index increases of 8.3 % (from 12.1 mN·m^2/g to 13.1 mN·m^2/g) and 9.6 % (from 7.3 mN·m^2/g to 8.0 mN·m^2/g), respectively, were found when 8 % A was added to the pulp. Xylan stability, known to have positive influence on tear index, could be the effect of this increase (Schwikal *et al.,* 2011; Tavast *et al.,* 2014).

The correlation between the addition of boron compounds and burst index of handsheets is presented in Figure 9. In European black pine, burst index of handsheets decreased when boron compounds were added to the cooking liquor. However, burst index losses were not statistically significant (P>0.05) when 4 % A was added to the pulp. The highest burst index loss

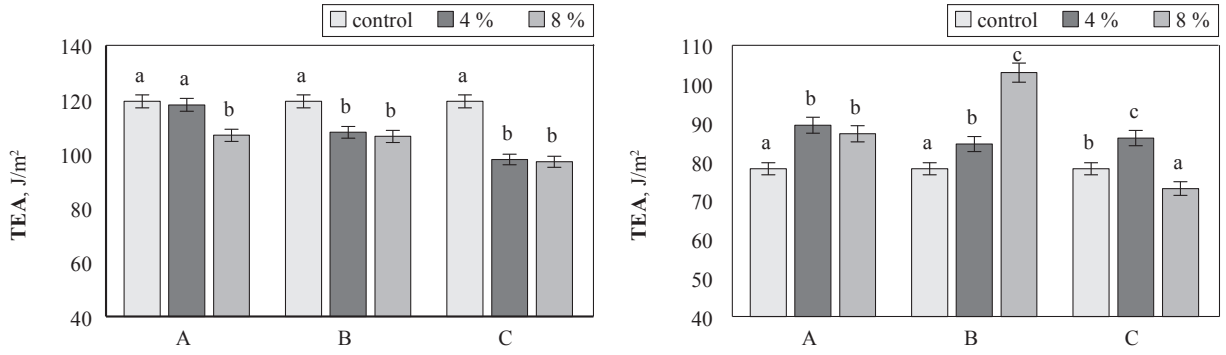

Figure 7 Effect of boron compounds on TEA of pine (a) and aspen (b) handsheets
Slika 7. Utjecaj spojeva bora na prekidnu jakost uzoraka papira od (a) bora i (b) jasike

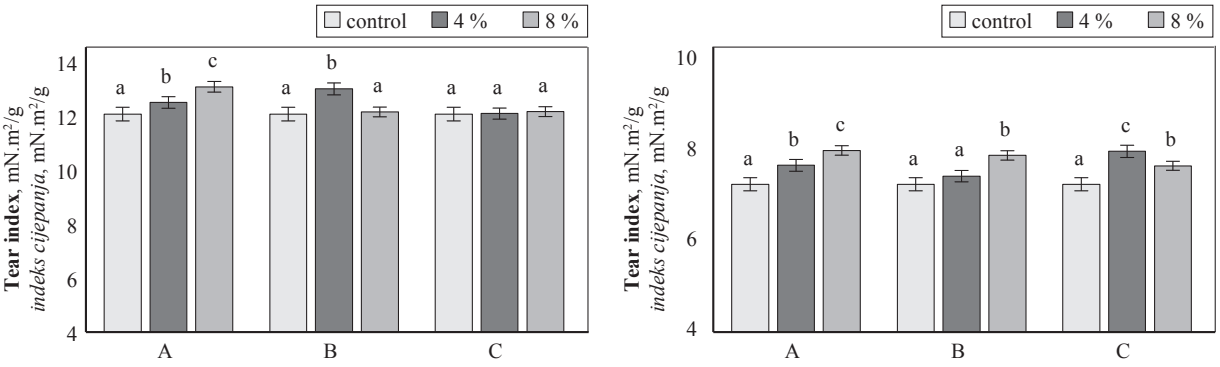

Figure 8 Effect of boron compounds on tear index of pine (a) and aspen (b) handsheets
Slika 8. Utjecaj spojeva bora na indeks cijepanja uzoraka papira od (a) bora i (b) jasike

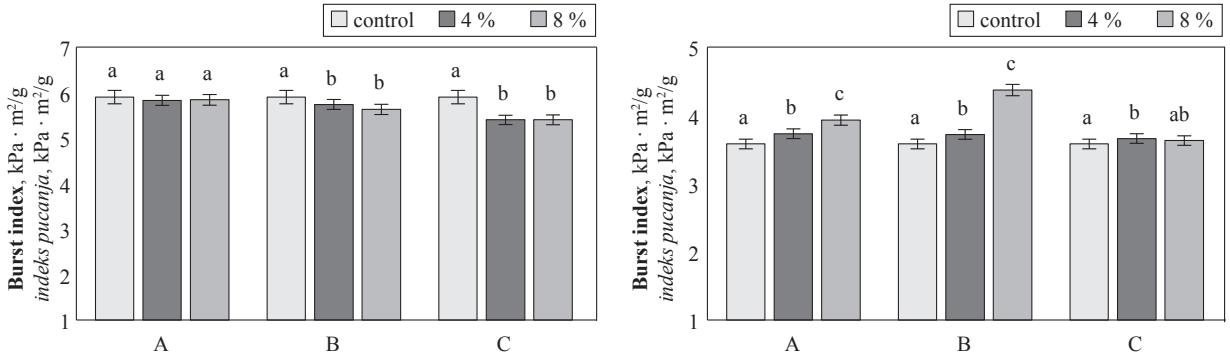

Figure 9 Effect of boron compounds on burst index of pine (a) and aspen (b) handsheets
Slika 9. Utjecaj spojeva bora na indeks pucanja uzoraka papira od (a) bora i (b) jasike

of 8.5 % (from 5.90 kPa·m²/g to 5.40 kPa·m²/g) was determined when 4 % and 8 % C was added to the pulp. In European aspen, burst index of handsheets significantly increased ($P<0.05$) with the addition of boron compounds (Figure 9). The highest burst index increase of 22.1 % (from 3.58 kPa·m²/g to 4.37 kPa·m²/g) was found when 8 % B was added to the pulp. The results are compatible with Table 4. Strength increases can also be attributed to more hemicellulose retention during cooking (Molin and Teder, 2002).

Table 4 Amount of sugar units in wood and pulps of European black pine and European aspen (mg/g dry sample).
Tablica 4. Količina jedinica šećera u drvu i pulpi europskoga crnog bora i europske jasike

Samples *Uzorci*	**Ara**	**Rha**	**Xyl**	**Man**	**Gal**	**Glc**	**GlcA**	**GalA**	**4-0-MeGlcA**	**Total**
Black Pine wood / *drvo crnog bora*	15.5	1.77	49.5	96.4	19.1	29.1	3.89	10.5	8.60	234
Black Pine pulp control *kontrolni uzorak pulpe od crnoga bora*	6.05	0.08	35.1	33.2	6.44	37.6	0	0	0.16	119
Black Pine 4 % A / *crni bor 4 % A*	4.69	0.04	35.3	33.6	4.74	34.2	0	0	0.12	113
Black Pine 8 % A / *crni bor 8 % A*	4.32	0.03	37.1	33.8	4.19	33.3	0	0	0.16	113
Black Pine 4 % B / *crni bor 4 % B*	4.76	0.07	36.0	32.8	4.74	32.3	0	0	0.22	111
Black Pine 8 % B / *crni bor 8 % B*	5.94	0.04	38.6	38.1	5.31	30.5	0	0	0.63	119
Black Pine 4 % C / *crni bor 4 % C*	6.04	0.05	37.1	31.6	5.61	33.6	0	0	0.15	114
Black Pine 8 % C / *crni bor 8 % C*	4.70	0.04	38.0	31.8	4.18	32.6	0	0	0.27	112
Aspen wood / *drvo jasike*	3.66	3.91	151	10.9	6.20	23.2	4.67	14.0	15	232
Aspen pulp control *kontrolni uzorak pulpe od jasike*	0	0.40	101	1.66	1.34	31	0	0	1.01	137
Aspen 4 % A / *jasika 4 % A*	0	0.31	100	1.61	1.09	29.3	0	0	1.76	135
Aspen 8 % A / *jasika 8 % A*	0	0.35	107	1.91	1.19	29.3	0	0	2.85	143
Aspen 4 % B / *jasika 4 % B*	0	0.41	105	1.95	1.26	31.2	0	0	2.42	142
Aspen 8 % B / *jasika 8 % B*	0	0.43	106	1.99	1.19	25.9	0	0	5.28	141
Aspen 4 % C / *jasika 4 % C*	0	0.30	97.4	1.66	1.10	29.5	0	0	1.78	132
Aspen 8 % C / *jasika 8 % C*	0	0.35	96.3	1.62	1.37	26.8	0	0	2.97	129

4 CONCLUSIONS
4. ZAKLJUČAK

The results of this study showed that using of A, B, and C in kraft pulping provides various benefits. The addition of 8 % B to the cooking liquor of both species resulted in higher screened and total yield increases compared to A and C. Also, the addition of 4 % A and 8 % B to the cooking gave the best results in European black pine and European aspen, respectively, in terms of paper strength properties. Especially, the addition of 8 % B significantly increased the pulp strength in European aspen samples.

Similar results were observed in the chemical composition. In European black pine kraft pulp, 8 % B increased the stability of Xylose, Mannose and 4-0-MeGlcA units compared to control samples. The addition of 8 % B and 8 % A also has a positive effect and enhanced the amount of sugar units and total amount of hemicelluloses in aspen. As mentioned before, this positive effect directly influenced the strength properties of handsheets.

The boron compounds used in this study are cheaper than other digester additives, such as $NaBH_4$ and AQ. After some additional studies e.g. using of these boron compounds with other lignocellulosic materials, their effects on recovery cycle and recoverability of boron compounds, these boron compounds (A, B and C) can be used in pulp mills.

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Cone Morphology as a Diagnostic Attribute of Resonant Properties of Standing Spruce Wood

Morfologija češera kao dijagnostički atribut rezonantnih svojstava drva smreke

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ABSTRACT • *The paper presents the results of dendroacoustic research and statistical and correlation analysis. The insights of heuristic identification based on biotechnology law are also given with the aim of defining the relationship of wood resonant properties with the form of seed scales of spruce growing in the Kama-Volga region of Russia.*

Key words: *sonorous spruce, cone biomorphology, wood macrostructure, density, sound velocity, acoustic constant, dendroacoustic indices identification*

SAŽETAK • *U radu su prikazani rezultati dendroakustičkog istraživanja te statističke i korelacijske analize. Autori također daju uvid u heurističku identifikaciju utemeljenu na primjeni biotehničkog zakona radi definiranja odnosa rezonantnih svojstava drva i oblika ljuske smrekova sjemena u ruskoj regiji Kama-Volga.*

Ključne riječi: *akustična smreka, biomorfologija češera, makrostruktura drva, gustoća drva, brzina zvuka, akustična konstanta, identifikacija dendroakustičkih indikacija*

1 INTRODUCTION
1. UVOD

It is well-known that the ways to diagnose and select wood for manufacturing both musical instruments and acoustic panels for theatres and conservatories (Fedyukov *et al*., 2011) can be conventionally classified into direct and indirect.

Direct methods are based on determining dendroacoustic indices with the help of ultrasonic and other instruments for measuring sound velocity in wood, its frequency-amplitude characteristics, and a number of other physical and mechanical properties (Bucur, 2006; Fedyukov and Makaryeva, 1992). Based on the results obtained, the main criterion of 'musicality' of the material, i.e. its acoustic constant of sound propagation K, is defined. In many countries, $K \geq 12$ $m^4/kg \cdot cm$ is accepted for resonant wood.

Direct methods involve some technical difficulties in conducting studies in the forest and are still used primarily in the laboratory environment.

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Indirect methods are based on visual tree assessment with respect to its species and biomorphological features, such as branching type and crown shape, bark color and structure, stem habit (Bagayev and Alexandrov, 1976; Gavris, 1938; Pchelin, 1961; Redulescu, 1969).

It is impossible to find reliable data on the way these attributes were used by Stradivari and other masters of the Old Italian school in the selection of wood for manufacturing unique musical instruments. However, it is wrong to exclude this, as later and modern ways of visually estimating the resonance quality of standing tree wood applied the attributes mentioned above.

Visual appearance and conditions of a tree

According to modern masters, a spruce tree selected for manufacturing musical instruments should meet the following requirements:
- be absolutely vertical;
- have symmetric, narrow and spiry crown;
- have a cylindrical trunk and branchless zone no less than 5-6 meters;
- not contain other visible defects and damages.

Thicker trunks are in demand: if the diameter at breath height is less than 35 cm, i.e. at the age of less than 100-120 years, the use of such a tree as a source of resonant material is considered counterproductive.

A Rumanian scientist, V. Grapini (1967), gives more detailed data for resonant spruce:
- the crown is in the form of a column, almost symmetric, gradually decreases from the basis to the top at an angle of 30-40° and is formed by thin branches oriented mainly downwards;
- the branches from the third part of the middle and the bottom of a crown are attached to the trunk at an angle of 30-40°; large branches are arranged in clusters;
- the second order branches are rather rare, thin, long, hanging down, ash-gray-green;
- the third order branches are also rare, thin, but light green.

A lot of individual masters also consider descending branches to be an attribute of a resonant spruce. The fact that it 'is not warped' is especially valued. It is determined by attentive inspection of a tree with regard to clusters arrangement, bark cracks, etc., which requires considerable experience.

Bark structure and color

These morphological attributes of spruce are often used by masters selecting the material for manufacturing musical instruments from the root and round assortments. However, there is no general opinion about any characteristic attribute that can be undoubtedly acceptable as diagnostic.

This is probably related to strong variability of the above attributes, which also correlate with biological and ecological features of individual trees (Onegin and Kuznetsova, 2012; Pat. № 2130611 RF, 1999; Pchelin, 1961; Pravdin, 1975).

Absence of a uniform method to give the diagnostics of acoustic properties of standing tree wood is caused by the elements of subjectivity in conclusions based on the results of observations by different authors, especially, in different soil, climate and geographical environment.

Selector Yablokov (1962) recommends to select spruce trees with smooth bark forms (low land, in his opinion) as resonant; this coincides with the opinion of Gavris (1938). Bagayev and Alexandrov (1967), who believe that smooth-barked spruce-trees with narrow crown of both Norway and Siberian species have the best resonance.

Sankin (1972) conducted a thorough research on determining the relations between the variability of macrostructure, anatomical structure of wood, physical, mechanical and acoustic properties depending on spruce tree bark appearance (rhytidoma) in the environment of the Vologda Region of Russia. Having studied the trees of two groups (with platy and scaly bark), he came to a conclusion that spruce with scaly bark is preferable due to greater genetic plasticity. Meanwhile, the relationship of late wood percentage and annual ring width with wood density, dynamic modulus of elasticity and acoustical constant is equally strongly expressed in both groups.

Basing on such biomorphological preconditions, some scientists consider that there is a certain phylogenetic biotype of resonant spruce (Grapini, 1967; Pravdin, 1975).

Further to the above review of scientific literature, it can be concluded that hereditary genetic factors prevail in the formation of wood quality. They manifest themselves in quite a sustained way through external biomorphological features of cones, including their size and seed scale forms (Bakshayeva, 1966; Danilov, 1943; Mamayev and Nekrasov, 1968; Onegin and Kuznetsova, 2012; Pchelin, 1961; Redulescu, 1969; Yablokov, 1962).

It is necessary to bear in mind that each master chooses, at his discretion, the characteristic attributes of wood 'musicality' as a criterion for visual estimation of the resonant raw material. The criteria used by individual masters or representatives of different schools are different as a rule, with rare exceptions.

In this connection, uniform diagnostic attributes should be established for mathematical modeling and development of an objective way of selection of standing spruce trees with resonant properties in certain nature-climate environment of its growth.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

Searching an objective biomorphological attribute, we chose the seed scale form from the middle part of the cone.

Danilov's (1943) and Bakshayeva's (1966) methods are taken as a basis for drawing up a matrix of initial data to differentiate the trees inside a population with respect to seed scale form, which results from their characteristic features.

Danilov's method is most detailed. It is based on the analysis of four attributes:

Table 1 Tree classification
Tablica 1. Klasifikacija stabala

Attributes / *Atributi*	**Symbolic representation** / *Simbolički prikaz*	
1. Scale edge angle / *rubni kut ljuske*	Mean	
up to 45°	30°	I
45°-75°	60°	II
75°-105°	90°	III
105°-135°	120°	IV
135° and more	150°	V
2. Angle form of a scale edge / *oblik kuta na rubu ljuske*	Obtuse / *tup*	O
	Acute, round /*oštar, okrugao*	A/R
3. Nature of generatrix / *izgled izvodnice*	Smooth-margined / *glatko omeđena*	SM
	Serrated / *nazubljena*	S
4. Outside edge type / *izgled vanjskog ruba*	Sinuous / *vijugav*	SN
	Even / *ravan*	E

a) b)

Figure 1 Spruce seed scale form: a) Siberian spruce; b) Norway spruce
Slika 1. Oblik ljuske sjemena smreke: a) sibirska smreka; b) norveška smreka

a) degree of scale edge tapering - the main attribute (5 classes);
b) angle form of a scale edge (obtuse, acute, round);
c) nature of generatrix (smooth-margined or serrated);
d) outside edge type (straight, sinuous, even).

The method of tree classification according to the above attributes is presented as a whole in Tab. 1.

As an example, *Siberian spruce* is characterized by rounded smooth-margined seed scales of cones, while the *Norway spruce* is characterized by lengthened, a little bit pointed hackly ones (Fig. 1).

However, hybrid forms of spruce can be met more often, and they can be classified in detail using the method given.

Using Bakshayeva's method of classification, it is comparatively simple and easy to translate the data into mathematical language. It is based on defining the factor through the ratio of height *H* of the seed scale top part to its width in the widest part *l* (Fig. 2).

All the variety of seed scales is reduced to three groups depending on the size of the factors obtained: groups I, II and III at $H / l = 1.32$ (*Norway spruce*); = 0.09 (*Siberian spruce*) and = 1.0 (hybrid form).

