DRVNA INDUSTRIJA

ZNANSTVENI ČASOPIS ZA PITANJA DRVNE TEHNOLOGIJE • ZAGREB • VOLUMEN 69 • BROJ 3
SCIENTIFIC JOURNAL OF WOOD TECHNOLOGY • ZAGREB • VOLUME 69 • NUMBER 3

Anisoptera **spp.**

3/18

UDK 674.031.677.7 CODEN: DRINAT ISSN 0012-6772

UDK 630*8+674 Coden: Drinat ISSN 0012-6772

DRVNA INDUSTRIJA

ZNANSTVENI ČASOPIS ZA PITANJA DRVNE TEHNOLOGIJE
SCIENTIFIC JOURNAL OF WOOD TECHNOLOGY

IZDAVAČ I UREDNIŠTVO
Publisher and Editor's Office
Šumarski fakultet Sveučilišta u Zagrebu
Faculty of Forestry, Zagreb University
10000 Zagreb, Svetošimunska 25
Hrvatska – Croatia
*Tel. (*385 1) 235 25 09*

SUIZDAVAČI
Co-Publishers
Exportdrvo d.d., Zagreb
Hrvatsko šumarsko društvo, Zagreb
Hrvatske šume d.o.o., Zagreb

OSNIVAČ
Founder
Institut za drvnoindustrijska istraživanja, Zagreb

GLAVNA I ODGOVORNA UREDNICA
Editor-in-Chief
Ružica Beljo Lučić

TEHNIČKI UREDNIK
Production Editor
Stjepan Pervan

POMOĆNICA UREDNIŠTVA
Assistant to Editorial Office
Dubravka Cvetan

LEKTORICE
Linguistic Advisers
Zlata Babić, prof. (hrvatski – Croatian)
Maja Zajšek-Vrhovac, prof. (engleski – English)

DRVNA INDUSTRIJA je časopis koji objavljuje znanstvene i stručne radove te ostale priloge iz cjelokupnog područja iskorištavanja šuma, istraživanja svojstava i primjene drva, mehaničke i kemijske prerade drva, svih proizvodnih grana te trgovine drvom i drvnim proizvodima.

Časopis izlazi četiri puta u godini.

DRVNA INDUSTRIJA contains research contributions and reviews covering the entire field of forest exploitation, wood properties and application, mechanical and chemical conversion and modification of wood, and all aspects of manufacturing and trade of wood and wood products.

The journal is published quarterly.

OVAJ BROJ ČASOPISA POTPOMAŽE:

Sadržaj
Contents

NAKLADA (Circulation): *700 komada* · **ČASOPIS JE REFERIRAN U (Indexed in):** *Science Citation Index Expanded, Scopus, CAB Abstracts, Compendex, Environment Index, Veterinary Science Database, Geobase, DOAJ* · **PRILOGE** *treba slati na adresu Uredništva. Znanstveni i stručni članci se recenziraju. Rukopisi se ne vraćaju.* · **MANUSCRIPTS** *are to be submitted to the editor's office. Scientific and professional papers are reviewed. Manuscripts will not be returned.* · **KONTAKTI s uredništvom (Contacts with the Editor) e-mail:** *editordi@sumfak.hr* · **PRETPLATA (Subscription):** *godišnja pretplata (annual subscription) za sve pretplatnike 55 EUR. Pretplata u Hrvatskoj za sve pretplatnike iznosi 300 kn, a za đake, studente i umirovljenike 100 kn, plativo na žiro račun 2360000 – 1101340148 s naznakom "Drvna industrija"* · **ČASOPIS SUFINANCIRA** *Ministarstvo znanosti, obrazovanja i sporta Republike Hrvatske.* · **TISAK (Printed by)** – *DENONA d.o.o., Getaldićeva 1, Zagreb, tel. 01/2361777, fax. 01/2332753, E-mail: denona@denona.hr; URL: www.denona.hr* · **DESIGN** Aljoša Brajdić · **ČASOPIS JE DOSTUPAN NA INTERNETU:** *http://drvnaindustrija.sumfak.hr* · **NASLOVNICA** *Presjek drva Anisoptera spp., ksiloteka Zavoda za znanost o drvu, Šumarski fakultet Sveučilišta u Zagrebu*

DRVNA INDUSTRIJA · Vol. 69, 3 · str. 205-294 · jesen 2018. · Zagreb
REDAKCIJA DOVRŠENA 2.09.2018.

Ayhan Ozcifci[1], Erkan Sami Kokten[2], Nadir Ayrilmis[3], Günay Özbay[1], Suat Altun[2]

Effects of Catalysts on Modulus of Rupture and Chemical Structure of Heat–Treated Wood

Učinci katalizatora na modul loma i kemijsku strukturu toplinski obrađenog drva

Original scientific paper • Izvorni znanstveni rad
Received – prispjelo: 9. 3. 2017.
Accepted – prihvaćeno: 13. 6. 2018.
*UDK: 630*812.; 630*813.4; 674.032.475.4*
doi:10.5552/drind.2018.1717

ABSTRACT • *Heat treatment process, which is widely used in the wood industry, has shown some negative effects on the mechanical strength of wood. The objective of this study was to investigate the effects of catalysts on the modulus of rupture (MOR), mass loss and chemical structure of heat–treated Scotch pine (Pinus sylvestris L.) samples. For this purpose, some catalysts (50 % NaOH and 47 % KOH solutions, solid KOH) were added to the heat treatment process. Heat treatment experiments were performed under the nitrogen atmosphere at the temperature of 212 °C for 2 h. The MOR and chemical changes monitored by FT-IR spectra were then examined for the test groups. According to the results of this study, the use of commercial solid potassium hydroxide (KOH) in heat treatment decreased the degree of strength loss and mass loss of heat-treated wood. The strength (MOR) loss of samples heat-treated in the presence of potassium hydroxide was found to be only 5.4 %, while the strength loss in non-catalytic treatment was found to be 12.5 %.*

Keywords: *heat treatment, Scotch pine, mechanical strength, catalyst, chemical properties*

SAŽETAK • *Proces toplinske obrade, koji se često primjenjuje u drvnoj industriji, pokazao je neke negativne učinke na mehaničku čvrstoću drva. Cilj ove studije bio je ispitati učinke katalizatora na modul loma (MOR), gubitak mase i kemijsku strukturu uzoraka toplinski obrađenog drva običnog bora (Pinus sylvestris L.). S tom namjerom u procesu toplinske obrade drva primijenjeni su katalizatori (50-postotna otopina NaOH i 47-postotna otopina KOH te kruti KOH). Eksperimentalna toplinska obrada drva provedena je u atmosferi dušika, pri temperaturi 212 °C tijekom 2 h. Modul loma i kemijske promjene praćene na spektrima FT-IR za odabrane su skupine uzoraka analizirani. Rezultati studije pokazali su da se primjenom komercijalnoga krutog kalijeva hidroksida (KOH) kao katalizatora pri toplinskoj obradi drva gubitak čvrstoće i gubitak mase toplinski obrađenog drva smanjuju. Utvrđeno je da je gubitak čvrstoće (MOR) uzoraka obrađivanih toplinom uz prisutnost kalijeva hidroksida samo 5,4 %, a gubitak čvrstoće u nekatalitičkom je tretmanu bio 12,5 %.*

Ključne riječi: *toplinska obrada, obični bor, mehanička čvrstoća, katalizator, kemijska svojstva*

[1] Authors are professor and associated professor at Faculty of Engineering, Aksaray University, Aksaray, Turkey. [2]Authors are research assistant and assistant professor at Faculty of Engineering, Karabuk University, Karabuk, Turkey. [3]Author is professor at Faculty of Forestry, Istanbul University, Istanbul, Turkey.
[1] Autori su profesor i izvanredni profesor Strojarskog fakulteta, Sveučilište u Aksarayu, Aksaray, Turska. [2]Autori su znanstveni asistent i docent Strojarskog fakulteta, Sveučilište u Karabuku, Karabuk, Turska. [3]Autor je profesor Šumarskog fakulteta, Sveučilište u Istanbulu, Istanbul, Turska.

1 INTRODUCTION
1. UVOD

Wood heat treatment by pre-pyrolysis is used to improve wood properties such as its decay durability and dimensional stability without chemical treatment (Rowell *et al.,* 2009; Kamdem *et al.*, 2002).

Wood heat treatment has become widespread in forestry and wood industry. According to statistics, the production volume of ThermoWood increased from 18799 m^3 in 2001 to 159333 m^3 in 2015. Also, almost half of the production volume implemented in 2015 was produced from pine wood (ThermoWood Production Statistics, 2015).

Thermal treatment at high temperature causes considerable changes in the chemical composition of wood. During heat treatment, hemicelluloses are degraded, ramification of lignin takes place, the relative amount of crystalline cellulose increases due to degradation of the amorphous components, extractive content decreases and wood acidity increases (Weiland and Guyonnet, 2003; Tumen *et al.,* 2010; Hakkou *et al.*, 2005; Boonstra and Tjeerdsma, 2006; Kocaefe *et al.*, 2008; Brito *et al.,* 2008; Kamdem *et al.,* 2002, Chen *et al.*, 2012).

Heat treatment process has shown some negative effects on the mechanical strength of wood. The reduction of mechanical strength may limit the use of heat-treated wood in fields requiring high strength (Shi *et al.,* 2007; Mburu *et al.,* 2008; Ates *et al.,* 2009; Şahin Kol, 2010; Guofu and Shengxia, 2012; Cao *et al.,* 2012; Kartal *et al.,* 2008).

During the heat treatment process, degradation of hemicelluloses releases acetic acid, which acts as a catalyst for decomposition of carbohydrate. Decomposition of carbohydrate results in strength and mass loss. Acid concentration, leading to strength loss in heat-treated wood increases with increasing treatment temperature and duration (Tjeerdsma *et al.*, 1998; McDonald *et al.,* 1999; Sivonen *et al.,* 2005; Sundqvist *et al.*, 2006).

In recent years, numerous studies have been performed by using various methods in order to improve the mechanical properties of heat-treated wood. Kartal *et al.* (2008) studied the effects of boron impregnation and heat treatment on chemical and mechanical properties of wood. Thus, wood samples treated with either boric acid (BA) or di-sodium octoborate tetrahydrate (DOT) solutions were exposed to heat treatment. They reported that BA and DOT treatments decreased the pH value of wood. Additionally, *MOR* losses after heat treatment in DOT-treated samples were found to be higher than in the untreated samples. Awoyemi and Westermark (2005) studied the effects of borate impregnation that were applied to wood before heat treatment on the strength properties of thermally modified wood. It was found that borate impregnation reduced the severity of the strength loss during heat treatment and this was attributed to the buffering effect of the alkali on the acidity of wood, which could have mitigated the degree of degradation. LeVan and Winandy (1990) stated that acidic fire retardant chemicals and high temperature increased the degree of acid hydrolysis in the wood, thereby causing a loss in strength. Wang *et al.* (2012) studied the effect of pH on chemical and mechanical properties of thermally modified wood. They found that disodium octoborate tetrahydrate (*pH* = 8.3) and buffering solutions reduced the mass loss of thermally treated wood and improved the modulus of rupture and modulus of elasticity. Chemical analyses also showed that degradation of hemicelluloses was inhibited by disodium octoborate tetrahydrate and boric acid/sodium hydroxide (buffering solutions) pretreatments within the temperature range of 180-200 °C, which may explain the mechanical property improvement. Winandy (1997) stated that using boron-based buffers before thermal treatment reduced the severity of thermal degradation. Percin *et al.* (2015) determined that the mechanical strength losses of samples impregnated with borax were generally lower than those of non-impregnated controls.

In previous studies, the strength loss in heat-treated wood was reported to be related to acid concentration. In this study, some basic catalysts (50 % NaOH and 47 % KOH solutions, solid KOH) were used in order to investigate the effects of the basic catalysts added to the heat treatment process on the modulus of rupture (*MOR*) and chemical changes revealed by FT-IR ATR spectroscopy.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Wood material
2.1. Drvo

Scotch pine (*Pinus sylvestris* L.) sapwood samples (non-deficient, without decay and insect damages) were selected as test materials. At least 28 samples with dimensions of 20 mm x 20 mm x 300 mm per treatment were oven dried at 103 ± 2 °C until a constant oven-dry weight was obtained prior to heat treatment experiments.

2.2 Catalysts
2.2. Katalizatori

The commercial catalysts used in the experiments were 50 % sodium hydroxide (NaOH) solution, 47 % potassium hydroxide (KOH) solution and solid potassium hydroxide (KOH). NaOH and KOH solutions were purchased from Merck, and solid KOH was purchased from Sigma-Aldrich.

The technical specifications of the catalysts are given in Table 1. (Sigma Aldrich Product Specification Sheet, 2013; MERCK Use Information Sheet, 2016a; MERCK Use Information Sheet, 2016b).

2.3 Heat treatment experiments
2.3. Provedba toplinske obrade

Heat treatment experiments were performed in a vacuum oven under the nitrogen atmosphere at the temperature of 212 °C for 2 h. During the experiments, the heating rate and temperature were controlled with a PID (Proportional–Integral–Derivative) controller. In a non-catalytic heat treatment experiment, the oven-

Table 1 Technical specifications of catalysts
Tablica 1. Tehnička obilježja katalizatora

Specification / *Obilježje*	**NaOH solution** / *Otopina NaOH*	**KOH solution** / *Otopina KOH*	**Solid KOH** / *Kruti KOH*
Melting point / *talište*	-	-	361 °C
Density / *gustoća*	1.53 g/cm³ (20 °C)	1.47 g/cm³ (20 °C)	2.04 g/cm³ (20 °C)
pH	>14 (20 °C)	>13.5 (20 °C)	>14 (20 °C)
Boiling point / *vrelište*	143 °C	135 °C	719 °C
Viscosity / *viskoznost*	79 mPa·s (20 °C)	8.7 mPa·s (20 °C)	-

Table 2 Test groups
Tablica 2. Ispitivane skupine uzoraka

Group code *Oznaka skupine*	**Catalyst** *Katalizator*	**Amount of catalyst** *Količina katalizatora* %	**Temperature** *Temperatura* °C	**Time** *Vrijeme* h
UT	NO / *bez katalizatora*	-	Untreated	-
HT	NO / *bez katalizatora*	-	212	2
N1	NaOH solution / *otopina NaOH*	15	212	2
N2	NaOH solution / *otopina NaOH*	30	212	2
K1	KOH solution / *otopina KOH*	15	212	2
K2	KOH solution / *otopina KOH*	30	212	2
SK1	Solid KOH / *kruti KOH*	15	212	2
SK2	Solid KOH / *kruti KOH*	30	212	2

*UT – Untreated / *netretirano drvo*, HT – Heat-treated / *toplinski obrađeno drvo*

dried samples were weighed and placed into the oven. In the catalytic heat treatment experiments, the oven was loaded with the samples and various amount of catalyst (15 %wt and 30 %wt). The samples were heated until a final temperature of 212 °C and maintained for 2 h at this temperature. The final, treatment system was stopped and allowed to cool down to a drying temperature of 103 °C under nitrogen atmosphere. The labeled test groups are given in Table 2.

2.4 Determination of mass loss and MOR
2.4. Određivanje gubitka mase i modula loma

The mass loss (*ML*) of the samples was determined according to equation (1).

$$ML = \frac{M_{ut} - M_t}{M_{ut}} \cdot 100 \qquad (1)$$

Where:
ML – mass loss (%),
M_{ut} – initial oven-dry mass of the sample before heat treatment (g),
M_t – oven-dry mass of the same sample after heat treatment (g).

The samples with dimensions of 20 mm x 20 mm x 300 mm were conditioned at 20 ± 2 ºC and 65 ± 5 % relative humidity for about 15 days to reach the equilibrium moisture content prior to MOR tests. MOR of the samples was tested according to Turkish standard (TS 2474, 1976). At least 28 samples were used for each treatment group to determine MOR.

2.5 Fourier transform infrared spectroscopy (FTIR)
2.5. Infracrvena spektroskopija s Fourierovom transformacijom (FTIR)

FT-IR spectra of untreated, heat-treated and catalytic heat-treated wood samples were determined by using an Alpha FTIR-ATR instrument (Bruker Alpha FTIR-ATR instrument).

Spectra were determined directly using ATR technique in the range from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

2.6 Statistical analysis
2.6. Statistička analiza

An analysis of variance ($p \leq 0.05$) was conducted to evaluate the importance of differences between experimental groups. In order to measure specific differences between pairs of means, post hoc test was performed. Significant differences between the groups and homogeneity groups were determined by Duncan's multiple range test (DMRT).

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1. Mass loss and modulus of rupture
3.1. Gubitak mase i modul loma

The mass loss and *MOR* test results of heat treatment experiments are given in Figures 1 and 2.

The analysis of variance ($p \leq 0.05$) was conducted to evaluate the effects of heat treatment performed in the presence of different catalysts on mass loss and *MOR*. The test results showed that the parameters that affect mass loss and *MOR* were statistically significant. Subsequently, the Duncan's multiple range test was applied in order to determine homogenous groups (Table 3).

According to Table 3 and Figure 1, the use of solid KOH resulted in the highest mass loss of heat-treated wood samples. Due to the acid–reducing effects of the catalysts used on wood, the mass loss of the samples generally reduced as compared to non-catalytic heat treatment.

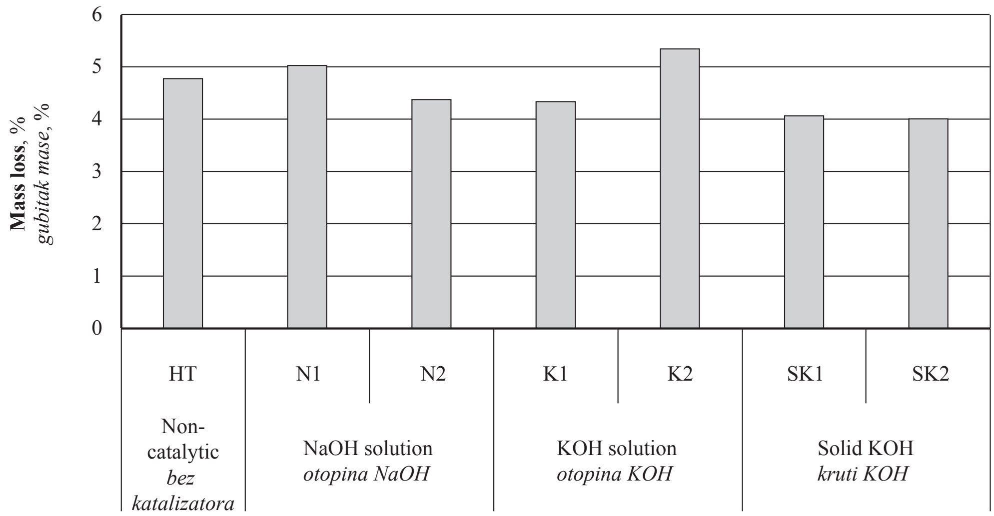


Figure 1 Mass loss of samples after heat treatment at temperature of 212 °C for 2 hours
Slika 1. Gubitak mase uzoraka nakon toplinske obrade pri temperaturi 212 °C tijekom 2 h