Based on cone classification according to Bakshayeva's method (1966), it was possible to establish unequivocally that 39 model trees selected were *Siberian Spruce*, and Danilov's classification made it pos-

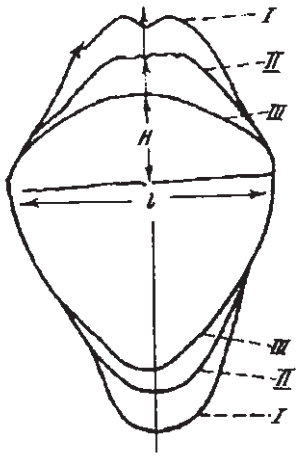
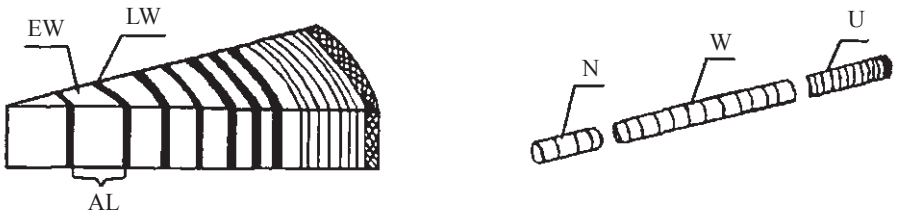


Figure 2 Scheme of spruce seed scale form variability according to Bakshayev (1966)
Slika 2. Shema varijabiliteta oblika ljuske smrekova sjemena prema Bakshayevu (1966.)



a) b)

Figure 3 General view of wood macrostructure according to the trunk zone: a - elements of wood macrostructure (EW - early wood; LW - late wood; AL - annual ring); b - scheme of core division according to zones (N – near-core zone; W – working zone; U – undercork zone)
Slika 3. Prikaz makrostrukture drva u zoni debla: a) elementi makrostrukture drva (EW – rano drvo, LW – kasno drvo, AL – god); b) shema osnovne podjele prema zonama (N – zona blizu srca, W – radna zona, U – zona ispod pluta)

sible to classify 10 types of combination of seed scale attributes distributed as follows:

Types of frequent occurrence, pcs.	Types of rare occurrence, pcs.
1. III (O+S+E) -8	1. IV (O+S+E) - 4
2. IV (A/R+SM+E) - 7	2. III (A/R+S+E) - 1
3. III (O+S+SN) - 6	3. III (O+SM+E) - 1
4. III (A/R+SM+E) - 5	4. II (O+S+SN) - 3
	5. IV (A/R+S+E) - 3
	6. V (A/R+SM+E)- 1

According to this classification, hybrid form trees having cone seed scales with obvious attributes of *Siberian spruce* are of frequent occurrence.

This was confirmed by the research site. The fact of the matter is that model trees were taken from ripe spruce groves of the Kirov Region in a taiga zone. In this region, *European spruce* is hardly ever met in its pure form, but rather in the hybrid form (Ovechkin, 1982).

Cross-section radial cores, 4.0 mm in diameter, selected with an increment borer at breath height from 16 model trees, after being felled, were the material for the research into dendroacoustic parameters. Simultaneously, diameters of trunks at relative heights of 0.2 H, 0.5 H and 0.7 H, as well as tree crown parameters (extension, first alive knot fastening height, etc.) were defined.

The method of determining the resonance of wood in standing trees against the cores has been introduced abroad (Bucur, 2006) and in Russia (Fedyukov and Makaryeva, 1992) rather recently.

As a rule, wood structure is different along the length of a radial core and, accordingly, wood physical and mechanical parameters are also different in medullary parts and in sapwood. This distinction is obvious even with a naked eye, first of all, judging from wood macrostructure: narrow annual rings are in trunk peripheral zone and wide ones are close to juvenile central zone (Fig. 3, a).

Rather homogeneous wood between undercork and near-core zones is usually taken for deck manufacturing. In view of this, the study was focused on the part of the trunk along the radius, conditionally denoted on cores as a 'working' zone (Fig. 3, b).

Basic physical and dendroacoustic properties of wood – humidity, density, macrostructure, and ultrasound velocity – were defined in laboratory environment. Recalculation of the results obtained against standard humidity of wood, $W = 12$ %, was made. The complex research is presented in Fig. 4.

The macrostructure of wood was studied with electronic dendrometer, which operates on the basis of

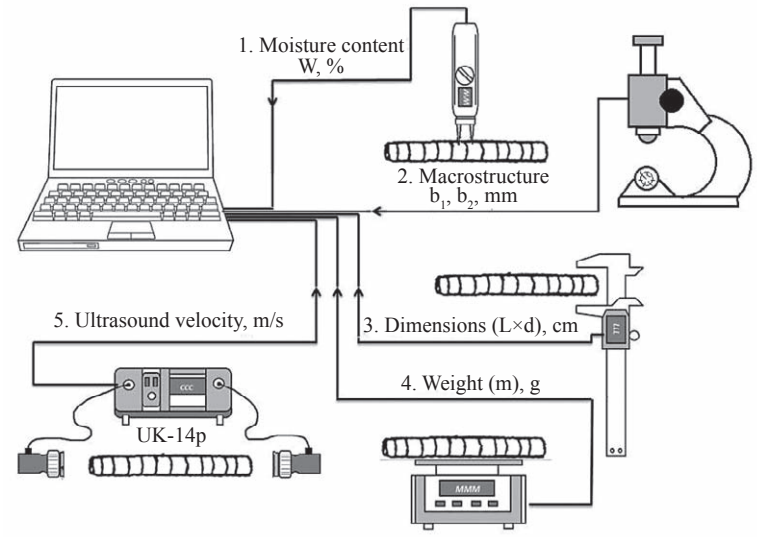


Figure 4 Principle diagram of experimental measurements
Slika 4. Shematski prikaz eksperimentalnih mjerenja

assessment of early (b_1) and late (b_2) wood zone width in annual rings according to their microhardness (Pat. № 2130611 RF., 1999).

Sound velocity in wood *(C)* was assessed with a pulse ultrasonic method by fixing the time *(τ)* of elastic longitudinal wave propagation along the sample *(l)*:

$$C = l/\tau \quad (1)$$

It should be noted that the device was equipped with a 60 kHz piezoelectric transducer, which is optimal for wood study.

Based on sound velocity in the material, *C*, and its density, it is possible to assess Young's dynamic modulus, *E,* on the basis of the following ratio:

$$C = \sqrt{\frac{E_{dyn}}{\rho}}, \quad \text{then } E_{dyn} = C^2 \cdot \rho \quad (2)$$

It is known that, today, acoustic constant of sound propagation *(K),* suggested by the Academician N.N. Andreyev, is accepted as the basic criterion of '*musicality'* of a given material in many countries:

$$K = \sqrt{\frac{E}{\rho^3}} \quad (3)$$

Threshold value is $K \geq 12.0$ m^4/kg·cm for resonant wood in a longitudinal direction along fibers, and under cross-section radial measurements $K \geq 3.5$ m^4/kg·cm (Ugolev, 2001).

Small transformations and joint solution of equations 2 and 3 allow to define the size of acoustical constant *K* through *C* and *ρ*:

$$\begin{cases} K = \sqrt{\frac{E}{\rho^3}} \Rightarrow K = \frac{C}{\rho} \\ C = \sqrt{\frac{E}{\rho}} \end{cases} \quad (4)$$

Thus, the physical essence of resonant wood represents a *combination of incongruous properties,* i.e., high parameters of rigidity, sound velocity and low density.

Processing of statistical data for determining the relationship of the cones (seed scales) form with physical, mechanical and acoustic properties of wood was supplemented with heuristic identification of the results obtained with a general model (Mazurkin, 1989):

$$y = a_1 \exp(-a_2 i_f) + a_2 i_f^{a_4} \exp(-a_5 i_f) + a_6 i_f^{a_7} \quad (5)$$

where $a_1 \ldots a_7$ are regression coefficients (model parameters); i_f is cone seed scale form code (individual rank); y is theoretical value of physical, mechanical and acoustic properties of wood parameters.

According to this technique, coding of morphological attributes of cone seed scales for the specified trees is developed to perform further calculations on the basis of Danilov's classification. Values of attributes are classified by transition from the Norway spruce to Siberian spruce.

Attribute values were classified in accordance with the transition from Norway spruce to Siberian spruce.

Rank scale 1...40 (5×2×2×2) is theoretically possible. The present (specific) scale contains 10 positions, as many combinations of attribute values are absent in the growth environment researched (Tab. 2).

Integer scales i_f and I_f are four-factorial in the given coding, scale $I_f = 1 \ldots 40$ taking into account specific morphological variety of spruce features in different regions of the country.

Using PC and *Eureka* mathematical environment, the results of corresponding parameters identification were obtained. Parameters adequacy values according to model 5 are shown in Tab. 4.

Maximal residual ε_{max} was calculated according to the formula:

$$\varepsilon_{max} = \max\{\hat{y}_i - y_i\} \quad (6)$$

where $\hat{y}_i$, y_i are experimental and theoretical parameter values.

Table 2 Position rank scale according to spruce cone seed scales
Tablica 2. Rangiranje češera smreke prema obliku ljuski sjemenki

Specific rank *Specifični rang*	**General rank** *Opći rang*	**Scale form parameters** / *Vrijednosti parametara oblika ljuske*			
		Angle sharpness class *Klasa oštrine kuta*	**Apex type** *Oblik vrha*	**Generatrix nature** *Izgled izvodnice*	**Outside edge type** *Izgled vanjskog ruba*
1	9	II	obtuse / *tup*	serrated / *nazubljena*	sinuous / *vijugav*
2	17	III	«	«	«
3	18	III	«	«	even / *ravan*
4	20	III	«	smooth-margin / *glatko omeđena*	«
5	22	III	acute / *oštar*	serrated / *nazubljena*	«
6	24	III	«	smooth-margin / *glatko omeđena*	«
7	26	IV	obtuse / *tup*	serrated / *nazubljena*	«
8	30	IV	acute / *oštar*	«	«
9	32	IV	«	smooth-margin / *glatko omeđena*	«
10	40	V	«	«	«

Note: Angle sharpness class value is 45 – 75° for class II; 75 – 105° for class III; 105 – 135° for class IV; more than 135° for class V./ *Napomena: Veličina kuta prema klasi oštrine jest 45 – 75° za klasu II; 75 – 105° za klasu III; 105 – 135° za klasu IV; više od 135° za klasu V.*

Maximal relative error Δ_{max} was calculated using the formula:

$$\Delta_{max} = 100 \frac{|\varepsilon_{max}|}{\hat{y}(\varepsilon_{max})} \quad (7)$$

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

Values of correlation coefficients *(R)* and correlation ratio *(η) of* dendroacoustic parameters and seed scales form, according to Bakshayeva (1966), are presented in Tab. 3.

According to the above table, there are certain relationships between a specific biomorphological attribute and the basic dendroacoustic parameters, all correlation coefficients being positive because the relationships are direct. However, the reliability of these relationships is less than 95 %; e.g. the relationship of correlation coefficients with seed scales form for *K* and *b* is only about 90 % reliable; as for *E* and *υ*, the reliability is much lower, and for *ρ* and *δ* it is close to zero.

The correlation ratio *η* against all parameters, except for *b,* is higher than the correlation coefficient *R.* Hence, a nonlinear relationship would be more appropriate than a linear one.

Table 3 Values of correlation coefficient (*R*) and correlation ratio (η) of dendroacoustic parameters and seed scale forms
Tablica 3. Vrijednosti koeficijenta korelacije (*R*) i omjera korelacije (η) dendroakustičkih parametara i oblika ljuske sjemena

Parameters / *Parametri*	***R***	***η***
Annual ring width *b* / *Širina goda, b*	0.599	0.593
Late wood proportion δ *Udjel kasnog drva,* δ	0.076	0.405
Density ρ / *Gustoća,* ρ	0.044	0.389
Ultrasound velocity υ / *Ultrazvučna brzina,* υ	0.460	0.593
Modulus of elasticity *E* *Modul elastičnosti, E*	0.408	0.482
Acoustical constant *K* *Akustična konstanta K*	0.565	0.767

In practice, when selecting a resonant raw material (standing tree), it should be noted that the correlation between acoustic constant coefficient and seed scales form (0.767) appeared to be maximum with high level of reliability (0.99 %).

Parameters adequacy values according to model 5 are shown in Table 4.

The results presented in Tab. 4 confirm that model 5 describes the relationship of scale form with parameters of physical, mechanical and acoustic properties of spruce wood, in this case with *δ*, *ρ*, *υ* and *K,* with rather small relative error Δ_{max} <10 % for practical purposes.

Basically, model 5 is characterized by three kinds of biotechnology law (Mazurkin, 1989). The first component describes the process of parameters *δ*, *ρ* and *υ* value recession in transition from Norway spruce to Siberian spruce. The width of annual rings depends on habitat conditions rather than on species diversity.

The second component of the model is characterized by stressful change of parameters *δ*, *b* and *υ.* Stressful influence of hybrid species strongly affects the width of annual rings and practically does not change the density. This fact does not mean the absence of relationship between wood density and width of annual rings; it mainly emphasizes the possibility of purposeful forming of resonant wood with specific macrostructure.

The third part of the model describes allometric growth of scale form influence.

Fig. 5 presents the graphs of parameters change depending on an integer scale i_f. Parameters *δ* and *b* change under the wave law (Fig. 5, a). Values ρ and υ (Fig. 5, b) are minimal at various codes (i_f = 7 and i_f = 3). Such unequal extremes of the graphs require accounting for the complex parameter *K,* which is defined as the *υ* / *ρ* ratio. Since i_f grows from 1 to 10, *K* value increases almost rectilinearly (Fig. 5, c).

Graph $K = f(i_f)$ shows that Siberian spruce has better resonant properties than Norway spruce. Sound velocity in a radial direction at breath height increases likewise.

The analysis of these graphs disproves the opinion of some researchers about the absence of heredi-

Table 4 Parameters adequacy values according to model 5
Tablica 4. Adekvatnost parametara prema modelu 5.

Parameters of models *Parametri modela*	**b, mm**	***δ*, %**	***ρ*, kg/m³**	***υ*, m/s**	***K*, m⁴/(kg·cm)**	***E*, kg/(m·s²)**
a_1	0	35.1	472.75	1640.3	3.0600	12.839
a_2	0	0.2605	0.01952	0.11238	0.01976	0.2509
a_3	8.284	0.003841	0	1.7693	0	0
a_4	4.3490	15.718	0	6.2744	0	0
a_5	2.7136	3.4173	0	1.0045	0	0
a_6	0.4641	0.2698	0.009907	3.0075	0.05205	0.4639
a_7	0.5469	2.0025	5.2846	2.4915	1.2503	1.3910
ε_{max}	0.203	1.365	22.61	100.6	0.243	1.94
Δ_{max}, %	12.3	5.72	5.23	7.10	7.04	21.0

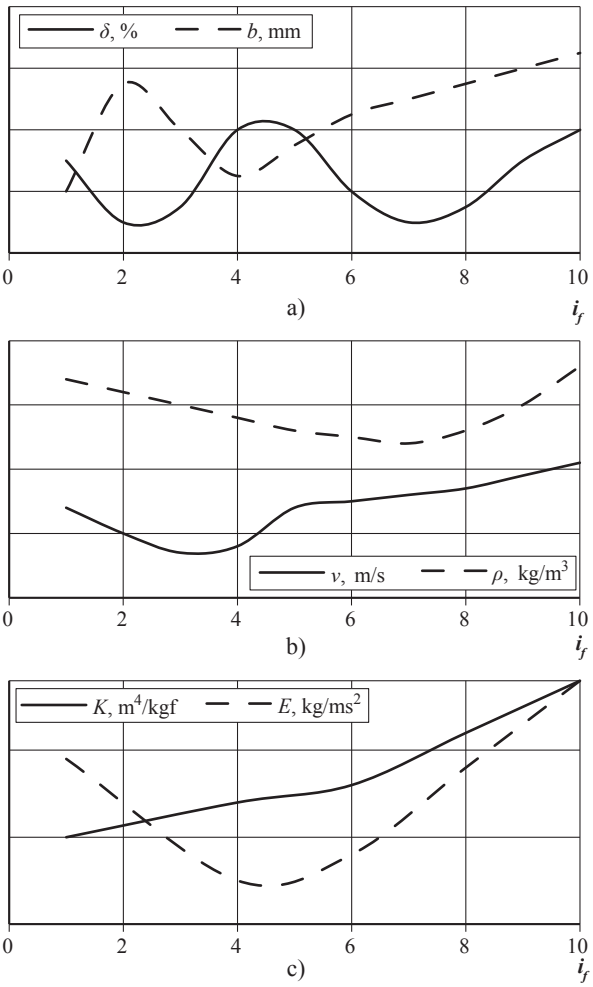


Figure 5 Parameters change depending on integer scale i_f
Slika 5. Promjena parametara ovisno o cijeloj vrijednosti i_f

tary-genetic factor role in the formation of wood resonant properties and, accordingly, their transfer to subsequent generations of spruce trees, saying that '*a resonant spruce is usual spruce wood that happened to grow in a certain specific environment'* (Onegin and Kuznetsova, 2012).

It is important to note that the probability of the occurrence of the best resonant properties in spruce is observed at $\upsilon > 1{,}400$ m/s. Further modeling of υ change depending on other factors, b and δ in particular, made it possible to derive the equation:

$$\vartheta = \left(1{,}165.67 + 8{,}352.49b\frac{\delta}{100}\right)\exp\left(-1.4626\right) \cdot \cdot \left(b\frac{\delta}{100}\right)^{0.3381} \quad (8)$$

Model (4) describes the law of aperiodic motion with fast attenuation under the influence of late wood as a damper of sound velocity in radial direction. Thus $\varepsilon_{max} = 17{,}278$ m/s; Δ_{max}=11.3 %.

The constant component of sound velocity (1,376.25 m/s) and influence of annual ring average width are taken into account under the biotechnology law in the model

$$\vartheta = 11{,}376.25 + 8{,}355.32b^{26.1478}\exp\left(-10.0818 \cdot b\right) \quad (9)$$

where $\varepsilon_{max} = 149.92$ m/s; Δ_{max}=9.82 %.

The graph in Fig. 6.a clearly illustrates a significant increase of sound velocity under $b > 1$ mm.

According to the complex law of aperiodic motion, the model for defining wood density (Fig. 6, b) is obtained as follows:

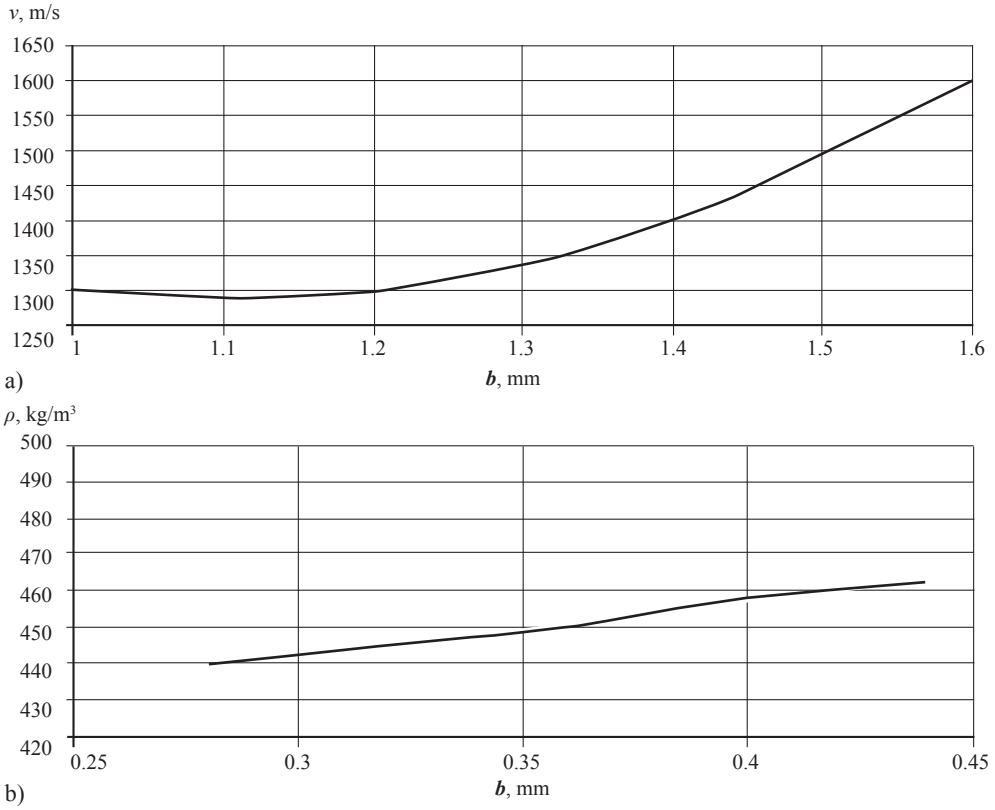


Figure 6 Dynamics of sound velocity (a) and density (b) depending on wood annual ring width
Slika 6. Dinamika brzine zvuka (a) i gustoće (b) ovisno o širini goda

$$\rho = (450 + 8359.05 \cdot b\frac{\delta}{100})\exp\left(-2.6014 \cdot b\frac{\delta}{100}^{0.3130}\right) - 0.09229 \cdot b^{1.3332} \quad (10)$$

where ε_{max} = 33.90 m/s; Δ_{max}=8.01 %.

A more simple aperiodic model for density is described by the equation:

$$\rho = (450 + 8359.05 \cdot b_d)\exp\left(-2.9520 \cdot b_d\right)^{0.3643} \quad (11)$$

where ε_{max} = 38.21 m/s; Δ_{max}=8.01%.

Models 9 and 11 are adequate at the 95 % level of reliability.

4 CONCLUSIONS
4. ZAKLJUČAK

In conclusion, the main results of the research can be summarized as follows:

1. Seed scales form of spruce is a rather significant biomorphological attribute describing genetic and, to a certain extent, phytocenotic predisposition of a tree to forming resonant wood with good acoustic properties.

2. Hybrid forms have lower acoustic parameters of wood than pure forms of Norway or Siberian spruce, resonant properties improving in the process of transition from Norway spruce to Siberian spruce.

3. Close correlation between the basic physical, mechanical and acoustic parameters of wood remain even against the background of its genetic and phytocenotic (ecological) variability.

4. Spruce seed scales form can be a characteristic attribute for non-destructive diagnostics of standing tree resonant properties.

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The Influence of Radial Slots on Dynamic Stability of Thermally Stressed Circular Saw Blade

Utjecaj radijalnih utora na dinamičku stabilnost termički napregnutog lista kružne pile

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ABSTRACT • *The influence of temperature distribution, temperature difference between the rim and centre of the saw blade and the number and size of radial slots on the dynamic stability of the circular saw blade was analysed in this work. The optimum number and size of radial slots for a circular saw blade with a diameter of 300 mm and a thickness of 2.18 mm is determined according to the least favourable temperature distribution and temperature difference. The critical rotational speed and lateral stiffness at the rim of the saw blade are considered as criteria for dynamic stability. According to the mentioned criteria, it was found that the optimum number and length of radial slots is 6 and 30 mm, respectively. In some cases, longer radial slots would further increase the critical rotational speed, but would also greatly decrease the lateral stiffness of the saw blade.*

Keywords: *circular saw blade, finite element method, radial slots, critical rotational speed, temperature distribution*

SAŽETAK • *U radu je analiziran utjecaj raspodjele temperature duž radijusa lista pile, temperaturne razlike između ruba i središta lista pile te utjecaj broja i veličine radijalnih utora na dinamičnu stabilnost kružne pile. Optimalan broj i veličina radijalnih utora za kružnu pilu promjera 300 mm i debljine 2,18 mm određuje se prema najmanje povoljnoj raspodjeli temperature i temperaturnoj razlici. Kritična brzina vrtnje i lateralna krutost na rubu lista pile smatraju se kriterijima za dinamičku stabilnost. Prema navedenim kriterijima, utvrđeno je da je optimalan broj radijalnih utora šest, a duljina radijalnih utora 30 mm. Dulji radijalni utori u nekim bi slučajevima dodatno povećali kritičnu brzinu vrtnje, ali bi se uvelike smanjila lateralna krutost pile.*

Ključne riječi: *kružna pila, metoda konačnih elemenata, radijalni utori, kritična brzina vrtnje, raspodjela temperature*

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1 INTRODUCTION
1. UVOD

In the past, a lot of research was focused on the stability of circular saw blade, which is one of the most frequently used woodworking tools. When cutting wood, 12 % of the wood is converted into chips and a further 7 % is lost due to planing required because of rough surfaces caused by low-quality sawing (Schajer and Mote, 1983). To increase the efficiency of circular sawing, manufacturers of circular saw blades tend to make thin and stable circular saw blades.

The stability of circular saw blades has been investigated since the 19th century when Kirchoff, in 1850, published his work about oscillation of elastic discs (Lamb and Southwell, 1921). The first researchers also included Lord Rayleigh (Rayleigh, 1945), who published the work entitled The Theory of Sound in 1877, also describing the vibration of circular discs.

However a more thorough research of the stability of circular saw blades appeared in the 80s and 90s, when the dynamic stability of circular saw blades was analysed by many authors (Mote and Szymani, 1977; Szymani and Mote, 1977; Leu and Mote, 1984; Schajer, 1986; Holøyen, 1987; Hutton, 1991; Nishio and Marui, 1996).

Some authors analysed the influence of rolling on the stability of circular saw blades (Szymani and Mote, 1974; Schajer and Mote, 1983, 1984; Stakhiev, 1999, 2003; Cristovao *et al.* 2012; Zhang *et al.* 2014; Li *et al*., 2015a, 2015b; Li *et al.* 2016; Li and Zhang, 2017), while others focused on the development of new geometries and modifications of circular saw blades (Beljo-Lucic and Goglia, 2001; Wasielewski *et al.,* 2012; Droba *et al.,* 2015; Kaczmarek *et al.,* 2016a). In addition, new methods for the verification of dynamic properties of circular saw blades emerged (Orlowski *et al.,* 2007; Vesely *et al.*, 2012; Svoren *et al.,* 2015; Kaczmarek *et al.,* 2016b; Skoblar *et al.,* 2016).

Despite the development of new geometries of circular saw blades, the conventional circular saw blade with radial slots, which compensate the compression of thermal stresses, remains the most common design of circular saw blades. To improve the stability, the impact of temperature distribution and radial slots on the dynamic behaviour of circular saw blades has been analysed by many authors (Mote and Nieh, 1973; Yu and Mote, 1987; Ishihara *et al.,* 2010; Ishihara *et al.,* 2012; Yuan; 2012). Some of them investigated the influence of temperature differences between the rim and centre of the saw blade on the dynamic stability of the saw blade, while others analysed how the saw blades could be stabilised by the guides (Mote *et al.,* 1981; Schajer, 1986; Hutton, 1991).

In addition to the above studies of temperature differences between the rim and centre of the saw blade, an important factor is also the shape of temperature distribution which can be more or less favourable or unfavourable to the dynamic behaviour of the circular saw blade. In wood cutting, the rim of the saw blade has a higher temperature than the rest of the blade, whereby the friction between the saw blade tooth and newly formed chips causes the heating of the rim. In certain cases, the centre of the saw blade is also heated due to the friction in the bearings, especially in long lasting processes, but the temperature is much lower than that at the periphery of the blade.

Despite of numerous studies, there is a lack of research that would include interaction of temperature distribution, temperature difference between the rim and centre of the saw blade, and the number and size of radial slots. This fact is even more evident in circular saw blades available on the market and made by different manufacturers, where saw blades of the same dimension and intended for the same purpose are found to have a different number and size of radial slots. In view of the above mentioned facts, the purpose of this work is to investigate the interactions of these factors, and to determine the optimal number and size of radial slots in the circular saw blade.

2 MATERIAL AND METHODS
2. MATERIJAL I METODE

A circular saw blade with a diameter of 300 mm, bore diameter of 30 mm and thickness of 2.18 mm was modelled with the finite element method (FEM) using Ansys software. The saw blade had 60 teeth, 9 mm in height, and it was clamped with a flange of 75 mm in diameter, which equals ¼ of the saw blade diameter and thus represents the minimum allowable flange diameter. The density of the steel was 7850 kg/m^3, Young modulus of elasticity 200 GPa, Poisson ratio 0.3, and Coefficient of Thermal Expansion $1.2\text{x}10^{-5}$ K^{-1}. The FEM model had a mesh with around 14400 elements, where default values were used for mesh generation. The saw blade had 4 to 6 radial slots of 15 mm to 35 mm in length, with increments of 5 mm.

The internal stresses due to temperature distribution has been incorporated in the saw blade, where (0, 40, 80 and 120) °C temperature differences between the rim and centre of the saw blade were used.

The finite element method modal analysis of the circular saw blade, incorporating internal stresses due to temperature distribution, was performed for all combinations of the number and length of the slots and temperature differences.

First the natural frequencies of the stationary saw blade were calculated, and then the calculation was repeated by incorporating additional internal stresses due to rotation, where the saw blade rotated at a rotating speed of 100 rps. In the latter case, the natural frequencies of the rotating saw blade were higher than in the case of the stationary saw blade.

By using the natural frequencies of the rotating and stationary saw blades, the rotational stiffness coefficient K can be calculated for each of the vibration modes, using Eq. 1 (Mote and Szymani, 1977),

$$K = \frac{\nu_{\mathrm{m,n}}^2 - \nu_{\mathrm{m,n}}^{(0)\,2}}{\nu_{\mathrm{rot}}^{\,2}} \qquad (1)$$

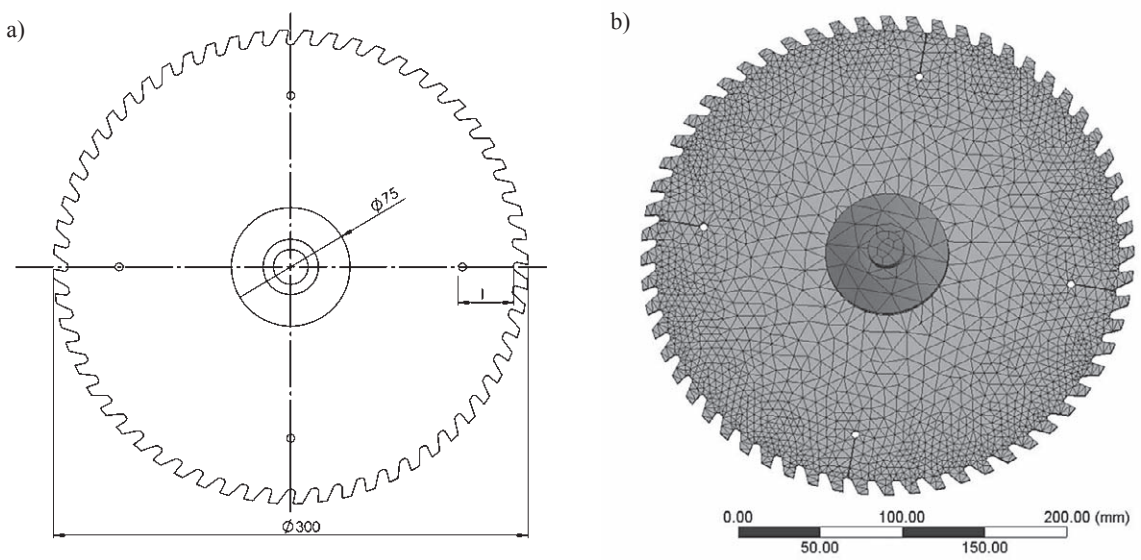

Figure 1 Modelled saw blade. a) Saw geometry, b) Mesh used for computation of FEM
Slika 1. Model lista kružne pile: a) geometrija lista, b) mreža za primjenu metode konačnih elemenata

where K is the rotational stiffness coefficient, $\nu_{m,n}$ the natural frequency (Hz) of the rotating saw blade for the vibrational mode with m nodal circles and n nodal diameters, $\nu_{m,n}^{(0)}$ is the natural frequency for the stationary saw blade for the vibrational mode with m nodal circles and n nodal diameters and ν_{rot} is the rotational speed.

The critical rotational speed ν_{crit} was calculated for vibrational modes with nodal diameters ranging between 0 and 6 from the calculated rotational stiffness coefficient K and natural frequencies of the stationary saw blades $\nu_{m,n}^{(0)}$, using Eq. 2 (Mote and Szymani, 1977),

$$\nu_{crit} = \frac{\nu_{m,n}^{(0)}}{\sqrt{n^2 - K}} \qquad (2)$$

Since various vibrational modes have different critical rotational speeds, the lowest calculated value was taken for circular saw blade critical rotational speed.

The buckling temperature was also calculated for each combination of the number and length of the slots. Different authors cite various temperature distributions in the circular saw blade (Mote and Nieh, 1973; Mote *et al.,* 1981; Schajer, 1986), which may be more or less unfavourable in terms of stability of the saw blade, and depend on the working conditions, temperature of the surrounding air, dust suction velocity, convection between the saw blade and air and others. In order to determine the least favourable temperature distribution, 4 additional distributions for the same temperature difference (40 °C) between the rim and centre of the saw blade were used in addition to the temperature distribution of Skoglund (Kollmann and Cote, 1975), as shown in Figure 2. Then the buckling temperatures for the saw blade without and with four 20 mm slots were calculated for all 5 distributions. The least favourable distribution was taken for further analysis, i.e., distribution, where the buckling temperature was the lowest.

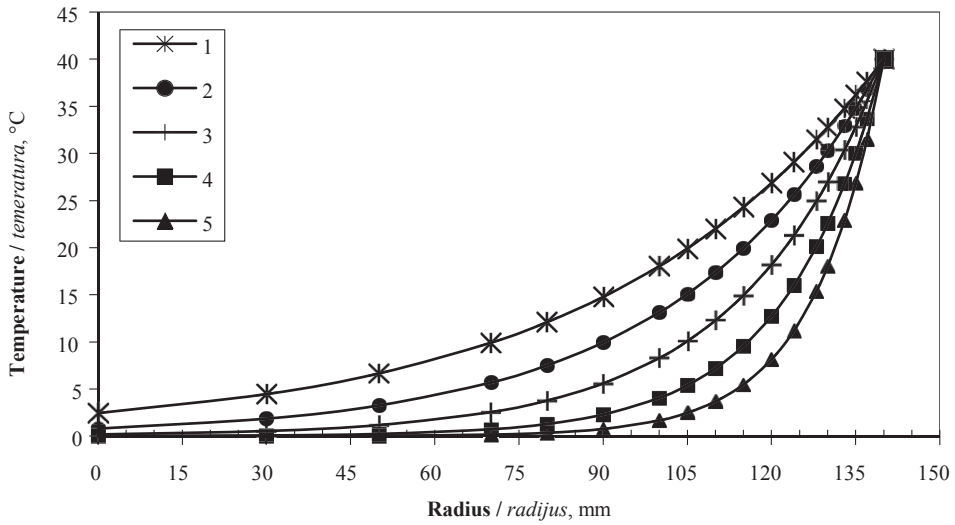

Figure 2 Temperature distributions for 40 °C temperature difference between the saw blade rim and centre. Distribution Nr. 5 was taken from Skoglund (Kollmann and Cote, 1975)
Slika 2. Raspodjela temperature pri temperaturnoj razlici od 40 °C između ruba i središta pile; raspodjela broj 5 preuzeta je iz Skoglunda (Kollmann i Cote, 1975.)

For each combination of the number and length of the slots, the lateral stiffness of the saw blade at the slot and between the slots was also calculated so that the saw blade was loaded with a force of 10 N at the place of interest, and the lateral stiffness *k* was calculated from the deformation.

3 RESULTS
3. REZULTATI

Table 1 shows the saw blade buckling temperatures for different temperature distributions shown in Figure 2, for a saw blade without slots and one with four 20 mm slots. It can be seen that temperature distribution No. 2 is the least favourable, since it has the lowest buckling temperature for the saw blade without slots as well as for the saw blade with slots, and it was used in all further analyses as the temperature distribution between the rim and centre of the saw blade as shown in Figure 3.