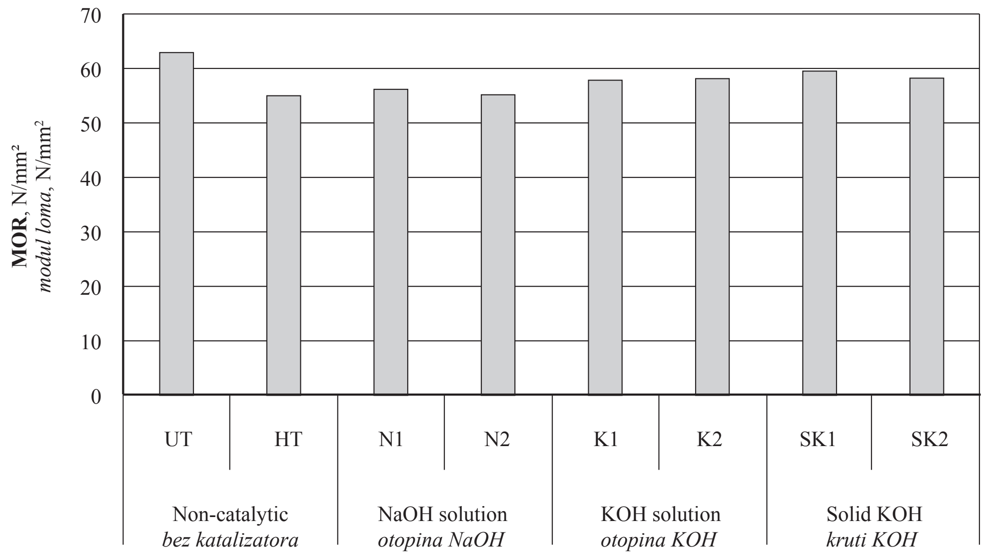


Figure 2 MOR test results of samples after heat treatment at temperature of 212 °C for 2 hours
Slika 2. Modul loma uzoraka nakon toplinske obrade pri temperaturi 212 °C tijekom 2 h

There were significant reductions in MOR of samples after heat treatment both in the catalytic and non-catalytic treatments (Table 3). As seen in Figure 2, heat treatment experiments performed in the presence of catalyst decreased the degree of strength loss of wood as compared to non-catalytic heat treatment. The strength (MOR) loss of samples heat-treated in the presence of solid KOH was found to be only 5.4 %, while the strength loss in non-catalytic treatment was found to be 12.5 %. However, the samples MOR was not significantly affected by the amount of catalyst, except for solid KOH, which was a bit different.

After heat treatment, the lowest mass loss (4 %) was found in samples heat-treated in the presence of solid KOH. Correspondingly, the highest MOR (59.56 N/mm^2) was found in the same samples and the lowest (55.04 N/mm^2) in non-catalytic (heat-treated) samples. The results showed that the use of catalyst (NaOH and KOH solutions, solid KOH) in heat treatment, especially solid KOH decreased the degree of strength loss. The most likely reason is that the use of catalyst reduces the release of acetic acid leading to strength loss in heat-treated wood. Awoyemi (2008) stated that the use of buffer reduces the release of acetic acid. Consequently, the degree of strength loss of heat-treated wood decreases significantly with increasing borate concentration from 0.1 to 0.3 M. This was undoubtedly due to the buffering effect of alkali on the strength properties of heat-treated wood.

3.2 Fourier transform IR analysis
3.2. FTIR analiza

Figure 3 presents the FTIR spectra of untreated, heat-treated and catalytic heat-treated pine wood samples. The peaks located at 805 cm^{-1}, 896 cm^{-1} and 1372 cm^{-1} corresponding to C-H deformation in cellulose and hemicelluloses decreased in the heat-treated samples when compared to the untreated samples (Tjeerdsma and Militz, 2005; Naumann *et al.,* 2005; Pandey and Pitman, 2003). However, the decreases of heat-treated samples with catalyst were less than those of heat-treated samples without the catalyst. This indi-

Table 3 Results of the Duncan's multiple range tests
Tablica 3. Rezultati Duncanovih testova

Group code *Oznaka skupine*	**Catalyst** *Katalizator*	**Amount of catalyst** *Količina katalizatora* %	**Temperature** *Temperatura* ºC	**Time** *Vrijeme* h	**SV**	**Mass loss** *Gubitak mase* %	**MOR** N/mm²
UT	NO / *bez katalizatora*	-	Untreated	-	Mean SD HG	-	62.97 8.70 B
HT	NO / *bez katalizatora*	-	212	2	Mean SD HG	4.77 0.77 BC	55.04 7.37 A
N1	NaOH solution / *otopina NaOH*	15	212	2	Mean SD HG	5.02 0.85 BC	56.22 11.01 A
N2	NaOH solution / *otopina NaOH*	30	212	2	Mean SD HG	4.37 1.56 AB	55.22 12.28 A
K1	KOH solution / *otopina KOH*	15	212	2	Mean SD HG	4.33 0.66 AB	57.88 8.50 A
K2	KOH solution / *otopina KOH*	30	212	2	Mean SD HG	5.34 1.05 C	58.17 7.57 A
SK1	Solid KOH / *kruti KOH*	15	212	2	Mean SD HG	4.06 0.84 A	59.56 9.64 AB
SK2	Solid KOH / *kruti KOH*	30	212	2	Mean SD HG	4.00 0.63 A	58.26 6.72 A

HG – Homogeneity group (groups with the same letters in the column indicate that there is no statistical difference (p<0.05) between the samples) / *grupa homogenosti (skupine s istim slovima u stupcu upućuju na to da među uzorcima ne postoji statistička razlika, p <0,05);* SD – Standard deviation / *standardna devijacija;* SV – Statistical values / *statističke vrijednosti*

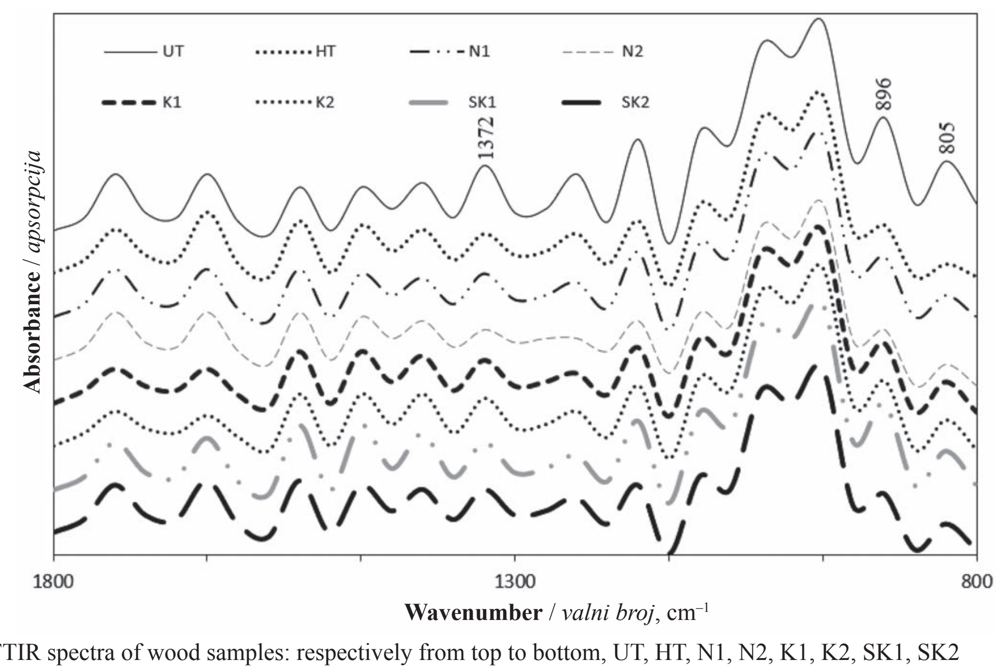


Figure 3 FTIR spectra of wood samples: respectively from top to bottom, UT, HT, N1, N2, K1, K2, SK1, SK2
Slika 3. FTIR spektri uzoraka drva; odozgo prema dolje: UT, HT, N1, N2, K1, K2, SK1, SK2

cates that the use of the catalyst in heat treatment reduced the hemicellulose degradation.

4 CONCLUSIONS
4. ZAKLJUČAK

The effects of heat treatment in the presence of catalyst on the chemical structure and *MOR* of scotch pine wood were investigated. Heat treatment in the presence of catalyst (NaOH and KOH solutions, solid KOH), especially commercial solid potassium hydroxide (KOH) could decrease the degree of strength loss and mass loss by reducing the release of acid leading to thermal degradation during heat treatment. According to FTIR analysis results, these differences could be attributed to the buffering effect of the catalysts on the strength properties of heat-treated wood.

The *MOR* losses of samples heat-treated in the presence of solid KOH (5.4 %) were lower than those in the presence of KOH solution (7.6 %), NaOH solution (10.7 %) and non-catalytic (12.5 %). However, significant differences between homogeneity groups were only found in treatments in the presence of solid KOH.

Acknowledgements – Zahvala

This study was supported by TUBITAK (The Scientific and Technological Research Council of Turkey) (Project grant number: 114O036).

5 REFERENCES
5. LITERATURA

1. Ates, S.; Akyildiz, M. H.; Ozdemir, H., 2009: Effects of Heat Treatment on Calabrian Pine (*Pinus Brutia* Ten.) wood. BioResources, 4 (3): 1032-1043.
2. Awoyemi, L.; Westermark, U., 2005: Effects of borate impregnation on the response of wood strength to heat treatment. Wood Sci. Technol., 39: 484-491. https://doi.org/10.1007/s00226-005-0001-5
3. Awoyemi, L., 2008: Determination of optimum borate concentration for alleviating strength loss during heat treatment of wood. Wood Sci. Technol., 42 (1): 39-45. https://doi.org/10.1007/s00226-007-0139-4
4. Boonstra, M.; Tjeerdsma, B., 2006: Chemical analysis of heat-treated softwoods. Holz Roh-Werkst., 64: 204-211. https://doi.org/10.1007/s00107-005-0078-4
5. Brito, J. O.; Silva, F. G.; Leão, M. M.; Almeida, G., 2008: Chemical composition changes in eucalyptus and pinus woods submitted to heat treatment. Bioresource Technology, 99 (18): 8545-8548. https://doi.org/10.1016/j.biortech.2008.03.069
6. Cao, Y.; Jiang, J.; Lu, J.; Huang, R.; Zhao, X.; Jiang, J., 2012: Effect of Steam-Heat Treatment on Mechanical Properties of Chinese Fir. BioResources, 7 (1): 1123-1133.
7. Chen, Y.; Fan, Y.; Gao, J. and Stark, N. M., 2012: The Effect of Heat Treatment on the Chemical and Color Change of Black Locust (*Robinia Pseudoacacia*) Wood Flour. BioResources, 7(1): 1157-1170.
8. Guofu, W.; Shengxia, H., 2012: Mechanical properties study on high temperature heat treatment of plantation Eucalypt wood. Chin. Agric. Sci. Bull., 28 (10): 59-62. https://doi.org/10.11924/j.issn.1000-6850.2012-0067
9. Hakkou, M.; Pétrissens, M.; Zoulalian, A.; Gérardin, P., 2005: Investigation of wood wettability changes during heat treatment on the basis of chemical analysis. Polymer Degradation and Stability, 89: 1-5. https://doi.org/10.1016/j.polymdegradstab.2004.10.017
10. Kamdem, D. P.; Pizzi, A.; Jermannaud, A., 2002: Durability of heat-treated wood. Holz Roh-Werkst, 60: 1-6. https://doi.org/10.1007/s00107-001-0261-1
11. Kartal, S. N.; Hwang, W.-J.; Imamura, Y., 2008: Combined effect of boron compounds and heat treatments on wood properties: Chemical and strength properties of wood. Journal of materials processing technology, 198: 234-240. https://doi.org/10.1016/j.jmatprotec.2007.07.001
12. Kocaefe, D.; Poncsak, S.; Boluk, Y., 2008: Effect of thermal treatment on the chemical composition and mechanical properties of birch and aspen. BioResources, 3 (2): 517-537.
13. LeVan, S. L.; Winandy, J. E., 1990: Effect of fire retardant treatments of wood strength: a review. Wood Fiber Sci., 22: 112-131.
14. Mburu, F.; Dumarçay, S.; Bocquet, J. F.; Pétrissans, M.; Gérardin, P., 2008: Effect of chemical modifications caused by heat treatment on mechanical properties of Grevillea robusta wood. Polymer Degrad. Stabil., 93: 401-405. https://doi.org/10.1016/j.polymdegradstab.2007.11.017
15. McDonald, A. G.; Gifford, J. S.; Dare, P. H.; Steward, D., 1999: Characterisation of the condensate generated from vacuum-drying of radiata pine wood. Holz Roh Werkst, 57 (4): 251-258. https://doi.org/10.1007/s001070050052
16. Naumann, A.; Gonzales, M. N.; Peddireddi, S.; Kues, U.; Polle, A., 2005: Fourier transform infrared microscopy and imaging: Detection of fungi in wood. Fungal Genetics and Biology, 42: 829-835. https://doi.org/10.1016/j.fgb.2005.06.003
17. Pandey, K. K.; Pitman, A. J., 2003: FTIR studies of the changes in wood chemistry following decay by brown-rot and white-rot fungi. International Biodeterioration & Biodegradation, 52: 151-160. https://doi.org/10.1016/S0964-8305(03)00052-0
18. Percin, O.; Sofuoglu, S. D.; Uzun, O., 2015: Effects of Boron Impregnation and Heat Treatment on Some Mechanical Properties of Oak (*Quercus petraea* Liebl.) Wood. BioResources, 10 (3): 3963-3978. https://doi.org/10.15376/biores.10.3.3963-3978
19. Rowell, R. M.; Ibach, R. E.; McSweeny, J.; Nilsson, T., 2009: Understanding decay resistance, dimensional stability and strength changes in heat treated and acetylated wood. Wood Material Science and Engineering, 4: 1-2. https://doi.org/10.1080/17480270903261339
20. Shi, J. L.; Kocaefe, D.; Zhang, J., 2007: Mechanical behaviour of Quebec wood species heat-treated using thermo wood process. Holz Roh Werkst, 65: 255-259. https://doi.org/10.1007/s00107-007-0173-9
21. Sivonen, H.; Maunu, S. L.; Sundholm, F.; Jamsa, S.; Viitaniemi, P., 2005: Magnetic Resonance Studies of Thermally Modified Wood. Holzforschung, 56 (6): 648-654. https://doi.org/10.1515/HF.2002.098
22. Sundqvist, B.; Karlsson, O.; Westermark, U., 2006: Determination of formic-acid and acetic acid concentrations formed during hydrothermal treatment of birch wood and its relation to colour, strength and hardness. Wood Sci. Technol., 40 (7): 549-561. https://doi.org/10.1007/s00226-006-0071-z
23. Şahin Kol, H., 2010: Characteristics of heat-treated Turkish pine and fir wood after ThermoWood processing. Journal of Environmental Biology, 31 (6): 1007-1011.
24. Tjeerdsma, B. F.; Militz, H., 2005: Chemical changes in hydrothermal treated wood: FTIR analysis of combined hydrothermal and dry heat-treated wood. Holz Roh Werkst., 63: 102-111. https://doi.org/10.1007/s00107-004-0532-8
25. Tjeerdsma, B. F.; Boonstra M.; Pizzi, A.; Tekely, P.; Militz, H., 1998: Characterisation of thermally modified wood: Molecular reasons for wood performance improvement. Holz Roh-Werkst., 56 (3): 149-153. https://doi.org/10.1007/s001070050287
26. TS 2474. 1976: Wood – Determination of Ultimate Strength in Static Bending. Turkish Standards Institution (TSE), Turkey.
27. Tumen, I.; Aydemir, D.; Gunduz, G.; Uner, B.; Cetin, H., 2010: Changes in the chemical structure of thermally treated wood. BioResources, 5 (3): 1936-1944.
28. Wang, W.; Cao, J.; Cui, F.; Wang, X., 2012: Effect of pH on chemical components and mechanical properties of thermally modified wood. Wood and Fiber Science, 44 (1): 46-53.
29. Weiland, J.; Guyonnet, R., 2003: Study of chemical modifications and fungi degradation of thermally modified

wood using DRIFT spectroscopy. Holz Roh-Werkst, 61 (3): 216-220.
https://doi.org/10.1007/s00107-003-0364-y
30. Winandy, J. E., 1997: Effects of fire retardant retention, borate buffers, and redrying temperature after treatment on thermal-induced degradation. Forest Products Journal, 47 (6): 79-86.
31. *** 2013: „Potassium hydroxide Sigma Aldrich Product Specification Sheet", Product Number: P5958. http://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Sigma/Product_Information_Sheet/1/p6310pis.pdf (Accessed March 10, 2017).
32. *** 2015: „ThermoWood Production Statistics", https://asiakas.kotisivukone.com/files/en.thermowood.kotisivukone.com/tiedostot/Productionstatistics2015.pdf (Accessed March 10, 2017).
33. *** 2016a: „Potassium hydroxide solution 47% for analysis MERCK Use Information Sheet", Catalogue No: 105545. http://www.merckmillipore.com/INTERSHOP/web/WFS/Merck-TR-Site/tr_TR/-/USD/ViewProductDocument-ReachUsesForSUBID?SUBID=100000020599 (Accessed March 10, 2017).
34. *** 2016b: „Sodium hydroxide solution 50% for analysis. MERCK Use Information Sheet", Catalogue No. 158793. http://www.merckmillipore.com/INTERSHOP/web/WFS/Merck-AT-Site/de_DE/-/EUR/ViewProduct-Document-ReachUsesForSUBID?SUBID=100000007990 (Accessed March 10, 2017).

Corresponding address:

Assoc. prof. GÜNAY ÖZBAY, Ph.D.