Table 1 Buckling temperatures for different temperature distributions for saw blade without slots and with four 20 mm slots
Tablica 1. Temperature izvijanja lista pile pri različitim raspodjelama temperatura za pilu bez utora i pilu s četiri utora duljine 20 mm

	Temperature distribution designation *Oznaka raspodjele temperature*				
	1	2	3	4	5
No slots *Bez utora*	106	99	100	107	119
4 x 20 mm	141	136	141	158	186

With increasing length of radial slots, the natural frequencies for vibrational modes from 0 to 6 nodal diameters are decreasing, the least for the vibrational

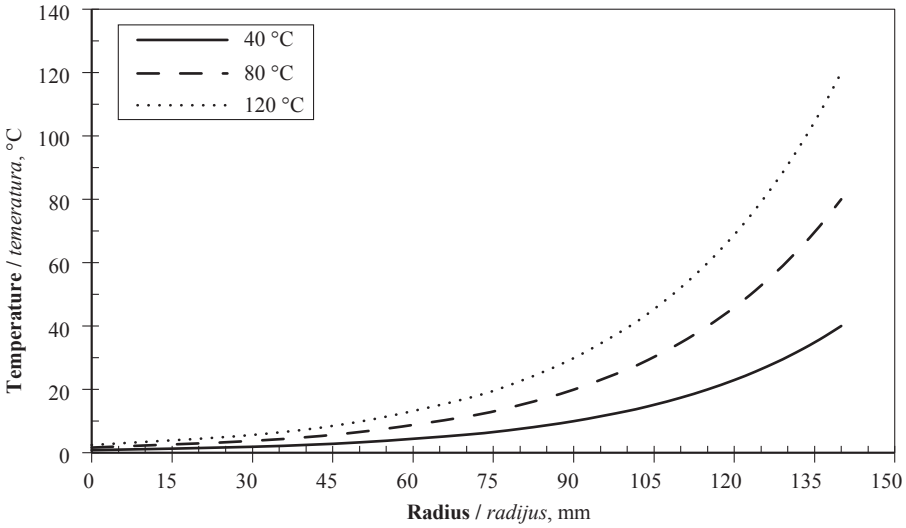

Figure 3 Temperature distributions for 40 °C, 80 °C and 120 °C temperature difference between the saw blade rim and centre
Slika 3. Raspodjela temperature pri temperaturnoj razlici između ruba i središta lista pile od 40, 80 i 120 °C

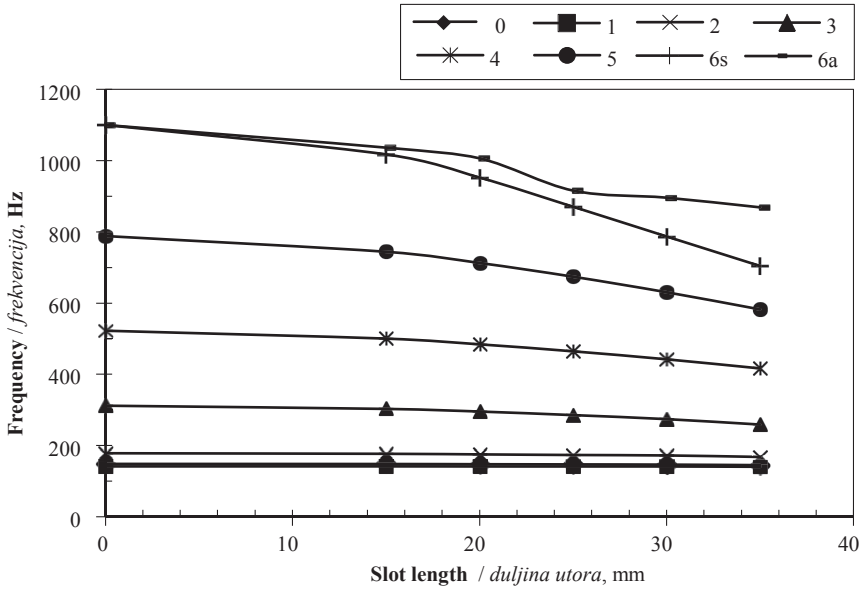

Figure 4 Natural frequencies for different slot lengths for a saw blade with 6 radial slots and zero to six nodal diameters. s-symmetrical mode, a-asymmetrical mode
Slika 4. Vlastite frekvencije lista pile sa šest radijalnih utora pri različitoj duljini utora i 0 – 6 čvornih promjera: s – simetrični mod, a – asimetrični mod

mode with 0 and 1 nodal diameters, and the most for the vibrational mode with 6 nodal diameters. This relationship for the circular saw with 6 radial slots and temperature difference of 0 °C is shown in Figure 4.

However, since the values of natural frequencies give less information than the values of critical rotational speed, the effects of temperature differences and slots on the critical rotational speed will be presented in this paper. Figure 5 shows the calculated critical rotational speeds for all combinations of number and length of the slots, as well as temperature differences between the rim and centre of the saw blade for vibrational mode with 3 nodal diameters, which was found to have the lowest critical rotational speed. It is clear that the critical rotational speed decreases with increasing temperature difference, both for the saw blade with no slots and for the saw blade with slots. It can also be seen that the critical rotational speed at a temperature difference of 0 °C greatly decreases with increasing length of the slots, namely from 136 rps in the case of the saw blade without slots to 112 rps for the saw blade with four 35 mm slots, or even down to 102 rps in the case of the saw blade with six 35 mm slots. However, in case of a temperature difference of 40 °C, the situation is different. In this case, the critical rotational speed for the saw blade without slots amounts to 105 rps, and remains more or less constant when the slot length is increased, while at the length of 35 mm, it is slightly reduced to 102 rps and 96 rps in the case of 4 and 6 slots, respectively.

Increasing the temperature differences between the rim and centre, the slots become even more necessary. At a temperature difference of 80 °C, the critical rotational speed of the saw blade without slots drops to 61 rps, whereas with increasing the slot length, the critical rotational speed increases to reach the maximum value of 91 rps and 92 rps for six 30 mm slots and 5 35 mm slots, respectively.

With further increase of the slot length in the saw blade with 5 slots, the critical rotational speed would

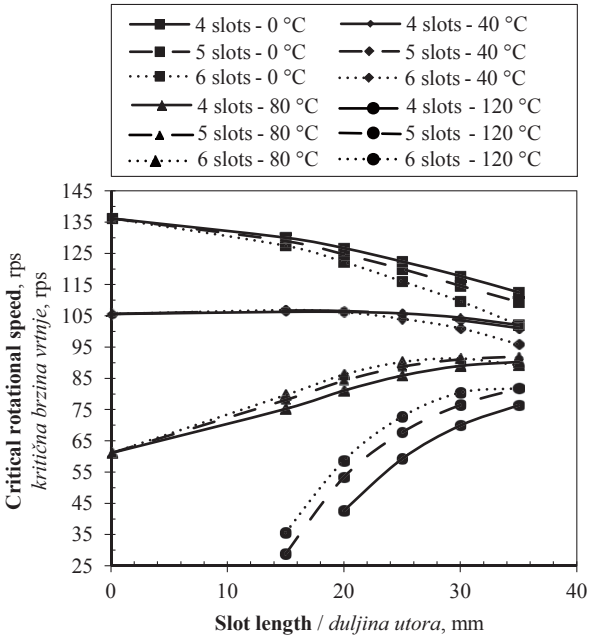

Figure 5 Critical rotational speeds of circular saw blades with different number and length of slots and various temperature differences

Slika 5. Kritične brzine vrtnje kružnih pila s različitim brojem i duljinom utora te pri različitim temperaturnim razlikama

continue to increase, but the lateral stiffness at the rim of the saw blade, as shown in Figure 6, must also be considered in the analysis. The figure indicates that the saw blade without slots has the maximum lateral stiffness amounting to 71 N/mm, whereas with increasing length and number of slots, the lateral stiffness decreases and it is lower near the slots than at the position between the slots. At six 30 mm slots, the lateral stiffness in the middle between slots and near the slot is 62 N/mm and 54.3 N/mm, respectively, whereas at five 35 mm slots, the lateral stiffness for the same location is

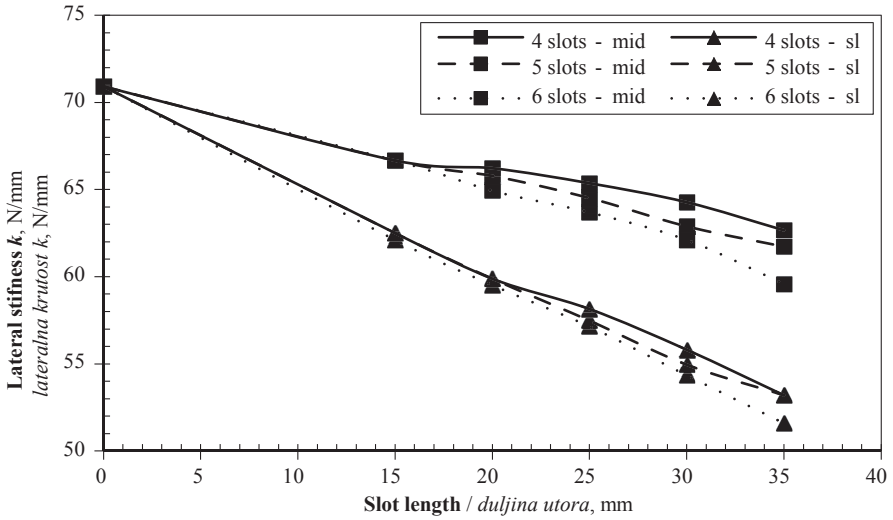

Figure 6 Lateral stiffness of the saw blade at temperature differences of 0 °C for a different number and length of slots. mid - position between the slots, sl - position near the slot

Slika 6. Lateralna krutost lista pile pri temperaturnim razlikama 0 °C za različit broj i duljinu utora: mid – položaj između utora, sl – položaj blizu utora

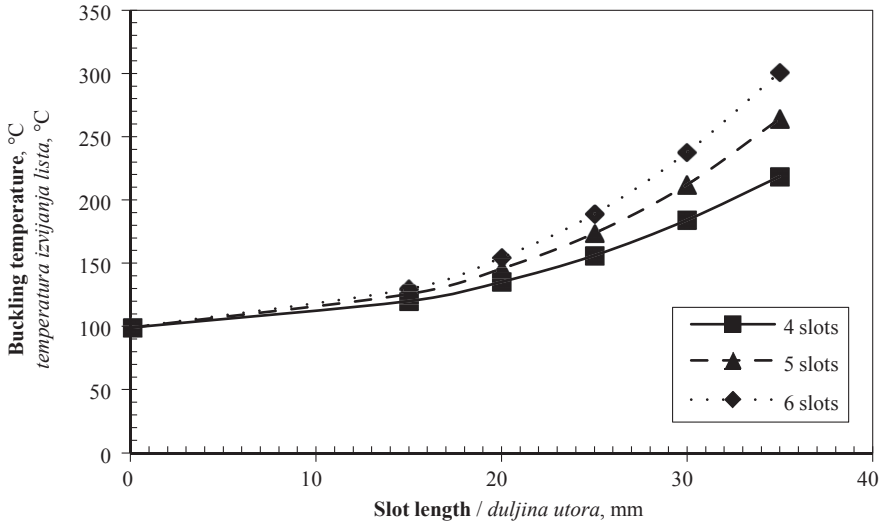

Figure 7 Saw blade buckling temperature for different number and length of slots
Slika 7. Temperatura izvijanja lista pile za različit broj i duljinu utora

61.7 N/mm and 53.2 N/mm. Taking into account the lateral stiffness, it follows that at a temperature difference of 80 °C, the configuration with six 30 mm slots is the most favourable combination, since this saw blade has a slightly greater lateral stiffness than that with five 35 mm slots. With further increase of the slot length in the 5-slot combination, the critical rotational speed would slightly increase, but the lateral stiffness of the saw blade would decrease significantly.

A similar situation occurs at the temperature difference of 120 °C. Here, the saw blade with six 30 and 35 mm slots has the maximum critical rotational speed of 80.4 and 81.8 rps, respectively, while in the case of five 35 mm slots, the critical rotational speed is 81.8 rps. As was the case with the temperature difference of 80 °C, the combination with six 30 mm slots is better than the combination with five 35 mm slots, due to slightly higher lateral stiffness, while the combination with six 35 mm slots is the worst because of much lower lateral stiffness, which amounts to 59.6 N/mm and 51.6 N/mm between the slots and near the slot, respectively.

In addition to the critical rotational speed and lateral stiffness, buckling temperatures at which the saw blade dishing occurs were also calculated. Figure 7 shows that, in the case of the saw blade without slots, buckling occurs at a temperature difference of 100 °C, which increases with the number of slots and slot length up to 231 °C at six 30 mm slots (Figure 8) or even up to 300 °C at six 35 mm slots.

Since the compressive stresses are the most significant for the saw blade stability, Figure 9 shows the tangential stresses in a stationary saw blade and in saw blade rotating at 100 rps for a temperature difference of 80 °C between the rim and centre of the saw blade. It can be seen that the tangential stresses are lower in the saw blade with six 30 mm slots than in the saw blade without slots.

The figure also shows lower compressive stresses of the rotating saw blade in the tangential direction due to the centrifugal effect, which is desirable, since the temperature difference between the rim and centre of the saw blade can be increased. However, it should be noted that, when the saw blade stops rotating, the tension due to the centrifugal effect disappears, and the saw blade could buckle. For this reason, it is important to analyse the saw blade in a worst case scenario, which is at rest, when there are no positive stresses caused by the centrifugal effect.

The distribution of internal stresses in the saw blade without slots and with six 30 mm slots at a temperature difference of 80 °C for a stationary circular saw blade is shown in Figure 10. It can be seen from the figure that the tangential stresses in the saw blade with slots are mainly compressive and amount to around 10 MPa in the radius range between 60 and 120 mm, which then increases to about 50 MPa under the teeth and up to 85 MPa under the gullets. In the saw blade without slots, the stress distribution is completely different: in the inner part of the blade up to the diameter of 90 mm, the stresses are tensile and amount to 20 MPa, while in the outer part of the blade, the stresses turn to compressive stress of up to 100 MPa below the teeth and up to 200 MPa under the gullets. The figure also shows the distribution of radial stresses, which are very similar for both saw blades and amount to around 50 MPa for saw

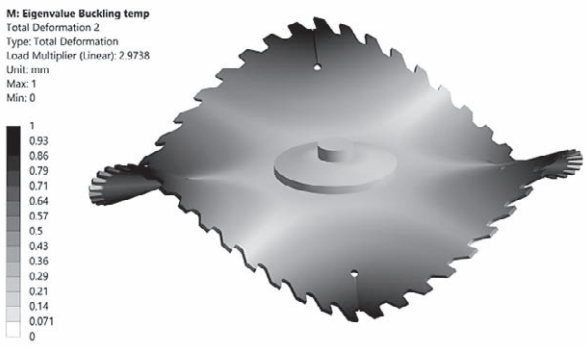

Figure 8 Saw blade buckling mode for 237 °C temperature difference and combination of six 30 mm slots
Slika 8. Mod izvijanja lista pile pri temperaturnoj razlici od 237 °C i kombinaciji od šest utora duljine 30 mm

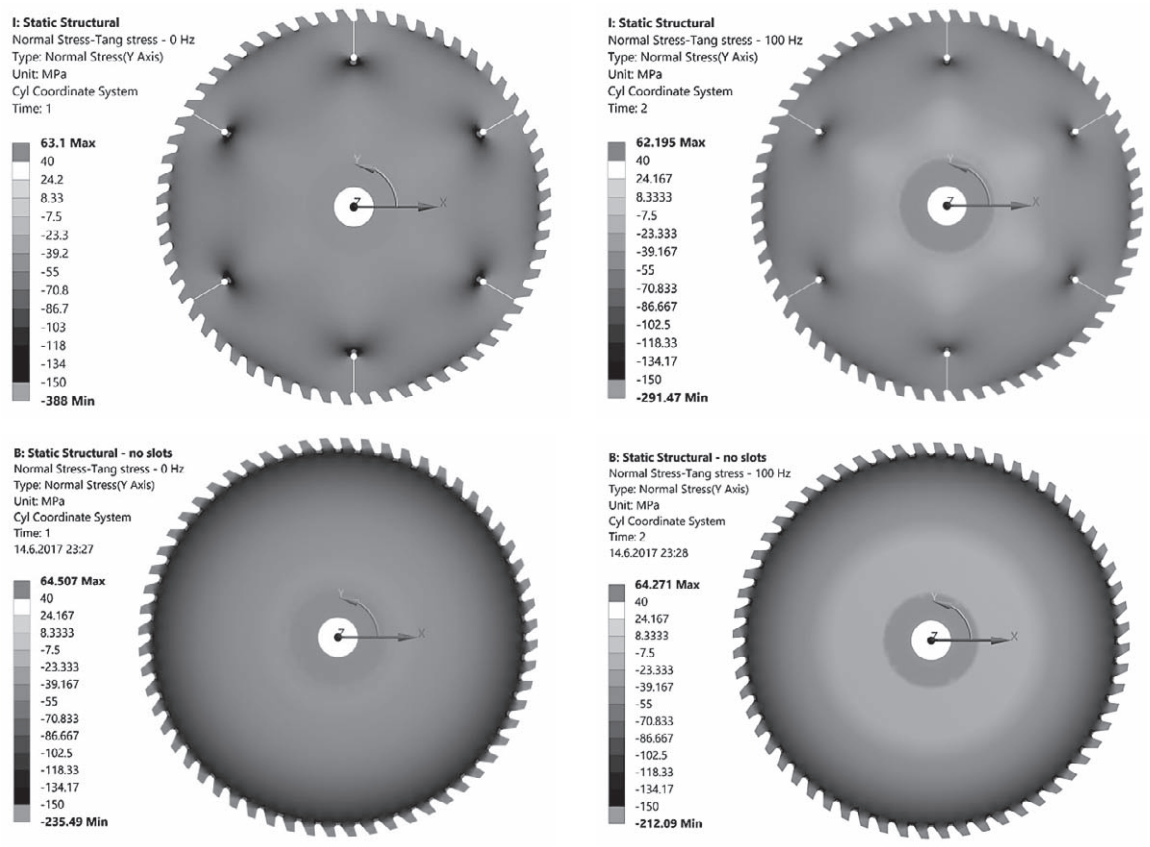

Figure 9 Tangential stresses of stationary and rotating saw blade at a rotational speed of 100 rps without slots and with six 30 mm slots and temperature difference of 80 °C
Slika 9. Tangencijalno naprezanje lista pile u mirovanju i rotirajućeg lista pri brzini vrtnje 100 okr./s bez utora i sa šest utora duljine 30 mm te pri temperaturnoj razlici od 80 °C

blades without slots and 35 MPa for saw blades with slots. The calculated compressive stresses are not significant in comparison to the yield strength of 75Cr1 steel, which is around 1400 MPa (Heisel, 2015). However, it should be emphasized that the saw blade is slim, and buckling may occur very quickly, particularly in the saw blade without any slots, where the buckling temperature of 100 °C was calculated.

4 CONCLUSION
4. ZAKLJUČAK

The research found that, for certain circular saw blade geometry, there is an optimum number of slots and slot length in case of temperature difference between the saw blade rim and centre. It was also found that different temperature distributions for the same temperature difference have various effects on the sta-

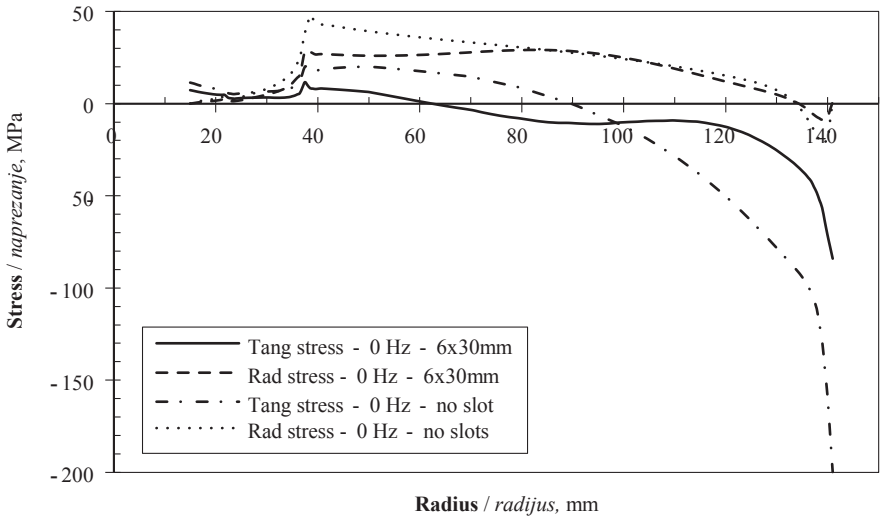

Figure 10 Tangential and radial stress distribution in the stationary circular saw blade without slots and with six 30 mm slots at a temperature difference of 80 °C
Slika 10. Tangencijalna i radijalna raspodjela naprezanja u listu kružne pile u mirovanju, bez utora i sa šest utora duljine 30 mm i pri temperaturnoj razlici od 80 °C

bility and critical rotational speed of the saw blade. The analysis first determined the least favourable temperature distribution, and then the optimum number of slots and slot length for various temperature differences for the same distribution. It was found that, for the temperature differences greater than 80 °C, the optimum combination for a circular saw blade with a diameter of 300 mm is six 30 mm slots. In the case of longer radial slots, the critical rotational speed begins to decrease due to lower lateral stiffness of the circular saw blade.

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Determination of the Effect of Liquid Glass (SiO_2) on Color Stability of Wood Stained by Natural Dyes

Određivanje učinka tekućeg stakla (SiO_2) na stabilnost boje drva obojenoga prirodnim bojama

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ABSTRACT • *In this exploratory study, the effect of liquid glass (SiO_2) treatment on color stability of wood stained by natural dyes was investigated. Mixing liquid glass with natural dyes produced durable, natural, and protective wood stain as expected. For natural dyes, Licorice (Glycyrrhiza glabra L.), Indigo (Isatis tinctoria L.) and pomegranate skin (Punica granatum L.) were chosen and their extracts were mixed with liquid glass and applied to Scots pine (Pinus sylvestris L.), chestnut (Castanea sativa Mill.) and mahogany (Khaya Ivorensis A. Chev.) specimens using immersion method. Coated wood specimens were tested to evaluate the protection degree of liquid glass + natural stains against discoloration using cold check test. The treated wood specimens were exposed to cold check test for different conditions; 1 h 50 °C (± 5), 1 h laboratory conditions, and 1 h -20 °C (± 2), for 20 cycles. As a result, the liquid glass treatment produced better performance against color change. However, for general definition, liquid glass was not found precisely effective on color stability.*

Key words: *Liquid glass, (SiO_2), natural plant dyes, wood protection, color stability, cold check*

SAŽETAK • *U provedenom je istraživanju ispitan učinak tekućeg stakla (SiO_2) na stabilnost boje drva obojenoga prirodnim bojama. Miješanjem tekućeg stakla s prirodnim bojama napravljen je trajni prirodni i zaštitni premaz za drvo, kako se i očekivalo. Za prirodne boje odabrani su sladić (Glycyrrhiza glabra L.), indigo (Isatis tinctoria L.) i šipak (Punica granatum L.), a njihovi su ekstrakti pomiješani s tekućim staklom i metodom uranjanja naneseni na uzorke drva običnoga bora (Pinus sylvestris L.), kestena (Castanea sativa Mill.) i mahagonija (Khaya Ivorensis A. Chev.). Na tako obrađenim uzorcima drva, primjenom testa hladne provjere, istražen je zaštitni utjecaj premaza od tekućeg stakla i prirodne boje na promjenu boje obrađenih uzoraka drva. Obrađeni su drvni uzorci bili izloženi testu hladne provjere u različitim uvjetima: 1 h pri 50±5 °C, 1 h pri laboratorijskim uvjetima i 1 h pri -20±2 °C u 20 ciklusa. Rezultati istraživanja pokazali su da je obrada tekućim staklom imala pozitivan učinak na zaštitu boje drvnih uzoraka obojenih prirodnim bojama, odnosno da nije došlo do promjene boje. Međutim, općenito se može zaključiti da rezultati istraživanja nisu dali uvjerljiv dokaz učinkovitosti tekućeg stakla na stabilnost boje obojenog drva.*

Ključne riječi: *tekuće staklo (SiO_2), prirodne biljne boje, zaštita drva, stabilnost boja, hladna provjera*

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1 INTRODUCTION
1. UVOD

Volatile organic compounds (VOCs) are chemicals used to manufacture and maintain building materials, interior furnishing, cleaning products, and personal care products. "Volatile" means that these chemicals evaporate or can easily get into the air at room temperature. "Organic" means that these chemicals are carbon based. The term "chemical emissions" refers to VOCs as they evaporate into the air from products (Greenguard, 2016).

VOCs are emitted as gases from certain solids or liquids. VOCs include a variety of chemicals, some of which may have short- and long-term adverse health effects. The majority of VOCs found in the indoor environments originate from building materials, indoor furnishings, cleaning supplies, consumer products and processes, such as printing, cooking, hobbies, cleaning, interior renovations and pesticide applications.

The human health risks can be decreased using organic chemicals instead of highly toxic, petroleum based ones. Human health risks may include: eye, nose and throat irritation, headaches, loss of coordination and nausea, damage to the liver, kidney and central nervous system; also some organics can cause cancer in animals, some are suspected or known to cause cancer in humans (EPA, 2016).

There are three main ways how people are exposed to chemicals: ingestion, dermal absorption, and inhalation. Ingestion occurs when materials including chemical content are swallowed or placed in the mouth. Dermal absorption occurs when chemicals come into contact with the skin. While these are both significant forms of chemical exposure, the majority of everyday chemical exposure occurs through the air we breathe in our homes, offices, schools and other indoor environments. As mentioned earlier in this paper, these airborne chemicals are commonly referred to as volatile organic compounds (VOC's). EPA's Office of Research and Development's "Total Exposure Assessment Methodology (TEAM) Study" found levels of about a dozen common organic pollutants to be 2 to 5 times higher inside homes than outside, regardless of whether the homes were located in rural or highly industrial areas (Dalsan, 2015; Greenguard, 2016).

Due to economical impacts, environmental concerns, and new regulations, paint and coating industries are significantly shifting toward water-borne formulations (Stoye *et al*., 2006; Dalsan, 2015). Nowadays, the interest in using water-borne paints or stains in furniture manufacturing has been significantly increased. Unfortunately, water-borne paints are not fully harmless because the colorants used in water-borne paints are frequently aniline based ones, where aniline is a toxic organic compound with the formula $C_6H_5NH_2$.

There is a variety of definitions like; "VOC Free Paint", "Zero VOC", "Green-Product" on paint bins. "Zero VOC" paint does not necessarily mean non-toxic, healthy, or safe. EPA allows the paint to be called "Zero VOC" even if the VOC content in it is actually not zero. EPA Method 24 allows for up to 5 g/L of VOCs as "Zero VOC" for oil-borne paints, 250 g/L as "Low-VOC" for latex paints, and 380 g/L, as "Low-VOC" for oil-borne paints (EPA, 2016).

As mentioned earlier in this study, VOCs are a cause of low indoor air quality. The United States Environmental Protection Agency (US EPA) recommended not using them in indoor environment". The synthetic dyes can be replaced with the natural ones to solve this problem. During the last few decades, growing interest in the use of natural colourants has been recognized, both in public awareness and scientific activity (Leitner *et al*., 2012; Khan *et al*. 2006). The majority of natural dyes are vegetable dyes from plant sources: roots, berries, bark, leaves, wood and other organic sources such as fungi and lichens. These alternative materials provide increased sustainability, renewable resources, environmentally friendly processing, reduced pollution, and green chemistry (Bechtold et al., 2003). Also, environmentally-friendly natural poisonous plant extracts, stains derived from natural dye plants, and water-based wood preservatives are being developed against wood damaging biotic and abiotic factors. There are scientific studies on using natural plant dye staff for wood materials. After applying natural dyes on wood specimens, color changing (Goktas *et al*., 2013; Peker, 2012; Goktas, 2009; Goktas, 2008[a]; 2008[b]), antimicrobial, and antifungal performances (Ozen, 2014) have been determined. Unfortunately, natural colorants and preservatives can be bleached and discolored by exposure to weather conditions. Therefore, introducing natural and durable colorant is a requirement that needs to be developed against bleaching and discoloration.

As a solution to this problem, applying liquid glass on wood materials was considered as a potential option. The liquid glass can be used to decrease the disadvantages of wood like lack of color stability and water interaction of wood (Lu *et al*., 2014). Also, another study showed that the addition of nano-SiO_2 modification to the wood structure provides decrease in external moisture penetration, which has a negative effect on color changes (Jiang *et al*., 2013). The liquid glass can be sprayed on the surface within seconds and can create an anti-microbial, easy-to-clean barrier that will last from one to several years, depending on the surface (Nanopool, 2012). In this study, the coated wood specimens were tested to evaluate the protection degree of liquid glass+natural stains against discoloration using cold check test.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Wood test specimens
2.1. Drvni uzorci

As wood material, Scots pine (*Pinus sylvestris*), chestnut (*Castanea sativa* Mill.), and mahogany (*Khaya Ivorensis A. Chev.*) wood specimens commonly used in furniture and decoration industries in Turkey

were chosen. The specimens were prepared from the sapwood parts of the first-class wood with smooth fiber, knotless and crack-free surfaces, no color and density differences, with annual rings perpendicular to the surfaces, in accordance with TS 2470 standards (2005).

In this study, the cold check test was used to observe and investigate the behavior of the finishing layer. The cold check test is a practical way to understand that the changes in finishing layer occured because of temperature changes (Wisnofurniture, 2013).

The cold check test specimens were prepared with dimensions of 100 mm x100 mm x10 mm and were kept under suitable temperature (20±2 °C) and suitable moisture (moisture of ±12 % and relative humidity of ±65 %) conditions until they became air-dried (the moisture value in furniture used under interior area conditions) in accordance with TS 2471, (2005).

2.2 Plant material and mordant agents
2.2. Biljni materijal i sredstva za fiksiranje boje

Plant materials were purchased from domestic markets located in Turkey. The Licorice (*Glycyrrhiza glabra* L.), Indigo (*lsatis tinctoria* L.) and Pomegranate Skin (*Punica granatum* L.) were chosen as natural dyes. In addition to creating affinity between dye and wood fibre, the use of mordants change the hue of certain dyes (Shahid, 2013). Different mordants used with the same dye may darken, brighten or drastically alter the final color of the dyed wood sample. The mordants used in this study were ferrous sulfate ($Fe_2(SO_4)_3.7H_2O$), aluminum sulfate ($Al_2(SO_4)_3.18H_2O$) and vinegar (Kimetsan Co.,Fersan Co./Turkey). Also, a synthetic dye (woodtex - Kayalar kimya Co./Turkey) has been used for comparison to natural dyes.

2.3 Extraction of dye
2.3. Ekstrakcija boje

A weighed amount of dry plant material was extracted with distilled water in a bath (Elmasonic X-tra 150 H). According to the standard procedure, the mass / volume ratio between plant material and liquid was 1:20; extraction was performed for approximately 180 min. at 45 °C. Due to the high liquor ratio, some manual stirring was applied to distribute the plant material homogenously in the liquid during the extraction period. The expected volume loss due to evaporation was compensated by the addition of water at the end of the extraction period to obtain the initial volume.

Aqueous solutions were mordanted by adding ferrous sulfate ($Fe_2(SO_4)_3.7H_2O$) 3 %, aluminum sulfate ($Al_2(SO_4)_3.18H_2O$) 5 %, and grape vinegar 10 % in order to stabilize the color of extracted dyes, ensure itsduralibilty on the applied material (to increase retention amount), and create color options. After mordanting, liquid glass was added to mordanted aqueous with 20 % by weight.

2.4 Dyeing experiments
2.4. Bojenje uzoraka

Air-dried wood specimens were placed into the dyebath container. The immersion method was applied for 60 min at 45 °C. Any extra solution left on the specimens was wiped with a clean cloth. Specimens were then left to air dry at 20±3 °C in a vertical position.

2.5 Cold check test
2.5. Test hladne provjere

The stain and liquid glass mixture treated wood specimens were exposed to cold check test for periods of 1 h 50 °C (± 5), 1 h laboratory conditions, and 1 h -20 °C (± 2), for 20 cycles according to ASTM D 1211-97 (2001).

2.6 Color measurements
2.6. Mjerenja boje

The colors of the cold check tested coated parts were identified prior to exposure using Konica Minolta CR–10 portable color reader device. Minumum four (4) repetitions (color measurmenets) were performed to analyze the colors on each specimen due to the non-homogenous color structure of wood. The identified color values were classified according to the coordinates Commission International de I'Eclaireage-CIELAB 1976 set in ISO 2470 standards (Figure 1). The obtained colors were indicated by numerical values of L, a, and b. Where; "L" indicates lightness from 0 % (black) to 100 % (white), "a" from green (-a) to red (+a), and "b" from blue (-b) to yellow (+b). Also, the coated parts were subjected to color measure prior to cold check test and stated as "color values prior to cold check".

2.7 Determination of color change values
2.7. Određivanje veličina promjene boje

In order to determine the color changes occured due to the cold check test cycle, Konica Minolta CR–1 (Japan) portable color reader device was used. Color changes were calculated with the following equations in accordance with ISO 2470 standards.

$$\Delta L^* = L^*_f - L^*_i \quad (1)$$

$$\Delta a^* = a^*_f - a^*_i \quad (2)$$

$$\Delta b^* = b^*_f - b^*_i \quad (3)$$

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (4)$$

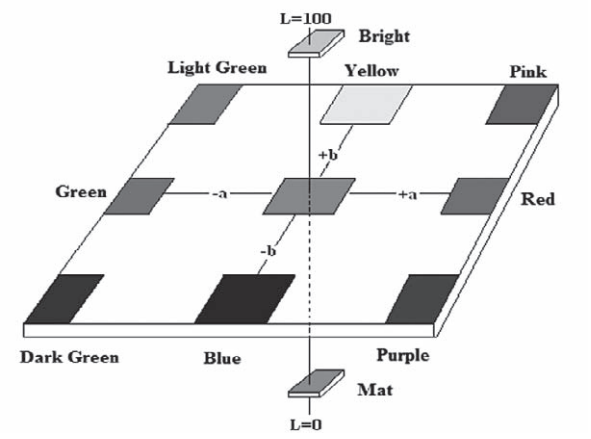

Figure 1 CIELAB–76 color system
Slika 1. Sustav boja CIELAB-76

Where; Δ*L**, Δ*a** and Δ*b** are the changes occurring between the initial state (i) and final state (f) of colors. Δ*E**, indicates total changes of colors occurring in *L*, *a*, and *b*. The highest value shows the highest color change.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

The color change values of the test specimens exposed to cold check test for periods of 1 h 50 °C (± 5), 1 h laboratory conditions, and 1 h -20 °C (± 2), for 20 cycles are numerically presented in Table 1, Table 2, and Table 3. Positive (+) values of Δ*L** show whitening, and negative (-) values of Δ*L** indicate the color turning to gray. Positive values of Δ*a** indicate reddening of the colors, and negative values of Δ*a** show a shift towards green. Positive values of Δ*b** represent yellowing in color, and negative values of Δ*b** represent the color turning blue.

The results showed that all wood specimens, exposed to cold check test, produced negative values of Δ*L**. This was attributed to chemical structure changes that occurred, especially in lignin, due to temperature differences applied through the cold check test.

For natural plant extracts, sensitive degrees to cold check test are Licorice (*Glycyrrhiza glabra* L.), Pomegranate skin (*Punica granatum* L.) and indigo (*lsatis tinctoria* L.) extracts. For Licorice, the best color stability (Δ*E** 3,14) was determined on chestnut wood with vinegar mordant. The biggest change (Δ*E** 49,08) for the same dyestuff was observed on chestnut wood treated with ferrous sulfate (Table 1). The best color stability (Δ*E** 3,71) for Pomegranate skin was determined on mahogany wood with vinegar mordant. The biggest change (Δ*E** 50,06) for the same dyestuff was observed on scots pinewood with ferrous sulfate (Table 2). For indigo, the best color stability (Δ*E**8,89) was determined on chestnut wood with control sample (without mordant). For indigo, the biggest change

Table 1 Color changing of wood specimens stained with Licorice (*Glycyrrhiza glabra* L.), extracts
Tablica 1. Promjena boje uzoraka drva obojenih ekstraktom sladića (*Glycyrrhiza glabra* L.)

Dye Staffs *Uzorak drva*	**Mordant** *Sredstvo za fiksaciju boje*	**Mixtures** *Smjese*	**Before stain** *Prije bojenja*			**After stain** *Nakon bojenja*				**After cold check test** *Nakon testa hladne provjere*			
			L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔE^*
Chestnut / *Kesten*	Control (without mordant) *kontrolni uzorak*	A	65.94	9.00	20.26	-2.64	-0.10	1.26	2.93	-3.14	-0.28	1.18	3.37
		B	65.18	8.80	20.48	-9.30	-1.90	-3.94	10.28	-9.66	-1.54	-2.04	9.99
	Ferrous sulfate *željezov sulfat*	A	68.26	8.10	19.54	-42.56	-8.10	-24.80	49.92	-42.08	-8.52	-20.58	47.61
		B	69.96	8.18	19.34	-45.30	-8.68	-23.74	51.88	-43.68	-8.80	-20.58	49.08
	Aluminum Sulfate *aluminijev sulfat*	A	62.54	8.80	20.54	-4.76	-1.22	2.20	5.38	-5.90	-1.28	2.36	6.48
		B	66.74	8.20	19.30	-3.22	-0.88	2.60	4.23	-4.54	-0.58	2.94	5.44
	Vinegar *ocat*	A	69.20	7.44	19.30	-3.80	0.74	2.44	4.58	-3.88	0.46	1.88	4.34
		B	65.08	9.14	20.18	-2.74	-0.46	0.80	2.89	-2.88	-0.64	1.08	3.14
	Synthetic stain *sintetičko bojilo*		70.02	8.44	19.56	-18.30	11.50	10.98	24.24	-18.38	11.34	11.14	24.30
Scots pine / *Obični bor*	Control (without mordant) *kontrolni uzorak*	A	82.62	5.66	23.82	-6.42	1.26	3.46	7.40	-8.14	1.52	2.54	8.66
		B	82.74	5.16	24.64	-5.44	0.08	2.10	5.83	-6.60	0.88	1.36	6.80
	Ferrous sulfate *željezov sulfat*	A	81.60	5.64	25.80	-20.04	0.88	-1.56	20.12	-23.34	1.54	-3.30	23.62
		B	81.62	5.26	27.84	-25.80	1.84	-3.90	26.16	-28.24	3.12	-5.46	28.93
	Aluminum Sulfate *aluminijev sulfat*	A	81.58	5.82	25.52	-4.82	1.58	6.44	8.20	-8.32	4.04	6.26	11.17
		B	80.60	6.22	26.48	-3.64	1.22	4.76	6.12	-8.64	5.24	4.72	11.15
	Vinegar *ocat*	A	82.16	5.16	26.72	-5.16	1.94	1.78	5.79	-6.72	1.56	2.92	7.49
		B	83.02	4.14	24.90	-5.20	0.22	2.18	5.64	-6.92	1.22	2.60	7.49
	Synthetic stain *sintetičko bojilo*		82.36	4.60	25.88	-26.58	19.86	10.36	34.76	-27.40	19.68	10.08	35.21
Mahogany / *Mahagonij*	Control (without mordant) *kontrolni uzorak*	A	51.30	15.68	18.86	-3.72	0.16	0.32	3.74	-7.80	-1.01	-0.24	7.87
		B	48.62	15.22	18.40	-1.94	-1.44	-0.76	2.53	-3.84	-2.40	-0.90	4.62
	Ferrous sulfate *željezov sulfat*	A	50.66	16.30	18.66	-19.34	-14.42	-11.44	26.70	-20.74	-12.92	-10.92	26.76
		B	50.46	15.12	18.48	-20.20	-13.96	-12.04	27.35	-20.10	-11.76	-10.56	25.57
	Aluminum Sulfate *aluminijev sulfat*	A	50.96	16.04	19.88	-0.64	-3.76	0.26	3.82	-3.58	-4.36	-1.28	5.78
		B	50.02	15.88	18.74	-1.88	-2.98	0.80	3.61	-4.96	-3.66	0.02	6.16
	Vinegar *ocat*	A	50.70	16.24	19.34	-2.86	-0.06	0.24	2.87	-5.42	-0.98	0.54	5.53
		B	50.74	15.38	19.22	-1.46	-0.46	0.20	1.54	-3.12	-1.16	0.02	3.33
	Synthetic stain *sintetičko bojilo*		50.56	15.96	18.76	-11.38	2.36	1.60	11.73	-12.44	1.10	0.20	12.49

A: Liquid glass / *s tekućim staklom*, **B:** Without liquid glass / *bez tekućeg stakla*

Table 2 Color changing of wood specimens stained with Pomegranate skin (*Punica granatum* L.) extracts
Tablica 2. Promjena boje uzoraka drva obojenih ekstraktom šipka (*Punica granatum* L.)