Department of Industrial Engineering
Faculty of Engineering
Aksaray University
68100 Aksaray, TURKEY
e-mail: gunayozbay@aksaray.edu.tr

Sima Sepahvand[1]*, Kazem Doosthosseini[1], Hamidreza Pirayesh[2], Behrooz Karamdoost Maryan[3]

Supplementation of Natural Tannins as an Alternative to Formaldehyde in Urea and Melamine Formaldehyde Resins used in MDF Production

Dodatak prirodnih tanina kao alternativa formaldehidu u urea-formaldehidnim i melamin-formaldehidnim ljepilima u proizvodnji MDF ploča

Original scientific paper • Izvorni znanstveni rad
Received – prispjelo: 23. 4. 2017.
Accepted – prihvaćeno: 13. 6. 2018.
*UDK: 630*813.111; 630*824.328; 630*863.312*
doi:10.5552/drind.2018.1726

ABSTRACT • *The aim of this study was to evaluate some mechanical and physical properties of medium density fiberboards (MDF) made from different adhesive types. Five panel types were made from mixtures of tannin (T) to urea formaldehyde (UF) and tannin to melamine formaldehyde (MF),* $TUF_{10\%}$, $TUF_{20\%}$, *MF,* $TMF_{10\%}$ *and* $TMF_{20\%}$, *respectively. Besides, the effect of press temperatures (170 and 180 °C) on the curing of the formulations was studied. Some mechanical properties (modulus of rupture, modulus of elasticity and internal bond strength), physical properties (thickness swelling and water absorption) and formaldehyde emission of the resulting panels were determined. The incorporation of tannin decreases the formaldehyde emission of the panels. However, flexural properties and internal bond strength decreased with increasing tannin ratio. The results indicated that panels can be manufactured using tannin up to 10 % in UF resin without falling below the minimum EN Standard requirements of mechanical properties for general purpose MDF panels.*

Key words: *Tannin, MF, UF, Formaldehyde emission, MDF*

SAŽETAK • *Cilj rada bio je procijeniti određena mehanička i fizikalna svojstva ploča vlaknatica srednje gustoće (MDF ploča) proizvedenih primjenom različitih vrsta ljepila. Pet vrsta ploča proizvedeno je uz primjenu smjese tanina (T) i urea-formaldehidne smole (UF) te tanina i melamin-formaldehidne smole (MF) u različitim omjerima, označenih kao TUF10%, TUF20%, MF, TMF10% i TMF20%. Osim toga, proučavan je utjecaj temperature prešanja (170 i 180 °C) na otvrdnjavanje tako dobivenih smjesa ljepila. Upoznata su i neka mehanička svojstva*

[1] Authors are Ph.D. student and professor at Department of Wood and Paper Science and Technology, Natural Resources Faculty, University of Tehran, Iran. [2]Author is professor at Wood Science & Technology Department, Faculty of Civil Engineering, Shahid Rajaee Teacher Training University (SRTTU), Tehran, Iran. [3]Author is research director at Shafarood institution of forest research and management, Gilan, Iran.

[1] Autori su doktorand i profesor Odjela za znanost i tehnologiju drva i papira, Fakultet prirodnih resursa, Sveučilište u Teheranu, Teheran, Iran. [2]Autor je profesor Odjela za znanost i tehnologiju drva, Građevinski fakultet, Učiteljsko sveučilište *Shahid Rajaee* (SRTTU), Teheran, Iran. [3]Autor je znanstvenik *Shafarood* institucije za istraživanje i upravljanje šumama, Gilan, Iran.

proizvedenih MDF ploča (modul loma, modul elastičnosti i čvrstoća raslojavanja), njihova fizikalna svojstva (bubrenje u debljinu i upijanje vode) te emisija formaldehida. Uz dodatak tanina proizvedene ploče imaju manju emisiju formaldehida. Međutim, čvrstoća na savijanje i čvrstoća raslojavanja tih ploča smanjuju se s povećanjem udjela tanina u ljepilu. Rezultati su pokazali da ploče mogu biti proizvedene s ljepilima u kojima je urea-formaldehidnim smolama dodano do 10 % tanina a da ploče i dalje udovoljavaju minimalnim EN standardnim zahtjevima mehaničkih svojstava za MDF ploče opće namjene.

Ključne riječi: *tanin, MF, UF, emisija formaldehida, MDF*

1 INTRODUCTION
1. UVOD

Over the past few decades, as a result of environmental awareness, the problem of air pollution in residential buildings increased more and more concerns on indoor air pollutants such as formaldehyde and acetaldehyde to be released from building materials and products. The release of formaldehyde from the panels used for internal applications is one of the main factors that cause sick building syndrome known indoor. Thus, the problem of formaldehyde emissions is one of the most important aspects of research of urea formaldehyde resin that should be seriously and thoroughly investigated and studied. On the other hand, the demand for wood composites such as medium density fiberboard, oriented strand board (OSB), plywood, hardboard and veneer products has recently increased significantly all over the world (Pirayesh and Saadatnia, 2015). Solving old and new challenges and movement towards green chemistry will require human unity and creativity. A new approach will also be needed to make better and greater use of renewable resources, and increase the resilience and diversity of production systems (Salari *et al*., 2013). A selection of bio wastes including wheat straw, sugarcane, sunflower seed hull, bamboo and palm have been successfully used in panel manufacturing and are already in the market under different trade names (Buyuksari *et al*., 2010).

Urea formaldehyde resin is the most important type of adhesive for manufacturing wood based composites (Kim and Kim, 2005; Nemli *et al*., 2008). Low price, good technological properties, absence of colors in cured polymer and easiness of application for a variety of curing conditions are the advantages of urea formaldehyde, while, formaldehyde emission and poor water resistance are its main disadvantages (Abdolzadeh *et al.,* 2011; Papadopoulos and Hague, 2003).With rising economic standards, concerns about human health and the environment have been raised due to the increasing demand for wood based panels (Habibi, 2008). Formaldehyde (HCOH) is a suspected human carcinogen that is known to be released from pressed-wood products used in home construction, including products made with urea-formaldehyde (UF) resins (Khanjanzadeh *et al*., 2013). Formaldehyde has also been found to produce nasal carcinomas in mice and rats after exposure to 14.1 and 5.6 ppm of formaldehyde, respectively, over a long period of time (Khanjanzadeh *et al*., 2013). Formaldehyde emission from panels in service is caused by residual formaldehyde present in the UF bonded panels trapped as gas in the structure and formaldehyde dissolved in the water present in the boards (Aydin *et al*., 2006; Doosthoseini, 2002). UF is water based wood adhesive whose shortcomings are low efficiency, poor water resistance and formaldehyde emission (Doosthoseini, 2002). Due to similar reasons, other water-based adhesives, including protein and starch based adhesives, are also not effective to bond directly grass-based particleboards (Roumeli *et al*., 2010)

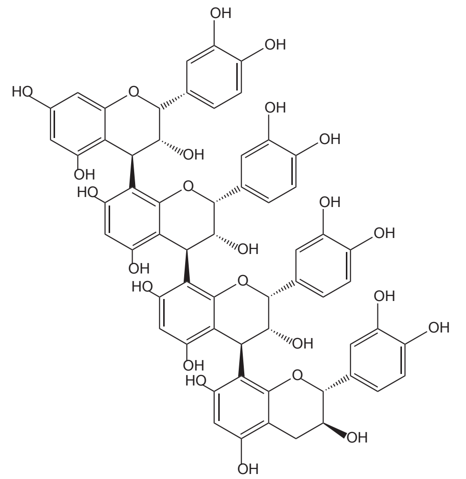


Figure 1 Condensed tannin
Slika 1. Kondenzirani tanin

Recently, there has been an interest in using tannin-based resins due to the more widespread availability of tannins, and the lower cost of tannin-based resins compared to CNSL. Tannins (Fig. 1) are naturally occurring phenolic compounds, which have been the subject of extensive research leading to the development of a wide range of industrial applications. The term ‘‘tannin” comes from the ancient Celtic word for oak, which still remains a popular source for tannins used in converting animal skin into leather (tanning). The objective of this study was to investigate the suitability of using natural tannins as an alternative to formaldehyde in urea and melamine formaldehyde resins used in MDF construction and to test the mechanical and physical properties of panels to determine if they have the required properties for general use.

2 MATERIAL AND METHODS
2. MATERIJAL I METODE

The raw material of this study included industrial wood fibers provided by a commercial fiberboard plant in Sari, Iran and tannin that was purchased from Merck, Germany. Thickness of panels was controlled by

Table 1 Experimental design
Tablica 1. Osnovni parametri eksperimenta

Panel type *Vrsta ploče*	*WS* wt.%	*MF* wt.%	$T_{10\%}$ *MF* wt.%	$T_{20\%}$ *MF* wt.%	$T_{10\%}$ *UF* wt.%	$T_{20\%}$ *UF* wt.%	Temperature press *Temperatura prešanja* °C
A_{170}	90	10	–	–	–	–	170
A_{180}	90	10	–	–	–	–	180
B_{170}	90	–	10	–	–	–	170
B_{180}	90	–	10	–	–	–	180
C_{170}	90	–	–	10	–	–	170
C_{180}	90	–	–	10	–	–	180
D_{170}	90	–	–	–	10	–	170
D_{180}	90	–	–	–	10	–	180
E_{170}	90	–	–	–	–	10	170
E_{180}	90	–	–	–	–	10	180

Table 2 Production parameters of MDFs
Tablica 2. Parametri proizvodnje MDF ploča

Parameter / *Obilježje*	**Value** *Vrijednost*
Pressing time / *Vrijeme prešanja*, min	7
Peak pressure / *Tlak prešanja*, kg/mm^2	35
Thickness / *Debljina*, mm	12
Dimensions / *Dimenzije*, mm	420×420
Number of panels for each type *Broj proizvedenih ploča za svaki tip ploče*	3

stop bars and panels target density was 0.7 g/cm^3. Three panels were produced for each group. The experimental design is shown in Table 1.

The dimensions of the produced panels were 42 × 42 × 1.2 cm. The produced MDF panels were conditioned at 20 °C and 65 % relative humidity to reach moisture content of about 12 % before trimming to final dimension of 40×40×1.2 cm. The panel production parameters are also displayed in Table 2.