Dye Staffs *Uzorak drva*	**Mordant** *Sredstvo za fiksaciju boje*	**Mix-tures** *Smje-se*	Before stain *Prije bojenja*			**After stain** *Nakon bojenja*				**After cold check test** *Nakon testa hladne provjere*			
			L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*	L^*	a^*	b^*	Δb^*	ΔE^*
Chestnut / *Kesten*	Control (without mordant) *kontrolni uzorak*	A	64.46	10.00	21.72	-2.38	4.48	5.86	7.75	-4.14	0.72	5.16	6.65
		B	68.18	7.36	19.84	-1.72	-0.78	7.30	7.54	-2.28	-0.52	7.42	7.78
	Ferrous sulfate *željezov sulfat*	A	66.10	8.42	20.42	-36.46	-9.52	-22.58	43.93	-36.88	-9.32	-19.56	42.77
		B	68.98	8.04	19.78	-40.56	-9.22	-21.94	47.03	-38.62	-9.20	-18.70	43.88
	Aluminum Sulfate *aluminijev sulfat*	A	63.40	9.50	21.60	-3.90	-1.46	8.52	9.48	-5.76	-0.98	8.28	10.13
		B	62.76	9.12	20.62	-1.80	-1.98	9.28	9.66	-2.96	-0.90	7.96	8.54
	Vinegar *ocat*	A	67.32	8.14	19.40	-2.96	0.54	8.32	8.85	-5.04	0.78	7.60	9.15
		B	65.40	8.64	20.24	-3.22	-0.96	6.48	7.30	-3.92	-0.76	6.42	7.56
	Synthetic stain *sintetičko bojilo*			8.44	19.56	-18.30	11.50	10.98	24.24	-18.38	11.34	11.14	24.30
Scots pine / *Obični bor*	Control (without mordant) *kontrolni uzorak*	A	82.46	4.64	24.80	-6.04	1.68	9.36	11.27	-8.36	2.11	8.98	12.45
		B	83.08	4.54	25.20	-6.54	0.74	11.38	13.15	-8.74	1.94	11.38	14.48
	Ferrous sulfate *željezov sulfat*	A	81.42	5.70	24.96	-45.66	-6.02	-23.42	51.67	-45.36	-5.42	-20.48	50.06
		B	82.92	4.66	24.82	-53.78	-5.86	-26.28	60.14	-21.72	4.06	10.56	24.49
	Aluminum Sulfate *aluminijev sulfat*	A	81.26	4.88	26.30	-9.92	0.90	15.56	18.48	-14.92	4.76	11.94	19.69
		B	82.32	4.90	25.60	-7.86	0.68	22.00	23.37	-43.80	-3.86	-15.36	46.58
	Vinegar *ocat*	A	82.04	5.00	25.94	-8.98	2.74	10.80	14.31	-11.34	4.16	10.72	16.15
		B	81.74	5.92	25.52	-9.26	1.48	9.50	13.35	-11.18	2.38	9.86	15.10
	Synthetic stain *sintetičko bojilo*			4.60	25.88	-26.58	19.86	10.36	34.76	-27.40	19.68	10.08	35.21
Mahogany / *Mahagonij*	Control (without mordant) *kontrolni uzorak*	A	49.28	15.92	19.50	-0.28	0.00	3.26	3.27	-2.96	-0.68	2.54	3.96
		B	51.32	16.12	18.60	-0.04	-1.42	3.12	3.43	-2.24	-3.04	2.58	4.57
	Ferrous sulfate *željezov sulfat*	A	49.90	15.60	18,44	-20.12	-13.36	-13.60	27.72	-21.36	-13.04	-13.20	28.29
		B	50.66	15.54	19.48	-24.66	-15.32	-18.54	34.45	-23.46	-13.58	-15.52	31.24
	Aluminum Sulfate *aluminijev sulfat*	A	50.76	15.24	19.04	-1.90	-3.60	6.52	7.69	-6.00	-2.92	3.98	7.77
		B	51.94	15.98	19.68	-1.54	-3.78	9.06	9.94	-4.26	-3.90	7.00	9.08
	Vinegar *ocat*	A	47.52	15.68	18.86	-1.38	-0.12	3.06	3.36	-4.06	-0.46	2.12	4.60
		B	50.46	15.50	18.98	-0.20	-1.50	3.06	3.41	-1.58	-2.12	2.60	3.71
	Synthetic stain *sintetičko bojilo*			15.96	18.76	-11.38	2.36	1.60	11.73	-12.44	1.10	0.20	12.49

A: Liquid glass / *s tekućim staklom*, **B:** Without liquid glass / *bez tekućeg stakla*

(ΔE^* 56, 74) for the same dyestuff was observed on the same wood with ferrous sulfate (Table 3).

Wood materials colored with metal mordant mixes produced darker colors. However, researchers did not determine that mordant had negative effect on color change performances. This can be explained by the reactions between wood material and mordant mixes and definitely by the effect of UV irradiation on different colors. Dark colors could absorb the light up to 98 %, and transparent colors up to 11 %. Therefore, darker wood species could have undergone more color changes (Yeniocak *et al*., 2015).

Among wood specimens, high color changing values for cold check test were respectively observed on Scots pine, chestnut and mahogany. The reason for the differences between wood species may be due to the differences of chemical composition of wood species, and interaction of natural dyes and mordant mixes extract compounds with wood test specimens, resulting in different photo-degradation effects of UV irradiation. Several factors, such as anatomical differences, growing characteristics, machining properties, pre-treatments (e.g. steaming, drying, etc.), can also affect the color stability (Temiz *et al*., 2005; Goktas *et al*., 2009). In addition, the treatment parameters, such as treatment time, percentage of dyes materials, application temperature and percentage of mordant may also affect the color stability.

All wood specimens exposed to cold check showed negative values of ΔL^*, which means that the color of all wood specimens partially turned to gray. Generally, the highest negative values (ΔL^*) were observed on specimens that were treated with ferrous sulfate mordant. This result is compatible with literature studies about color changing (Yeniocak, *et al*., 2015) of natural dyes. The use of ferrous sulfate mordant produced high color

Table 3 Color changing of wood specimens stained with Indigo (*Isatis tinctoria* L.) extracts
Tablica 3. Promjena boje uzoraka drva obojenih ekstraktom indiga (*Isatis tinctoria* L.)

Dye Staffs *Uzorak drva*	**Mordant** *Sredstvo za* fiksaciju boje	**Mixtures** *Smjese*	**Before stain** *Prije bojenja*			**After stain** *Nakon bojenja*				**After cold check test** *Nakon testa hladne provjere*			
			L*	a*	b*	ΔL*	Δa*	L*	a*	b*	Δa*	Δb*	L*
Chestnut / *Kesten*	Control (without mordant) *kontrolni uzorak*	A	65.94	9.20	20.64	-4.30	-4.38	-3.38	7.01	-7.36	-4.08	-2.86	8.89
		B	64.96	9.82	20.30	-5.10	-7.12	-6.06	10.65	-6.58	-8.06	-6.20	12.11
	Ferrous sulfate *željezov sulfat*	A	66.76	8.00	20.20	-38.94	-8.76	-29.10	49.40	-38.00	-9.52	-23.54	45.70
		B	67.26	9.02	21.24	-5.10	-7.12	-6.06	10.65	-39.34	-39.34	-11.14	56.74
	Aluminum Sulfate *aluminijev sulfat*	A	63.86	9.50	20.72	-13.64	-12.12	-13.70	22.82	-15.34	-11.68	-12.78	23.13
		B	68.00	9.26	20.68	-13.92	-11.96	-12.64	22.28	-16.42	-11.94	-11.40	23.28
	Vinegar *ocat*	A	64.54	8.58	20.30	-16.90	-10.40	-16.56	25.85	-17.80	-10.14	-13.90	24.76
		B	64.78	9.45	21.50	-24.96	-17.35	-25.12	39.43	-25.04	-17.27	-21.60	37.31
	Synthetic stain *sintetičko bojilo*			8.44	19.56	-18.30	11.50	10.98	24.24	-18.38	11.34	11.14	24.30
Scots pine / *Obični bor*	Control (without mordant) *kontrolni uzorak*	A	82.34	4.62	26.34	-11.78	-8.88	-9.56	17.58	-13.68	-7.86	-9.32	18.32
		B	82.38	7.92	25.98	-16.10	-15.18	-17.16	28.00	-19.02	-14.32	-17.42	29.50
	Ferrous sulfate *željezov sulfat*	A	80.46	5.54	27.08	-24.60	-7.86	-16.70	30.75	-28.90	-4.38	-15.86	33.26
		B	82.18	6.52	25.50	-16.10	-15.18	-17.16	28.00	-27.48	-27.48	-6.94	39.48
	Aluminum Sulfate *aluminijev sulfat*	A	82.04	4.92	24.08	-24.54	-13.98	-24.08	37.11	-26.96	-12.08	-22.20	36.95
		B	80.50	7.86	25.88	-18.96	-13.86	-19.58	30.58	-25.78	-10.26	-19.48	33.90
	Vinegar *ocat*	A	81.30	6.38	26.10	-23.86	-14.02	-22.98	35.97	-25.68	-12.42	-21.10	35.48
		B	81.60	7.36	24.82	-39.88	-20.64	-39.48	59.79	-41.86	-20.00	-39.30	60.80
	Synthetic stain *sintetičko bojilo*			4.60	25.88	-26.58	19.86	10.36	34.76	-27.40	19.68	10.08	35.21
Mahogany / *Mahagonij*	Control (without mordant) *kontrolni uzorak*	A	48.92	15.80	18.78	-3.64	-2.42	-1.94	4.78	-9.10	-5.20	-4.06	11.24
		B	47.78	16.62	18.12	-3.36	-3.84	-1.24	5.25	-7.98	-4.90	-1.86	9.55
	Ferrous sulfate *željezov sulfat*	A	51.30	16.04	18.64	-17.48	-16.50	-14.68	28.17	-18.63	-14.09	-12.94	26.70
		B	49.40	15.92	18.74	-3.36	-3.84	-1.24	5.25	-17.26	-17.26	-13.60	27.94
	Aluminum Sulfate *aluminijev sulfat*	A	48.40	15.84	18.50	-11.36	-15.90	-16.82	25.78	-13.82	-14.12	-14.32	24.40
		B	49.48	17.06	18.70	-8.38	-11.30	-8.02	16.19	-11.26	-11.74	-9.34	18.76
	Vinegar *ocat*	A	51.24	16.26	19.16	-6.94	-11.82	-9.26	16.54	-13.42	-10.10	-7.84	18.54
		B	47.72	16.84	18.28	-12.04	-18.84	-16.04	27.52	-15.82	-17.24	-14.88	27.73
	Synthetic stain *sintetičko bojilo*			15.96	18.76	-11.38	2.36	1.60	11.73	-12.44	1.10	0.20	12.49

A: Liquid glass / *s tekućim staklom*, **B:** Without liquid glass / *bez tekućeg stakla*

changing (Δ*E**) values, too. These changes can be explained by the interaction of ferrous sulfate ions and wood components. Metal mordant produced color stability. Metal ions promote free radical formation (Feist and Hon, 1984; Peker *et al*., 2012) of wood components even when they are exposed to light. The stabilization of lignin by ferrous was reported to occur through the formation of complex (Kamdem and Grelier, 2002).

4 CONCLUSIONS
4. ZAKLJUČAK

The natural dyes produced lower color changes than the synthetic dyes with a few exceptions. This is a very promising result for the use of natural dyes as alternative colorants in near future.

The vinegar mordant applications provided resistance as much as other mordant applications. The natural dyestuff for wood surfaces was successfully developed by using natural mordant in natural dye application. Ferrous sulfate was observed to be the mordant type with the highest color change among all wood species in general. Sometimes this property is desired on decorative applications. It is worth noting that ferrous sulfate mordant should be avoided for some wet and hot environment, or that it can be preferred in places where the color change is not important.

The future work will be focused on the use of various natural dyes and mordants in the production of wooden products, especially for the children's furniture and wooden houses.

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Cross Laminated Timber (CLT) as an Alternative Form of Construction Wood

Lamelirano drvo (CLT) kao alternativni oblik drva za gradnju

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ABSTRACT • *Wood, which is a natural and renewable material, is gaining increasing appreciation again and it is more and more commonly used in the building industry. The use of wood has been improved due to the application of modern bonding technologies (e.g. Glued Laminated Timber, Cross Laminated Timber), the development of modern production technology and improved methods of wood protection from fire. As large-size assortments of constructional timber in the form of light beams and boards are available on the market, it is possible to make stable and durable joints between individual constructional elements of a building. Among wood materials used for construction, CLT is increasingly used. It is applied in the construction of single-family houses, residential buildings, multi-storey buildings, public buildings, industrial and retail buildings as well as bridges. CLT was developed as a result of European research how to use short wood, left after the elimination of faults, for private construction. The trend very soon spread to the building industry in North America, Australia and Japan. CLT was more and more commonly used in multi-storey buildings due to its higher seismic resistance. At the beginning of the 30-year history of CLT, the use of this building material was minimal. However, due to the ecological trend and a wide range of economic factors (the value of material used and costs of production combined with high precision of finished products), this technology gained significant popularity. The surge of interest in wooden constructions also resulted from better distribution channels and technical approvals for different concepts of wooden construction boards. The following countries are leaders in the production and use of CLT: Austria, Germany, Switzerland, Sweden, Norway and the United Kingdom. In recent years, New Zealand and Australia have joined this group. CLT boards are exported to North America, Japan and Russia. The surge of producers and investors' interest in CLT boards results from the production process diversity and construction variability. In consequence, there is an increasing number of concepts specifying the range of product application, depending on its strength and resistance.*

Key words: *wood construction material, Cross Laminated Timber*

SAŽETAK • *Drvo kao prirodni i obnovljivi materijal ponovo dobiva sve veću vrijednost i sve se češće upotrebljava u graditeljstvu. Upotreba drva poboljšana je zbog primjene suvremenih tehnologija vezanja (npr. lamelirano drvo), razvoja suvremene proizvodne tehnologije i poboljšanih metoda zaštite drva od požara. Budući da je ponuda građevnog drva u obliku laganih greda i ploča na tržištu velika, njime je moguće izvesti stabilne i izdržljive spojeve među pojedinim konstrukcijskim elementima zgrade. Među drvnim materijalima koji se rabe za gradnju sve je zastupljenije unakrsno lamelirano drvo (CLT). Primjenjuje se u izgradnji obiteljskih kuća, stambenih zgra-*

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da, višekatnica, javnih zgrada, industrijskih i maloprodajnih zgrada, kao i mostova. CLT je razvijen kao rezultat europskih istraživanja uporabe drvnih elemenata malih dimenzija, preostalih nakon uklanjanja grešaka drva, i to mahom za privatnu gradnju. Trend se vrlo brzo proširio na građevnu industriju u Sjevernoj Americi, Australiji i Japanu. CLT se zbog svoje velike seizmičke otpornosti sve više upotrebljava u višekatnim zgradama. Na početku sada već 30-godišnje povijesti CLT-a uporaba toga građevnog materijala bila je minimalna. Međutim, zbog ekološke prihvatljivosti i širokog spektra ekonomskih čimbenika (cijena upotrijebljenog materijala i troškovi proizvodnje, u kombinaciji s velikom preciznošću gotovih proizvoda) ta je tehnologija postigla veliku popularnost. Osim toga, sve veće zanimanje za drvene konstrukcije rezultat je i boljih distribucijskih kanala te dobivanja tehničkih odobrenja za različite koncepte drvenih građevnih ploča. U proizvodnji i upotrebi CLT-a vodeće su zemlje Austrija, Njemačka, Švicarska, Švedska, Norveška i Ujedinjeno Kraljevstvo. U posljednjih nekoliko godina toj su se skupini zemalja pridružili Novi Zeland i Australija. CLT ploče izvoze se u Sjevernu Ameriku, Japan i Rusiju. Povećanje broja proizvođača i zanimanje ulagača za CLT ploče rezultat je raznolikosti proizvodnih procesa i varijabilnosti gradnje. Stoga postoji sve veći broj koncepata koji određuju raspon primjene proizvoda, ovisno o njegovoj čvrstoći i otpornosti.