Some mechanical properties: modulus of rupture (*MOR*), modulus of elasticity (*MOE*) (EN 310), internal bond strength (*IB*) (EN 319), and physical properties: thickness swelling (*TS*) and water absorption (*WA*) were determined for the produced fiberboards (EN 317). The average of 10 and 20 measurements were reported for mechanical and physical properties, respectively. The formaldehyde emission of the samples was measured according to the EN 717-3 standard. Six sheets of test pieces (with dimensions of 12 × 25 × 25 mm) were clamped 40 mm above water level using a plastic support in a 500-ml polyethylene bottle containing 50 ml of distilled water. The flask containing the specimens was loaded in the oven at 40 °C for 180 min. Formaldehyde released from the specimens was absorbed by the distilled water, which was subsequently used as the sample solution. The formaldehyde concentration in the sample solution was determined using acetylacetone–ammonium acetate solution and the acetylacetone method, with colorimetric detection at 412 nm. The data obtained was statistically analyzed using analysis of variance (ANOVA). Duncan's grouping was also included.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

Table 3 shows the results of mechanical properties of produced MDF panels. The highest *MOR* (27.12 N/mm^2) and *MOE* (2685 N/mm^2) values were measured for fiberboard produced employing neat MF resin. Besides, the lowest *MOR* (22.78 N/mm^2) and *MOE* (2285 N/mm^2) values were determined for panels type E, including 20 % tannin in UF resin. The result indicated that, with increasing tannin content in the mixture, the *MOR* and *MOE* values of fiberboards significantly decreased. Statistical analysis found some significant differences (P<0.01) between some group means for *MOR* and *MOE* values. Significant differences between groups were determined individually for these values by Duncan's multiple comparison tests. The results of Duncan's multiple range tests are shown in Table 3, denoted by letters. Depending on the amount of tannin content in the panels, average decreases in *MOR* values varied from 1.4 % to 16.1 % as compared to the average of the panel type A. All panel types showed significant differences (P<0.01) from each other in their *MOR* properties. *MOE* values showed relatively similar trends to those of *MOR*. The average *MOE* values of the panels with tannin content decreased from 10.4 % to 14.9 % as compared to values of the panels made with unmodified MF resin (panel type A). With the exception of panel types B and C, as well as D and E, other panel types showed statistically significant differences (P<0.01) from each other in their *MOE* properties. Addition of tannin content to panels had more adverse effect on *MOR* than on *MOE* values. The average *MOR* values of all panel types met the minimum requirement (22.78 MPa) of EN 622–5 for general-purpose MDF panels for use in dry conditions. However, only average *MOE* values of the panel type A met the minimum requirements for general purpose MDF (2500 MPa) of EN 622–5.

IB values of the experimental panels ranged from 0.53 to 0.70 N/mm^2. The highest IB value was observed for panel A, while the lowest was recorded for E type panel. IB values decreased with the increasing tannin content in the panels. The average decreases of

Table 3 Mechanical properties of MDF panels made from UF/tannin and MF/tannin and wood fibers and test results of ANOVA and Duncan's mean separation
Tablica 3. Mehanička svojstva MDF ploča proizvedenih od smjese UF/tanina odnosno MF/tanina i drvnih vlakanaca te rezultati testa ANOVA i Duncanova testa srednjih vrijednosti

Mechanical properties *Mehaničko svojstvo*	**Panel type** *Vrsta ploče*	**Mean**[a] *Srednja vrijednost*	**Std. deviation** *Standardna devijacija*	**Std. error** *Standardna pogreška*	X_{Min} [b]	X_{Max} [c]	p[d]
MOR (N/mm^2)	A	27.12 [s]	0.289	0.130	25.10	24.92	*
	B	26.75 [u]	0.235	0.089	24.60	24.65	*
	C	25.19 [t]	0.119	0.041	23.80	23.54	*
	D	24.45 [v]	0.127	0.052	23.02	22.41	*
	E	22.78 [w]	0.228	0.088	20.90	21.90	*
MOE (N/mm^2)	A	2685[s]	34.995	13.975	2480.00	2580.00	*
	B	2407 [u]	13.754	5.545	2468.00	25200.00	*
	C	2395 [u]	33.389	13.980	2414.00	2490.00	*
	D	2412 [t]	27.003	9.995	2348.00	2385.00	*
	E	2285 [t]	11.680	4.855	2292.00	2376.00	*
IB (N/mm^2)	A	0.70 [s]	0.028	0.011	0.59	0.66	*
	B	0.68 [s]	0.012	0.005	0.58	0.63	*
	C	0.62 [u]	0.018	0.007	0.54	0.60	*
	D	0.55 [u]	0.016	0.006	0.52	0.58	*
	E	0.53 [t]	0.014	0.005	0.50	0.53	*

[a] Mean values are the average of 10 specimens. / *Srednje vrijednosti dobivene su na temelju mjerenja provedenih na 10 uzoraka*. [b] Minimum value / *minimalna vrijednost*; [c] Maximum value / *maksimalna vrijednost*;
[d] Significance level of 0.01 (for ANOVA) / *razina značajnosti 0,01 (za test ANOVA)*.
[s,u,t,v,w] Values having the same letter are not significantly different (Duncan test). / *Vrijednosti koje imaju isto slovo nisu statistički signifikantno različite*.

IB value, upon increasing the tannin content, were 12.9 % to 24.3 % as compared to values of the panels made using neat MF resin (panel type A). With the exception of panel types A and B, as well as C and D, other panel types showed statistically significant differences (P<0.01) from each other in their *IB* properties. Out of the produced panels, only panel types A, B and C met the *IB* requirement (0.60 MPa) of EN 622–5 for general-purpose MDF panels for use in dry conditions.

The strength properties of wood products depend on many factors such as physical and mechanical properties as well as compact ratio of employed wood species, the configuration (orientation) and interfacial adhesion or interphase quality (Aydin *et al*., 2006; Ciannamea *et al*., 2010; Papadopoulos and Hague, 2003). Employed resin (bonder) plays a crucial role in wood based panels so that the quality of bonding, and hence the properties of the resulting materials, are dominantly determined by the type and quality of the bonder. There is close relationship between the ratio of urea and formaldehyde so that, with decreasing formaldehyde below a certain point, mechanical strength properties of the resulting UF resin will be seriously affected (Copur *et al.,*2008). Besides, chemical composition (lignin, cellulose and hemicellulose contents) of wood species has a strong influence on mechanical properties (Habibi *et al*., 2008) so that cellulose as well as hollocellulose contents have an impressive effect on surface wettability and hence adhesion (Aghakhani *et al*., 2013).

Unidirectional cellulose microfibrils constitute the reinforcing elements in the matrix blend of hemicellulose and lignin (Dunky and Pizzi, 2002). The effect of press temperature on mechanical properties of the resulting MDFs was not significant and this is why the result has not been included in the result and discussion part. The reason can be due to narrow temperature range used in this study.

Similar results have been published by different authors, who used various bio wastes (Aydin *et al*., 2006; Nemli and Colakoglu, 2005; Nemli *et al*., 2009). The results of ANOVA and Duncan's mean separation test for TS and WA of panels, made using the mixture of different adhesive formulations and wood fibers for 2 and 24 h water immersion times, are given in Table 4.

Adding tannin into MDF improved water repellency. With increasing tannin in the panels, the TS and WA values decreased from 3.3 % to 33.1 % and 4.5 % to 21.8 % for 2 h water immersion time, respectively. Likewise, for 24 h water immersion time, these figures were 3.4 % to 14.7 % and 2.1 % to 17.1 %, respectively. The average TS values of all panel types showed significant difference (P<0.01) from each other with the exception of panels D and E in TS after 2 h water immersion time. Besides, average WA values of all panel types showed significant difference (P<0.01) from each other after 2 and 24 h water immersion time. TS values of all panels did not meet maximum property requirements of 15 % for 24h water immersion for general purpose MDF panels specified by EN 622–5 (2005) standard.

The water resistance properties of wood based composites are affected by both water uptake capacity of lignocellulosic raw material and adhesive bonding quality (Roumeli*, et al.,* 2010). The effect of press temperature on physical properties of the resulting MDFs was not significant and this is why the result has not been included in the result and discussion part. The reason can be due to narrow temperature range used in this

Table 4 Test results of thickness swelling (TS) of MDF panels produced from UF/tannin and MF/tannin and wood fibers and of ANOVA and Duncan's mean separation
Tablica 4. Bubrenje u debljinu MDF ploča proizvedenih od smjese UF/tanina odnosno MF/tanina i drvnih vlakanaca te rezultati testa ANOVA i Duncanova testa srednjih vrijednosti

Physical properties *Fizikalno svojstvo*	**Panel type** *Vrsta ploče*	**Soaking time** *Vrijeme potapanja* min	**Mean**[a] *Srednja vrijednost*	**Std. deviation** *Standardna devijacija*	**Std. error** *Standardna pogreška*	X_{Min} [b]	X_{Max} [c]	p[d]
Thickness swelling *bubrenje u debljinu* (TS)	A	2	12.01 [s]	0.201	0.089	10.26	12.40	*
	B	2	11.63 [u]	0.525	0.195	10.20	11.65	*
	C	2	8.85 [t]	0.354	0.112	10.06	11.05	*
	D	2	8.50 [v]	0.343	0.085	9.54	10.62	*
	E	2	8.10 [v]	0.338	0.124	9.65	9.58	*
	A	24	21.25 [s]	0.404	0.123	20.35	21.80	*
	B	24	20.52 [s]	0.352	0.135	19.67	21.30	*
	C	24	19.83 [u]	0.235	0.068	18.54	20.52	*
	D	24	19.02 [t]	0.429	0.163	18.33	19.30	*
	E	24	18.12 [v]	0.295	0.095	16.63	18.30	*
Water absorption *upijanje vode* (WA)	A	2	25.80 [s]	0.358	0.224	25.60	26.16	*
	B	2	24.65 [u]	0.457	0.186	24.02	25.12	*
	C	2	23.62 [t]	0.364	0.224	23.41	23.52	*
	D	2	21.36 [v]	0.428	0.163	21.39	22.36	*
	E	2	20.18 [w]	0.309	0.096	20.01	20.56	*
	A	24	34.41 [s]	0.421	0.136	33.56	34.50	*
	B	24	33.68 [u]	0.402	0.128	31.02	33.22	*
	C	24	31.48 [t]	0.708	0.298	30.54	32.52	*
	D	24	29.36 [v]	0.375	0.104	28.37	29.00	*
	E	24	28.54 [w]	0.319	0.095	28.09	28.45	*

[a] Mean values are the average of 10 specimens. / *Srednje vrijednosti dobivene su na temelju mjerenja provedenih na 20 uzoraka*. [b] Minimum value / *minimalna vrijednost*; [c] Maximum value / *maksimalna vrijednost*; [d] Significance level of 0.01 (for ANOVA) / *razina značajnosti 0,01 (za test ANOVA)*.
[s,u,t,v,w] Values having the same letter are not significantly different (Duncan test). / *Vrijednosti koje imaju isto slovo nisu statistički signifikantno različite*.

study. Similar results have been reported for different bio wastes (Aydin, *et al*., 2006; Kim and Kim, 2005).