Ključne riječi: *drvni građevni materijal, unakrsno lamelirano drvo*

1 INTRODUCTION
1. UVOD

Wood, as one of natural and renewable materials used by man, has gained more and more recognition and applications in construction. Over the last 30-years Europe has seen a considerable increase in the share of laminated wood in building structures. One should mention here not only the use of GLT (Glued Laminated Timber), but also CLT (Cross Laminated Timber) produced in the form of panels. As soon as such assortments of structural wood emerged on the construction market, they were quickly used at the mass scale and included in the European standards connected with construction in the private and public sectors. CLT manufactured in the form of light panels is a multilayer wooden panel, where every layer is arranged at right angle to the adjacent layers. This assures the appropriate rigidity and stability of final material. CLT panels are usually made of three to seven layers; typically there is an odd number of layers arranged symmetrically to the middle layer. The joints between the individual layers of structural timber owe their stability and strength to the application of suitable, ecological glues. Amongst the composite wood materials used for structural purposes and in comparison to traditional building materials, CLT is a product characterised by many advantages, of which the most important are:

– sustainable consumption of raw material used for its production;
– an energy-efficient production process, which makes the material environmentally friendly;
– superb static, mechanical and insulation properties;
– lightness, which makes the building structure incomparably lighter than other structures made of conventional materials;
– the possibility of producing prefabricated elements, which results in a short time of completion of the whole building regime;
– the possibility of combination with other building materials (steel, glass, plastics, etc.), resulting in maximum freedom of architectural design.

The above-mentioned advantages make the CLT application range very broad, i.e. from single-family houses and residential buildings, through multi-storey public buildings, to industrial and commercial buildings, and even bridge structures.

Hitherto in Europe CLT has been primarily a material used for construction of low buildings, i.e. one- or two-storey houses. Despite the growing popularity of CLT in single-family housing, more and more often it is also used to accomplish more ambitious tasks of erecting multi-storey buildings, where it is the basic construction material, e.g. a seven-storey Stadthaus condominium in London (2008), a ten-storey residential building in Melbourne (2012), and a fourteen-storey high rise in Bergen (2015). The latest project is a USA design –Owings and Merrill Company designed a forty-two-storey condominium. In some regions, buildings made of CLT enjoy special interest due to their enhanced seismic endurance (Popovskii *et al.*, 2010; Pei *et al.*, 2010, 2012).There are many reasons why wood is better than any other building material. The most important is sequestration and accumulation of carbon dioxide, the fast pace of structure building, compatibility with other materials (Risen 2014). Steel, glass and concrete revolutionised the 19th and 20th century construction. De Rijke believes that wood will do the same for the 21st century construction, and that wooden buildings made of CLT are the future.

2 WOOD COMPOSITES
2. DRVNI KOMPOZITI

The initial development and success of CLT was connected to the first analyses of the use of multi-layer timber in roof structures (Cziesielski, 1974). Further efforts to introduce composite wood materials into construction were made in the period 1981-1989. Those efforts were supported by numerous studies conducted in Lausanne and Zürich at the beginning of 1990 (Colling, 1990; Colling *et al.*, 1992; Frampto and Cava, 1995). The modern CLT technology started to develop rapidly after 1996 in Austria as a result of cooperation between industry and science. For the first

few years the development of wood panel application was progressing slowly (Espinoza *et al.*, 2015). At the beginning of 2000, the demand for CLT increased thanks to green building, which was developing at that time. The high efficiency of wood material processing and favourable changes of regulations had a positive effect on the development of that technology (Brandner, 2014; Brandner *et al.*, 2016; Pavlyukovskiy, 2012). Those factors directly translated into CLT production, which amounted to approximately 600 000 m^3 in 2014, only to exceeded 1 million m^3 in successive years and maintain an upward trend (Muszyński, 2015; Plackner, 2015). A significant factor limiting the use of CLT in building systems in the European Union was the requirement to obtain European Technical Assessment certificate (ETA). The basic standards define the requirements for CLT wooden structure cover of multifamily residential buildings and public buildings (Augustin *et al.*, 2010; Zumbrunnen and Fovargue, 2012). Austria, Germany, Switzerland, Sweden, Norway, and the United Kingdom are the countries leading in terms of CLT production and application (Schickhofer, 2010). In recent years, a rapid growth of CLT production and use has been recorded in North America (Canada and the United States), as well as in Japan, Taiwan, New Zealand (Crews, 2011; Lewis *et al.*, 2014), and Russia (Vdovin and Karpov, 1999; Pilagin, 2006). The development of CLT construction has also been observed in China and Australia, countries that import CLT from Europe.

It is worth mentioning that the CLT system is also known as "X-lam" ("cross lam"), "plywood boards" (PBs), and "Massivholz". The main European manufacturers of CLT are Austrian, German, and Scandinavian companies (Tab.1).

Each of the presented companies uses a similar production process, whose core stage is procurement and quality sorting of timber. Those activities largely come down to the assessment of the strength properties of timber. The production process also encompasses the manner of joining boards into panels, which are a semi-product for further production of panels, whose adjacent layers are arranged at right angle to one another, thus wood grain is cross-arranged. Significant technological differences between the individual producers primarily come down to the thickness of manufactured layers, their strength class, and the systems of joining timber in terms of length, width and thickness. Glues and limit dimensions of the obtained elements also play an important role (Falk, 2010, 2011; Brandner and Schickhofer, 2008, 2010, 2012; Brandner, 2014; Brandner *et al.*, 2016).

Recently, research on the properties of CLT panels and their use in structures has become very intensive, which results from current business conditions that have a direct effect on the increased interest in new wood materials and their possible applications in construction. Major advantages of the CLT technology encompass the use of fast-renewed resources and less contamination of the environment, compared to alternative materials,

Table 1 Comparison of technical specifications of CLT panels by producers
Tablica 1. Usporedba tehničkih specifikacija CLT ploča različitih proizvođača

Company *Proizvođač*	**Maximum panel dimensions, m** *Maksimalne dimenzije ploča,* m			**Classification of raw material** *Klasifikacija sirovine*	**Class of raw materials EN 1995-1-1** *Klasa sirovine prema EN 1995-1-1*	**Product name** *Naziv proizvoda*
	Maximum length *Maksimalna duljina*	**Maximum width** *Maksimalna širina*	**Maximum thickness** *Maksimalna debljina*			
KLH (Austria, United Kingdom, Sweden)	16.50	2.95	0.50	classification by EN 338 and EN 13017-1	EN 338 C24	KLH
Binderholz (Austria)	24	3.50	0.34	classification by DIN EN 13017-1	EN 338 C18/C24	BBS-125, BBS-XL
Martinsons (Sweden)	6	1.20	0.259	classification by NS- EN 13017-1	NS -EN 338 C14 – C24	KL-trä
Stora Enso (Austria)	16	2.95	0.32	classification by EN 14080	EN 338 C16/C24/C30	C-panels, L-panels
Thoma Holz GmbH (Austria)	8	3	0.80	classification by ETA - 13/0785	EN 338 C16 C24	H100
Finnforest Merk (Germany / United Kingdom)·	20	4.80	0.297	classification by EN 338 and EN 13017-1	EN 338 C24	-
HMS (Germany)	16	3.90	0.32	classification by EN 338 and EN 13017-1	EN 338 C24	-
NORDPAN SPA AG (Italy)	5	2.05	0.27	DIN EN 14081 DIN 4074-1	SK27/SK30	Nordpan
Züblin Timber Bauelemente (Germany)	7	3	0.31	DIN EN 14081 DIN 4074-1	EN 338 C24	LENO
LIGNOTREND AG (Germany, Switzerland)	18	0.625	0.247	DIN EN 14081 DIN 4074-1	EN 338 C20/24	LIGNO HBV

Source: Technical Approval No. Z-9.1-209, Z-9.1-482, Z-9.1-501, Z-9.1-534, Z-9.1-555, Z-9.1-574, Z-9.1-602, Z-9.1-559, Z-9.1-640

which is connected with the production technology. A review of literature on CLT suggests that the research concerns primarily the following matters:
– determining the mechanical properties of CLT (Massivträ: Handboken, 2006; Brandner and Schickhofer, 2008, 2012; Stürzenbecher, 2010; Falk and Buelow, 2011);
– defining possible applications of CLT as structure members of hybrid multi-storey buildings (Falk, 2011);
– searching for new methods of joining both panels and ready products in the assembly process (Follesa *et al.*, 2010);
– performance of CLT structures during seismic vibrations (Bogensperger *et al.*, 2010, 2011);
– determining the durability of CLT structures subjected to fire (Frangi *et al.*, 2009);
– determining the resistance of CLT panels to other destructive factors (Werner and Richter, 2007).

Nevertheless, most of research and studies on CLT concern technical verifications (Massivträ: Handboken, 2006; Bejder *et al.*, 2010, 2011, 2012). CLT panel elements assure that applications are multipurpose within the designed structure thanks to the improved technical properties, as confirmed by a series of tests (Gold and Rubik, 2008; Roos *et al.*, 2010). In terms of the product's aesthetics (Bell, 2006), there are many possible modifications of the product, which allow considerable elimination of natural flaws found in the initial raw material (Fragiacomo, 2014; van de Lindt *et al.*, 2013).

Taking into consideration the technical possibilities provided by the wood industry as regards large-scale CLT production as well as considerable dimensions of the offered products (thickness up to 0.5m, width up to 4m, and length up to 20 m), it could be said that building engineering has been given a new material, which has made it possible to use solid wood in a mass-scale construction to a much greater extent than before. Apart from the technical advantages of CLT panels in terms of design, the major asset of this material is the low cost of structural timber processing, i.e. minimal cost prior to gluing. Although sawing of raw material to obtain 16-40 mm thick timber entails some loss of material, taking into consideration the available sections of logs, such sawing allows the use of so-called side boards, hitherto considered by-product.

The logistics of building structure erection is also of importance. The wall and floor panels may be produced with a high degree of prefabrication, which assures not only a material cost decrease, but also a shortened construction period.

In terms of structural functions, CLT panels may be divided into the following types:
– panels intended for ceilings and floors, designed to bear the structure-specific load, where the main direction of load is perpendicular to the axis of the panel middle layer;
– panels intended for structural members of walls, designed to bear the loads resulting from, inter alia, the height of the building, where the main direction of load is in line with, i.e. parallel to the axis of the panel middle layer;
– combined structures, based on 3-D arrangement, for three-dimensional projects forming the spaces of building using CLT panels, which bear loads in different directions.

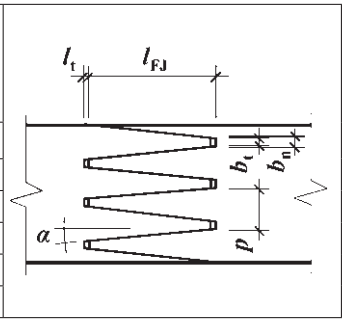
3 MATERIAL AND TECHNOLOGY
3. MATERIJAL I TEHNOLOGIJA

A standard CLT panel is composed of 12 ÷ 45 mm thick timber (EN 16351). Currently, in the context of adopted standardization, the thickness of a CLT layer ranges from 20 to 40 mm (Z-9.1-482 2010, Z-9.1-559). Such thickness range is used, inter alia, by the producers in Austria and Germany. Further standardization, particularly as regards the mechanical properties of CLT, concerns the stresses within the plane (for application in ceiling, floor, and roof structures) and the internal structure (for application in walls). As regards those tests, it could be said that there is no upper limit of the panel width; however, due to the shear stresses occurring between the layers composed of minimum-width timber (40 ÷ 300 mm), the following standards were assumed: 0.6, 1.2, 2.25, 2.4, 2.7, and 2.95 m (maximally up to 4 m). Those assumptions are allowed for in the effective Technical Approvals. Special emphasis is placed on the assurance of identical thicknesses of all the layers making a CLT panel. This is connected to current assumptions that all CLT planes are exposed to the same transverse stresses. Some researchers have also conducted studies on changeable layer arrangements with the use of wood of various strength classes (Li, 2015; Li and Lam, 2016). In terms of strength classification, the use of the available assortments of timber with various thickness parameters and characterised by admissible standards, suggests higher strength parameters of CLT panels compared to the comparable groups of glued laminated timber GLT (table 3) (Thiel, 2014; Fragiacomo, 2014).

Presently, the main softwood species used by the European CLT producers is Norway spruce (*Picea abies*), also often found in association with silver fir (*Abies alba*). Apart from spruce and fir, the following species are also used: Scots pine (*Pinus sylvestris*), European larch (*Larix decidua*), Douglas fir (*Pseudotsuga menziesii*), and Swiss pine (*Pinus cembra*). The last two species are often used for the surface layer of CLT panel due to their high decorative values. It is possible to use other species as well, e.g. maritime pine (*Pinus pinaster*), harvested mainly in Sardinia (Italy), or the wood of deciduous species, as long as it fulfils the quality and strength criteria. An example of such species diversity in CLT panels are the structures erected within the project "massive_living" in Austria, where one of the buildings was completely made of wall elements using silver birch (*Betula pendula*). Further possibilities of using hardwood allow for poplar (*Populus spp.*), ash (*Fraxinus excelsior*), and other species, which are interesting in terms of wood harvesting for economic purposes in a given region (Z-9.1-721).

Table 2 Dimensions and finger joint profiles, and geometrical dimensions of a section acc. to the standard EN 387
Tablica 2. Dimenzije i profili zupčastih spojeva te geometrijske dimenzije spoja prema standardu EN 387

Finger length *Duljina zubaca*	**Pitch** *Korak*	**Width** *Širina*	**Base width** *Širina baze*	**Tip gap** *Zazor*	**Flank angle** *Kut zubaca*	**Loss in cross section** *Gubitak poprečnog presjeka*
l_{FJ}	*p*	*bt*	*bn*	*lt*	*α*	*v(bn)*
mm					°	%
15	3.8	0.42	0.52	5	5.6	13.6
20	5.0	0.50	0.60	5	5.7	12.0
20	6.2	1.00	1.11	5	6.0	17.8
50	12.0	2.00	2.48	3	4.6	20.7



One of the parameters characterising raw material and determining its strength is density, which ranges from 480 to 500 kg/m^3 on average for CLT panels. This range corresponds to the density of softwood species intended for structural purposes. Thereby, the weight of typical CLT in a wall panel of a thickness of 103 or145 mm ranges from 67 to 72 kg/m^2 or 49 to 52 kg/m^2, respectively, (Ceccotti, 2010; Popovski, 2010; FPInnovations, 2010).

Correctly conducted heat treatment is an important element of the technological procedure for preparing structural raw material for CLT production. Due to the gluing processes and the conditions in which the final structure is used, wood for CLT production should be dried and conditioned until it reaches a technologically required moisture content of 12 ± 2%. The prepared material is then classified in terms of strength in the process of optical or/and mechanical sorting in accordance with the standard EN 14081-1 or, in the case of German producers, the standard DIN 4074-1. This is of utmost importance considering typical production requirements for CLT panels, where all pieces of timber within a layer should be of the same species and strength class (Schickhofer, 1994; Wathén, 2006; Augustin *et al.*, 2010). In other cases, where various species of wood are used, the defined strength of a single layer used for panel manufacture should be reduced to the lowest class of the timber used. A system of structural timber classification currently used in Europe is based on timber bending strength. According to the system, timber is classified in the range from C16 toC40 (acc. to EN 338). The system was defined for solid softwood and falls within a range of 16-40N/mm^2. According to the requirements of the European Technical Assessment, timber of class C24 is usually used in the production of CLT panels of homogenous structure. At the same time, 10 to 30 % of layers located closer to the middle of the panel can be of lower strength class, which does not result in worsening of the CLT mechanical properties (DIN 4074-1:2012-06). In the case of combined CLT panels, the surface layer is manufactured of timber of the strength class C24 and the transverse inner layer is made of C16/C18 timber. In reality, the assumed load bearing capacity of CLT in bending is connected with the strength of the outer layers (EN 384). Strength stability observed in the plane of CLT panel stems from the composition and properties of transverse layers, which make up a cross arrangement. Based on the available test results, it was ascertained that the strength properties of products belonging to the GLT or CLT system stabilise in comparison to initial material, i.e. solid wood, which has often numerous structural flaws. The process of flaw elimination consists in the elimination of so-called inadmissible sections from the transverse structural materials. Next, those materials are joined in length using finger joints of specific finger lengths defined for GLT and CLT (table 2). The prepared timber elements, which have been classified and optimised for the production of glued timber, are milled to obtain finger joints of a finger length ranging from 15 to 20 mm. To obtain strong joints, facilitating the obtainment of a desired strength of CLT elements, it is preferred that fingers of a length of $L_{FJ} \geq 45$ mm be introduced (table2). An important role in load bearing falls to the fingers' slenderness, which allows reduction of the pressure strength and enhancement of the joint strength (Colling and Ehlbeck, 1992; Radovic and Rohlfing, 1993; Groom and Leichti, 1994; Smardzewski, 1996).

The growing interest in CLT panels, noted amongst the producers and investors, is justified by a series of economic factors, including primarily the value of the raw material used and the production cost.

The important aspects of the CLT production process are the quality of raw material corresponding to the requirements for the longitudinal planes and proper preparation of a layer set. At this stage of production, the selection of glue systems is the key. Amongst the glues used in the process, there are such as amine glues (fulfilling the requirements of the standard EN 301), melamine-formaldehyde glues (MF), melamine-urea-formaldehyde glues (MUF), and single-component polyurethane glues (1K-PUR) – fulfilling the requirements of the standard EN 15425. Panels are also produced using the Emulsion Polymer Isocyanate adhesives (EPI), which fulfil the requirements of the standard EN 15425 and the European Technical Assessment, which allows their use in load-bearing wooden structures in accordance with the standard EN 16351. Maintaining technological regime during the gluing of wood layers (e.g. maintaining the correct pressure during hydraulic, vacuum or mechanical pressing) provides obtaining correct strength values and stability of the joint. The admissible hydraulic pressure falls within a range of 0.10 ÷ 1.00 N/mm^2; whereas in the case of vacuum presses and the pressure

Table 3 Examples of strength classes of CLT panels (acc. to standard EN 14080)
Tablica 3. Razredi čvrstoće CLT ploča (sukladno standardu EN 14080)

Strength class / *Razred čvrstoće*			
Lamella	GLT	CLT	
		Lamella $CV_{(ft,0,l)}$	
		The coefficient of variation	
		25 % ± 5 %	35 % ± 5 %
T14	GL24h	CL24h	CL28h
T18	GL28h	CL30h	CL34h

$CV_{(ft,0,l)}$ - Accuracy of mechanical grading process with reference to visual grading / *točnost metode mehaničkog klasiranja s obzirom na vizualno ocjenjivanje*

applied using screws, the pressure value should fall within the range of 0.05 ÷ 0.10 N/mm² and 0.01 ÷ 0.20 N/mm², respectively (Kairi, 2008; Brandner and Schickhofer, 2010). The strength of joint between the planes depends on the accuracy of surface machining, pressure of pressing, and adhesive system used.

Studies on the effect of the thickness of materials used for the production of CLT panels are one of the elements of verification of panel strength parameters. Table 4 presents the standard strength indicators for homogenous CLT panel made of 14 mm thick timber of classes C24 and C28 (Jöbstl and Schickhofer, 2007; Brandner and Schickhofer, 2008). The obtained strength parameters in association with thermal insulation indicators, fire resistance (R30 to R90) (Frangi *et al.*, 2009) and ecological aspects, bring CLT products to the forefront of structural materials manufactured from natural raw materials.

While producers and investors show much interest in CLT panels, as mentioned above, the interest of engineers and designers is definitely limited. This stems from the rigorous requirements as to the quality and strength provided by building standards concerning that product. Not long ago, standards concerning the use of CLT were only effective in Germany, Austria, and Switzerland. The development of so-called Eurocode5 (EN-1995-1) made it possible for CLT to

Table 4 Characteristic of the basic mechanical properties of homogenous glued timber CLT
Tablica 4. Obilježja osnovnih mehaničkih svojstava homogenoga lijepljenog drva CLT

Proporties *Svojstva*	**Material T14** / *Materijal T14*			
	Accuracy of mechanical grading process with reference to visual grading *Točnost metode mehaničkog klasiranja s obzirom na vizualno ocjenjivanje* $CV_{(ft,0,l)}$		**Coefficient of variation** *Koeficijent varijacije*	
			25% ±5%	35% ±5%
			CLT strength class *Razred čvrstoće CLT-a*	
	symbol		CL24h	CL28h
Bending strength / *savojna* čvrstoća	$f_{m,CLT,k}$	N/mm²	24	28
Tensile strength / *vlačna* čvrstoća	$f_{t,0,CLT,net,k}$		16	18
	$f_{t,90,CLT,k}$		0.5	
Compression strength / *tlačna* čvrstoća	$f_{c,0,CLT,net,k}$		24	28
	$f_{c,90,CLT,k}$		2.85	
Shear strength (shear) - in plane *smicajna čvrstoća u ravnini*	$f_{v,CLT,IP,k}$		5.0	
	$f_{T,mode,k}$		2.5	
Shear strength - out of plane *smicajna* čvrstoća *izvan ravnine*	$f_{v,CLT,OP,k}$		3.0	
	$f_{r,CLT,k\ -\ b/t \geq 4:1}$		1.25	
	$f_{r,CLT,k\ -\ b/t < 4:1}$		0.70	
Modulus of elasticity *modul elastičnosti*	$E_{0,CLT,mean}$		11 000	
	$E_{0,CLT,05}$		9 167	
	$E_{90,CLT,mean}$		300	
	$E_{90,CLT,05}$		250	
	$E_{c,90,CLT,mean}$		450	
	$E_{c,90,CLT,05}$		375	
Shear modulus / *modul smicanja*	$G_{CLT,mean}$		650	
	$G_{CLT,05}$		540	
Rolling shear modulus *kotrljajući smični modul*	$G_{r,CLT,mean}$		65	
	$G_{r,CLT,05}$		54	
Density / *gustoća*	$\rho_{CLT,k}$	kg/m³	350	
	$\rho_{CLT,mean}$		385	

enter the building markets of the other European Union member states. Those standards are guidelines for design and use of CLT. Building regulations, currently effective in Europe, determine, inter alia, the requirements as to combustibility of building materials, including primarily wooden elements. The issue of CLT panel combustibility is one of the major issues as regards the design and exploitation of multi-storey buildings. For that reason, the highest CLT buildings were erected outside Europe. In accordance with building requirements, modern structures made of CLT wood are designed in line with guidelines determining the exploitation conditions of a building (EN-1995-1-2). The tests take into consideration the strength conditions, transfer of vibrations, thermal insulation, and fire resistance. CLT is preferred for building purposes because of the favourable ratio of mass to strength, rigidity, and a reduced transverse effect of strength reduction. The adjustment of the American National Standards ANSI/APA PRG 320-2012, which determine the standards of efficiency assessment, production details, and the requirements concerning functional features, in order to assure the required quality, facilitated the use of CLT wood to the full extent in the United States. Thanks to standardization and pro-ecological activities, CLT should also be allowed for in the International Building Code (IBC) (http://www.rethinkwood.com 2013).

One of the basic advantages of CLT panels produced for construction purposes is the low production cost related to low energy-consumption. Therefore, the production process has a positive effect on the reduction of carbon emission to the atmosphere, and thus holding carbon within the cycle. According to comparative studies, the manufacture of 1 tonne of bricks requires four-time-higher energy expenditure than the manufacture of 1 tonne of coniferous timber, the manufacture of 1 tonne of concrete five-time-higher, and the manufacture of a steel or aluminium structure 24-time and 126-time higher, respectively. Wood also demonstrates better insulating properties: five-time higher than concrete and approximately 350-time higher than steel. This means that energy consumption required for heating up and cooling down a wooden building is much lower (Risen, 2014).

4 CONCLUSION
4. ZAKLJUČAK

Speaking about the development of construction based on raw wood material, it can be stated that the use of glued wood (GLT, CLT) indisputably contributed to the broadening of the application of natural raw materials in both single- and multi-storey structures. The use of CLT panels, characterised by highly stable strength parameters, resulted in the introduction of standardization acts organising the scope of CLT panel application. Regulating the production and structural conditions of CLT panels was accompanied by limitations on their use due to wood combustibility. A series of research conducted in order to reduce the susceptibility of wood to combustion suggests that glued wood fulfils the requirements for multi-storey structures. An important asset of constructions based on CLT panels is their strength and stability in the conditions of seismic activity. The scope of applications of wood in the form of CLT panels in construction is affected by the introduction of directives concerning the reduction of CO_2emission into the atmosphere. The success of CLT panels on the world markets derives from factors such as their high receptivity to machining, positive indicator of thermal insulation, and possibilities of modification of their functionality in terms of use and design.

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Autranella congolensis A. Chev.

NAZIVI

Vrsta drva *Autranella congolensis* A. Chev. pripada porodici *Sapotaceae*. Trgovački naziv vrste je mukulungu (Francuska, Gabon, Kongo, Nizozemska, Njemačka, Španjolska, Velika Britanija), anzala, kolo (Nigerija), elang, elanzok (Kamerun), bonga, ovango, bwanga (Srednjoafrička Republika), m'fua, angulu, fino, kungulu, kabulungu (Kongo), muku, mafamuti (Mozambik), autracon, yoli (SAD).

NALAZIŠTE

Vrsta drva *Autranella congolensis* A. Chev. prirodno je rasprostranjena u zapadnoj i srednjoj Africi, pretežito u Kamerunu i Kongu. Nalazimo je u nizinskim tropskim zimzelenim kišnim šumama i u nižim predjelima zimzelenih tropskih planinskih kišnih šuma.

STABLO

Na svom staništu stabla narastu od 30 do 40 metara visoko, duljina debla kreće im se od 15 do 25 metara, a prsni im je promjer debla od 1,0 do 1,5 metara. Deblo je pravilnoga, cilindričnog oblika. Vanjska je kora drva sivosmeđa, uzdužno izbrazdana, a unutarnja je crvenkastosmeđa i sadržava lateks. Debljina kore je 1,5 – 3,5 centimetara.

DRVO

Makroskopska obilježja

Drvo je rastresito porozno. Godovi su običnim okom slabo uočljivi, a pore jedva uočljive. Drvni su traci vidljivi pod povećalom. Tekstura drva je jednolična i pravilna. Drvo je ravne žice. Bjeljika je uska, svjetlosmeđa do žutocrvenkasto smeđa, široka samo 2 – 3 cm. Srž drva je crvenkastosmeđa, ružičastoga do ljubičastog tona.

Mikroskopska obilježja

Traheje drva raspoređene su radijalno, odnosno u kosim radijalnim nizovima. Promjer traheja iznosi 60...105...140 mikrometara, a gustoća traheja 7...23...36 na 1 mm^2 poprečnog presjeka. Volumni je udio traheja oko 18 %. Traheje srži često su ispunjene tamnim sržnim tvarima. Drvni su traci heterocelularni, visine 230...460...700 mikrometara, odnosno 8...15...22 stanice; širine 25...40...60 mikrometara, odnosno od 1 do 2 - 3 stanice. Gustoća drvnih trakova je 5...7...9 na 1 mm, a njihov volumni udio iznosi oko 25 %. Aksijalni je parenhim apotrahealno difuzan do mrežast, širine 1 – 3 stanice. Volumni udio aksijalnog parenhima iznosi oko 17 %. Drvna su vlakanca libriformska. Dugačka su 658...1195...1555 mikrometara. Debljina staničnih stijenki vlakanaca je 3,5...6,0...8,5 mikrometara, a promjer lumena vlakanaca 0,7...3,0...7,7 mikrometara. Volumni udio vlakanaca je oko 40 %.

Fizička svojstva

Gustoća standardno suhog drva, ρ_o	760...940...1030 kg/m^3
Gustoća prosušenog drva, $\rho_{12\text{-}15}$	780...960...1040 kg/m^3
Gustoća sirovog drva, ρ_s	1000...1250 kg/m^3
Poroznost	oko 38 %
Totalno radijalno utezanje, β_r	3,9...4,9...6,9 %
Totalno tangentno utezanje, β_t	4,1...5,5...7,6 %
Totalno volumno utezanje, β_v	18,1...10,6...14,9 %

Mehanička svojstva

Čvrstoća na tlak	73,5...107,0 MPa
Čvrstoća na vlak, u smjeru pružanja vlakanaca	100...166 MPa
Čvrstoća na vlak, tangencijalno	oko 5,2 MPa
Čvrstoća na savijanje	100...178 MPa
Čvrstoća na smicanje	6,5...13,5 MPa
Tvrdoća prema Brinellu, paralelno s vlakancima	65,0...108,0 MPa
Tvrdoća prema Brinellu, okomito na vlakanca	34,0...62,0 MPa
Modul elastičnosti	12,0...15,0 GPa

TEHNOLOŠKA SVOJSTVA

Obradivost

Premda je drvo znatnije gustoće, dobro se strojno i ručno obrađuje, no za obradu je potreban veći utrošak energije. Alati i brusna sredstva relativno se brzo troše. Piljevina i bruševina pri obradi najčešće prouzročuju upalu sluznice, pa se preporučuje upotreba uređaja s pojačanim odsisom. Drvo se dobro reže i ljušti. Prije

obrade trupce je potrebno pariti. Drvo se također dobro tokari te dobro prima čavle i vijke, no potrebno ga je prethodno izbušiti. Dobro se lijepi i politira.

Sušenje

Preporučuje se prirodno i polagano sušenje drva kako bi se izbjeglo vitoperenje i pucanje. U sušionicama je najbolje sušiti piljenice do 50 mm debljine.

Trajnost i zaštita

Prema normi HRN 350-2, 2005, srž drva vrlo je otporna na gljive uzročnice truleži (razred otpornosti 1) te je otporna na termite (razred otpornosti D). Srž je slabo permeabilna (razred 3). Prema normama, drvo se bez ograničenja može upotrebljavati u razredu opasnosti 4 (u dodiru s tlom ili vodom).

Uporaba

Upotrebljava se za izradu rezanih i ljuštenih furnira, u proizvodnji namještaja i laboratorijskih stolova, za izradu stubišta, oplata i parketa, a rabi se kao konstrukcijsko građevno drvo za vanjsku i unutarnju uporabu, za vagone, u brodogradnji i mostogradnji.

Sirovina

Drvo *Autranella congolensis* A. Chev. isporučuje se u obliku trupaca dužine od 4 do 5 metara, najčešćega srednjeg promjera od 0,8 do 1,2 metra.

Napomena

Drvo nije na popisu ugroženih vrsta međunarodne organizacije CITES.

Slične su vrste *Baillonella toxisperma* Pierre, *Dumoria heckelii* A. Chev., D. a*fricana s* A. Chev.

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prof. dr. sc. Jelena Trajković
doc. dr. sc. Bogoslav Šefc

Upute autorima

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Upute

Predani radovi smiju sadržavati najviše 15 jednostrano pisanih A4 listova s dvostrukim proredom (30 redaka na stranici), uključujući i tablice, slike te popis literature, dodatke i ostale priloge. Dulje je članke preporučljivo podijeliti na dva ili više nastavaka. Tekst treba biti u *doc formatu*, u potpunosti napisan fontom *Times New Roman* (tekst, grafikoni i slike), normalnim stilom, bez dodatnog uređenja teksta.

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Latinska imena trebaju biti pisana kosim slovima (italicom), a ako je cijeli tekst pisan kosim slovima, latinska imena trebaju biti podcrtana.

U uvodu treba definirati problem i, koliko je moguće, predočiti granice postojećih spoznaja, tako da se čitateljima koji se ne bave područjem o kojemu je riječ omogući razumijevanje ciljeva rada.

Materijal i metode trebaju biti što preciznije opisane da omoguće drugim znanstvenicima ponavljanje pokusa. Glavni eksperimentalni podaci trebaju biti dvojezično navedeni.

Rezultati trebaju obuhvatiti samo materijal koji se izravno odnosi na predmet. Obvezatna je primjena metričkog sustava. Preporučuje se upotreba SI jedinica. Rjeđe rabljene fizikalne vrijednosti, simboli i jedinice trebaju biti objašnjeni pri njihovu prvom spominjanju u tekstu. Za pisanje formula valja se koristiti Equation Editorom (programom za pisanje formula u MS Wordu). Jedinice se pišu normalnim (uspravnim) slovima, a fizikalni simboli i faktori kosima (italicom).

Formule se susljedno obrojčavaju arapskim brojkama u zagradama, npr. (1) na kraju retka.

Broj slika mora biti ograničen samo na one koje su prijeko potrebne za objašnjenje teksta. Isti podaci ne smiju biti navedeni i u tablici i na slici. Slike i tablice trebaju biti zasebno obrojčane, arapskim brojkama, a u tekstu se na njih upućuje jasnim naznakama ("tablica 1" ili "slika 1"). Naslovi, zaglavlja, legende i sav ostali tekst u slikama i tablicama treba biti napisan hrvatskim i engleskim jezikom.

Slike je potrebno rasporediti na odgovarajuća mjesta u tekstu, trebaju biti izrađene u rezoluciji 600 dpi, crno-bijele (objavljivanje slika u koloru moguće je na zahtjev autora i uz posebno plaćanje), formata jpg ili tiff, potpune i jasno razumljive bez pozivanja na tekst priloga.

Svi grafikoni i tablice izrađuju se kao crno-bijeli prilozi (osim na zahtjev, uz plaćanje). Tablice i grafikoni trebaju biti na svojim mjestima u tekstu te originalnog formata u kojemu su izrađeni radi naknadnog ubacivanja hrvatskog prijevoda. Ako ne postoji mogućnost za to, potrebno je poslati originalne dokumente u formatu u kojemu su napravljeni (*excel* ili *statistica* format).

Naslovi slika i crteža ne pišu se velikim tiskanim slovima. Crteži i grafikoni trebaju odgovarati stilu časopisa (fontovima i izgledu). Slova i brojke moraju biti dovoljno veliki da budu lako čitljivi nakon smanjenja širine slike ili tablice. Fotomikrografije moraju imati naznaku uvećanja, poželjno u mikrometrima. Uvećanje može biti dodatno naznačeno na kraju naslova slike, npr. "uvećanje 7500 : l".

Diskusija i zaključak mogu, ako autori žele, biti spojeni u jedan odjeljak. U tom tekstu treba objasniti rezultate s obzirom na problem postavljen u uvodu i u odnosu prema odgovarajućim zapažanjima autora ili drugih istraživača. Valja izbjegavati ponavljanje podataka već iznesenih u odjeljku *Rezultati*. Mogu se razmotriti naznake za daljnja istraživanja ili primjenu. Ako su rezultati i diskusija spojeni u isti odjeljak, zaključke je nužno napisati izdvojeno. Zahvale se navode na kraju rukopisa. Odgovarajuću literaturu treba citirati u tekstu, i to prema harvardskom sustavu (*ime – godina*), npr. (Bađun, 1965). Nadalje, bibliografija mora biti navedena na kraju teksta, i to abecednim redom prezimena autora, s naslovima i potpunim navodima bibliografskih referenci. Popis literature mora biti selektivan, a svaka referenca na kraju mora imati naveden DOI broj, ako ga posjeduje (http://www.doi.org) (provjeriti na http://www.crossref.org).

Primjeri navođenja literature

Članci u časopisima: Prezime autora, inicijal(i) osobnog imena, godina: Naslov. Naziv časopisa, godište (ev. broj): stranice (od – do). Doi broj.

Primjer

Kärki, T., 2001: Variation of wood density and shrinkage in European aspen (*Populus tremula*). Holz als Roh- und Werkstoff, 59: 79-84. http://dx.doi.org/10.1007/s001070050479.

Knjige: Prezime autora, inicijal(i) osobnog imena, godina: Naslov. (ev. izdavač/editor): izdanje (ev. svezak). Mjesto izdanja, izdavač (ev. stranice od – do).

Primjeri

Krpan, J., 1970: Tehnologija furnira i ploča. Drugo izdanje. Zagreb, Tehnička knjiga.

Wilson, J. W.; Wellwood, R. W., 1965: Intra-increment chemical properties of certain western Canadian coniferous species. U: W. A. Cote, Jr. (Ed.): Cellular Ultrastructure of Woody Plants. Syracuse, N.Y., Syracuse Univ. Press, pp. 551- 559.

Ostale publikacije (brošure, studije itd.)

Müller, D., 1977: Beitrag zür Klassifizierung asiatischer Baumarten. Mitteilung der Bundesforschungsanstalt für Forstund Holzvvirt schaft Hamburg, Nr. 98. Hamburg: M. Wiederbusch.

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Latin names shall be printed in italics and underlined.

Introduction should define the problem and if possible the framework of existing knowledge, to ensure that readers not working in that particular field are able to understand author's intentions.

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The results should involve only material pertinent to the subject. The metric system shall be used. SI units are recommended. Rarely used physical values, symbols and units should be explained at their first appearance in the text. Formulas should be written by using Equation Editor (program for writing formulas in MS Word). Units shall be written in normal (upright) letters, physical symbols and factors in italics. Formulas shall be consecutively numbered with Arabic numerals in parenthesis (e.g. (1)) at the end of the line.

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Journal articles: Author's second name, initial(s) of the first name, year: Title. Journal name, volume (ev. issue): pages (from - to). DOI number.

Example:
Kärki, T., 2001: Variation of wood density and shrinkage in European aspen (*Populus tremula*). Holz als Roh- und Werkstoff, 59: 79-84. http://dx.doi.org/10.1007/s001070050479.

Books:
Author's second name, initial(s) of the first name, year: Title. (ev. Publisher/editor): edition, (ev. volume). Place of publishing, publisher (ev. pages from - to).

Examples:
Krpan, J. 1970: Tehnologija furnira i ploča. Drugo izdanje. Zagreb: Tehnička knjiga.
Wilson, J.W.; Wellwood, R.W. 1965: Intra-increment chemical properties of certain western Canadian coniferous species. U: W. A. Cote, Jr. (Ed.): Cellular Ultrastructure of Woody Plants. Syracuse, N.Y., Syracuse Univ. Press, pp. 551-559.

Other publications (brochures, studies, etc.):
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