3.1 Formaldehyde emission
3.1. Emisija formaldehida

The addition of Tannin into the panels significantly decreased formaldehyde emission value (Fig. 3.). Depending on addition of tannin in the panels, the formaldehyde emission values ranged from 15 % to 35% lower than the panels made with neat MF resin. The minimum value of formaldehyde gas emission was measured for panels made with 20 % tannin in melamine formaldehyde resin. To be specific, panel type C had the lowest formaldehyde emission value with 6.5 mg/100 g (35 % less than panel type A), followed by panel type B (8.5 %), panel type D (9 %), panel type E (9.3 %), and finally panel type A (10.2 mg/100 g) (Fig. 3.).

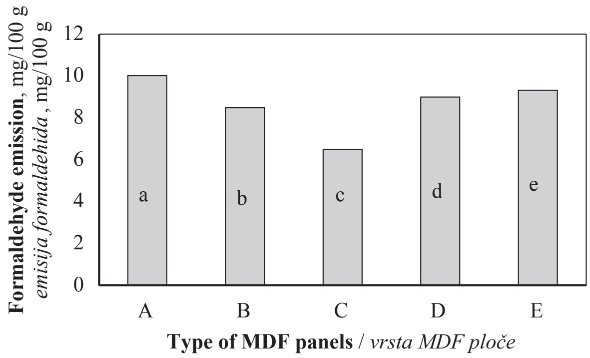


Figure 3 Percent decrease in average value of formaldehyde emission of panel types
Slika 3. Postotno smanjenje prosječne emisije formaldehida za sve vrste proizvedenih ploča

The results showed that the free-formaldehyde emission values of MDF panel types (E and C) for E1 class met the requirement of maximum 8 mg/100 g (Aydin *et al*., 2006). The decrease in formaldehyde emission of MDF panels with increasing tannin can be attributed to the scavenging effect of tannin and its chemical bonds with formaldehyde (Aydin *et al*., 2006). The similar results were reported in previous studies (Ayrilmis *et al*., 2009; Nemli and Aydin , 2007).They reported that the decrease in formaldehyde emission values in the panels may be due to high amounts of polyphenolic extractives in bark, especially tannins (Lei *et al*., 2009). It was found that incorporation of mimosa bark particle greatly reduces formaldehyde emission of particleboards. Post-treatment methods, aimed at decreasing and minimizing formaldehyde release, are based on compounds like ammonia, ammonium salts, or urea (Nemli and Aydin , 2007). Another effective way to reduce formaldehyde release is the addition of formaldehyde-binding substances ("scavengers") to the resin or to wood particles (Aydin *et al*., 2006). Ammonium chloride acts as an acid catalyst of the curing reaction and as a formaldehyde scavenger (Kim, 2009). Coating panel surfaces with decorative overlays are to eliminate the release of formaldehyde (Lei *et al*., 2009). The environmentally friendly tannin–formaldehyde resins are among the cheapest binders and cause low-formaldehyde emission (Ayrilmis *et al*., 2009). Besides, processing conditions of wood based panels have a serious impact on relative formaldehyde emission so that the higher the press cycle time, the lower the formaldehyde emission at service (Aghakhani, 2013). It is to be noted that using nanoparticles, such as nano-Sio_2 and nanoclay, due to their strong absorbability and high barrier properties (shielding effect) as formaldehyde catchers, will soon gain much attention (Kim, 2009; Papadopoulos and Hague, 2003).

4 CONCLUSION
4. ZAKLJUČAK

This study revealed that value-added MDF panels containing tannin can be considered as an alternative solution for decreasing carcinogenic gas of formaldehyde from wood based panels and for moving towards green chemistry. The incorporation of tannin greatly improved the formaldehyde emission of the panels; however, mechanical properties decreased with increasing tannin ratio. Using silane, dewaxing or raw material washing, the properties of wood based panels could be improved. Decreasing formaldehyde emission from MDFs containing tannin should be considered for furniture materials used indoor and this would be significant movement towards green chemistry and products.

Acknowledgment – Zahvala

The authors are grateful to the anonymous reviewers who provided useful comments to improve the clarity of the manuscript.

5. REFERENCES
5. LITERATURA

1. Abdolzadeh, H.; Doosthoseini, K.; Karimi, A. N.; Enayati, A. A., 2011: The effect of acetylated particle distribution and type of resin on physical and mechanical properties of poplar particleboard. Eur J Wood Prod, 69 (1): 3-10. https://doi.org/10.1007/s00107-009-0390-5
2. Aghakhani, M.; Enayati, S. H.; Nadalizadeh, H.; Pirayesh, H., 2013: The potential for using the sycamore (Platus orientalis) leaves in manufacturing particleboard. Int J Environ Sci Technol, 11 (2): 417-422. https://doi.org/10.1007/s13762-013-0327-8
3. Aydin, I.; Gursel, C.; Semra, C.; Cenk, D., 2006: Effects of moisture content on formaldehyde emission and mechanical properties of plywood. Building and Environment, 41 (10): 1311-1316. https://doi.org/10.1016/j.buildenv.2005.05.011
4. Ayrilmis, N.; Buyuksari, U.; Avci, E.; Koc, E., 2009: Utilization of pine (*Pinus pinea* L.) cone in manufacture of wood based composite. Forest Ecol Manage, 259 (1): 65-70. https://doi.org/10.1016/j.foreco.2009.09.043
5. Buyuksari, U.; Ayrilmis, N.; Avci, E.; Koc, E., 2010: Evaluation of the physical, mechanical properties and formaldehyde emission of particleboard manufactured from waste stone pine (*Pinus pinea* L.) cones. Bioresource Technology, 101 (1): 255-259. https://doi.org/10.1016/j.biortech.2009.08.038
6. Ciannamea, E. M.; Stefani, P. M.; Ruseckaite, R. A., 2010: Medium-density particleboards from modified rice husks and soybean protein concentrate-based adhesives. Bioresource Technology, 101 (2): 818-825. https://doi.org/10.1016/j.biortech.2009.08.084
7. Copur, Y.; Guler, C.; Tascioglu, C.; Tozluoglu, A., 2008: Incorporation of hazelnut shell and husk in MDF production. Bioresource Technology, 99 (15): 7402-7406. https://doi.org/10.1016/j.biortech.2008.01.021
8. Doosthoseini, K., 2002: Wood composite materials, manufacturing, applications. Vol. 1 (Fundamentals). University of Tehran Press, Tehran, Iran [in Persian].
9. Dunky, M.; Pizzi, A.; 2002: Wood adhesives. In: Chaudhury, M.; Pocius A. V. (eds.) Adhesive science and engineering: surfaces, chemistry and applications, chap. 23. Elsevier, Amsterdam, pp. 1039-1103. https://doi.org/10.1016/B978-044451140-9/50023-8
10. Faruk, O.; Bledzki, A. K.; Fink, H. P.; Sain, M., 2012: Biocomposites reinforced with natural fibers: 2000 – 2010. Progress in Polymer Science, 37 (11): 1552-1596. https://doi.org/10.1016/j.progpolymsci.2012.04.003
11. Habibi, Y.; El-Zawawy, W. K.; Ibrahim, M. M.; Dufresne, A., 2008: Processing and characterization of reinforced polyethylene composites made with lignocellulosic fibers from Egyptian agro-industrial residues. Compos Sci Technol, 68 (7-8): 1877-1885. https://doi.org/10.1016/j.compscitech.2008.01.008
12. Khanjanzadeh, H.; Pirayesh, H.; Salari, A., 2013: Long term hygroscopic characteristics of polypropylene based hybrid composites with and without organo-modified clay. J Wood Sci, 71 (2): 211-218. https://doi.org/10.1007/s00107-012-0661-4
13. Kim, S., 2009: The reduction of indoor air pollutant from wood-based composite by adding pozzolan for building materials. Construction and Building Materials, 23 (6): 2319-2323. https://doi.org/10.1016/j.conbuildmat.2008.11.008
14. Kim, S.; Kim, H. J., 2005: Effect of addition of polyvinyl acetate to melamine-formaldehyde resin on the adhesion and formaldehyde emission in engineered flooring. International Journal of Adhesion and Adhesives, 25 (5): 456-461. https://doi.org/10.1016/j.ijadhadh.2005.01.001
15. Lei, H.; Du, G.; Pizzi, A.; Celzard, A., 2008: Influence of Nanoclay on Urea-Formaldehyde Resins for Wood Adhesives and Its Model. Journal of Applied Polymer Science, 109 (4): 2442-2451. https://doi.org/10.1002/app.28359
16. Nemli, G.; Aydin, A., 2007: Evaluation of the physical and mechanical properties of particleboard made from the needle litter of Pinus pinaster Ait. Ind Crops Prod, 26 (3): 252-258. https://doi.org/10.1016/j.indcrop.2007.03.016
17. Nemli, G.; Colakoglu, G., 2005: Effects of mimosa bark usage on some properties of particleboard. Turkish Journal of Agriculture and Forestry, 29: 227-230.
18. Nemli, G.; Demirel, S.; Gümüokaya, E.; Aslan, M.; Acar, C., 2009: Feasibility of incorporating waste grass clippings (*Lolium perenne* L.) in particleboard composites. Waste Management, 29 (3): 1129-1131. https://doi.org/10.1016/j.wasman.2008.07.011 https://dx.doi.org/10.1016/j.wasman.2008.07.011.
19. Nemli, G.; Yildiz, S.; Gezer, E. D., 2008: The potential for using the needle litter of Scotch pine (*Pinus sylvestris* L.) as a raw material for particleboard manufacturing. Bioresource Technology, 99 (4): 6054-6058. https://doi.org/10.1016/j.biortech.2007.12.044
20. Papadopoulos, A. N.; Hague, J. R. B., 2003: The potential for using Xax (*Linum usitatissimum* L.) shiv as a lig-

nocellulosic raw material for particleboard. Industrial Crop and Products, 17: 143-147. https://doi.org/10.1016/S0926-6690(02)00094-8
21. Roumeli, E.; Pavlidou, E.; Papadopoulou, E.; Vourlias, G.; Bikiaris, D.; Paraskevopoulos, K. M.; Chrissafis, K., 2010: Synthesis, characterization and thermal analysis of Urea Formaldehyde/nanoSiO2 resins, Thermochimica Acta, 527: 33-39. https://doi.org/10.1016/j.tca.2011.10.007
22. Salari, A.; Tabarsa, T.; Khazaeian, A.; Saraeian, A., 2013: Improving some of applied properties of oriented strand board (OSB) made from underutilized low quality paulownia (*Paulownia fortunie*) wood employing nano-SiO2. Industrial Crops and Products, 42: 1-9. https://doi.org/10.1016/j.indcrop.2012.05.010
23. Zheng, Y.; Pan, Z.; Zhang, R.; EI-Mashad, H. M.; Pan, J.; Jenkins, B. M., 2009: Anaerobic digestion of saline creeping wild ryegrass for biogas production and pretreatment of particleboard material. Bioresour Technol, 100 (4): 1582-1588. https://doi.org/10.1016/j.biortech.2008.08.048
24. FAO, 2012: State of the World's Forests. Rome. www.fao.org.
25. *** 1993: BS-EN 310: Wood-based panels, determination of modulus of elasticity in bending and bending strength. Brussels (Belgium); European Committee for Standardization.
26. *** 1993: BS-EN 317: Particleboards and fiberboards, determination of swelling in thickness after immersion. Brussels (Belgium): European Committee for Standardization.
27. *** 1996: BS- EN 717-3: Wood-based panels. Determination of formaldehyde release. Formaldehyde release by the flask method.

Corresponding address:

SIMA SEPAHVAND, Ph.D. student

Department of Wood and Paper Science
and Technology
Natural Resources Faculty
University of Tehran
IRAN
e-mail: seppahvand.s@ut.ac.ir

Jacek Baranski[1], Marcin Jewartowski[1], Jan Wajs[1], Kazimierz A. Orlowski[2], Tomasz Pikala[3]

Experimental Examination and Modification of Chip Suction System in Circular Sawing Machine

Eksperimentalno ispitivanje i modifikacija sustava za odsis drvnih čestica na kružnoj pili

Original scientific paper • Izvorni znanstveni rad
Received – prispjelo: 10. 7. 2017.
Accepted – prihvaćeno: 13. 6. 2018.
*UDK: 630*822.331.9*
doi:10.5552/drind.2018.1743

ABSTRACT • *The article presents the results of experimental examination of the wood chip suction system in the existing sliding table saw before and after its modification. The studies focused on the extraction hood of the mentioned system. The methodical experimental research of the pressure distribution inside the hood during wood chip removal for the selected rotational speed of saw blades of 3500 and 6000 min*$^{-1}$ *with a diameter of 300 mm and 450 mm were carried out. The analysis of the results allowed estimating the areas with insufficient vacuum pressure hindering the organized transport of wood chips in the sliding table saw. That pressure was the main factor influencing the decision to adjust the hood construction. To achieve the efficient performance, several changes in the hood geometry were implemented. The results obtained from the experiments were used at the stage of shape modification of the extraction hood. As a result, a new design of the chip suction system was obtained, vastly improving the chip extraction from the tool.*

Key words: *sliding table saw, chip removing system, experimental study*

SAŽETAK • *U radu su prikazani rezultati eksperimentalnog istraživanja sustava za odsis drvnih čestica na stolnoj kružnoj pili prije njegove izmjene i nakon nje. Istraživanja su bila usmjerena na usisno ušće istraživanog sustava. Provedeno je metodološko eksperimentalno istraživanje raspodjele tlaka unutar usisnog ušća tijekom rada sustava za odsis drvnih čestica pri brzini vrtnje kružne pile od 3500 i 6000 min*$^{-1}$ *i uz promjer lista pile od 300 i 450 mm. Analiza rezultata omogućila je procjenu područjâ s nedovoljnim podtlakom unutar kojih je onemogućen učinkovit odsis drvnih čestica na stolnoj kružnoj pili. To je i bio glavni razlog odluke o prilagodbi konstrukcije usisnog ušća. Kako bi se postigao učinkovit odsis drvnih čestica, napravljeno je nekoliko promjena u geometriji usisnog ušća. Rezultati dobiveni eksperimentalnim istraživanjem upotrijebljeni su u fazi modificiranja oblika usisnog ušća. Kao rezultat toga dobiven je novi dizajn usisnog ušća kojim je znatno poboljšan odsis drvnih čestica iz radnog prostora alata.*

Ključne riječi: *stolna kružna pila, sustav za odsis drvnih čestica, eksperimentalna istraživanja*

[1] Authors are assistant professors at the Gdansk University of Technology, Faculty of Mechanical Engineering, Department of Energy and Industrial Apparatus, Gdansk, Poland. [2]Author is a full professor at the Gdansk University of Technology, Faculty of Mechanical Engineering, Department of Manufacturing Engineering and Automation, Gdansk, Poland. [3]Author is a chief process engineer in REMA SA in Reszel, Poland.

[1] Autori su docenti Tehnološkog sveučilišta u Gdansku, Strojarski fakultet, Odjel za energetske i industrijske uređaje, Gdansk, Poljska. [2]Autor je redoviti profesor Tehnološkog sveučilišta u Gdansku, Strojarski fakultet, Odjel za energetske i industrijske uređaje, Gdansk, Poljska. [3]Autor je glavni procesni inženjer u tvrtki REMA SA, Reszel, Poljska.

1 INTRODUCTION
1. UVOD

Currently, design development of woodworking machines, introduction of new technologies, and above of all the machining and feed speed result in the need to provide more effective wood waste (chips) removing systems. A modern wood cutting machine, which operates without a properly designed suction system loses immediately its performance and service life (Barański *et al.*, 2016). Woodworking machines and cutting parameters as well as wood material properties strongly determine the particle size distribution of chipped wood.

In the technological processes of machine wood chipping, a by-product is also formed besides the main product. These are chips whose shape, size and amount mainly depend on the form, physical and mechanical properties of sawed wood as well as on the shape, dimensions, type of machine, sharpness of the cutting blade, and technical and technological conditions of the sawing process (Wasielewski, 1999; Wasielewski and Orlowski, 2002; Orłowski, 2010; Beljo Lučić *et al.*, 2005; Očkajova *et al.*, 2006; Kopecký and Rousek, 2007; Klement and Detvaj, 2007).

Particles of wood, which are formed in individual processes of chipping and machining, are called "bulk wood substance" (Dzurenda, 2007). Thus, wood industry workers exposed to airborne wood dust particles in the surrounding air of the workplace may face different occupational health hazards (Kohler, 1995). Actually, the nature of the production and properties of chips require their continuous removal from the place where they are formed. As far as sanding dust is concerned, it is removed by means of an air-technical device - suction system. To develop such an appropriate suction system, it is important to know the size and shape of bulk particles, which are the basic data for characterizing the bulk material. The above characteristics affect the physical and mechanical properties of the bulk material (bulk density, bulk angle, tilt angle, aerodynamic properties of particles in the piping of the suction system) and conditions of separation or filtration in the separating device (Dzurenda, 2007). Also, those characteristics strongly affect the service life of the equipment in the workplace, where dust is generated as well as transportation equipment and filtering elements and, last but not least, the safety of the working environment.

Many authors investigate the possibility of reducing the (airborne) particles by controlling the machining parameters and by varying the cutting speed, feed speed, tool type and tool size, cutting angles, number of blades and processed material (Fujimoto and Takano, 2003; Hemmilä *et al.*, 2003). According to the results of these researches, the average chip thickness is one of the most important parameters of wood machining (Wieloch and Osajda, 2007). Furthermore, the sanding process, as a major source of airborne dust, was investigated by Rogoziński and Dolny, 2004; Očkajová and Beljaková, 2004; Beljaková and Očkajová, 2007; Rončka and Očkajová, 2007).

Depending on the machine type and the shape and size of its dust zone, serious problems may arise concerning the effective discharge of dust through a suction system during certain sanding positions. The machine type and method of processing significantly influence the increase of dust concentration in the air (Kos *et al.*, 2004). It is very difficult to remove dust when the working zone is large and when the tool operates at relatively high velocity. The dispersion of chips in different directions in the space of the treatment zone is very unfavorable in this respect. When the movement direction of the chips created during machining does not coincide with that of the air flow created by an extraction system, many chips are still not removed and can become dispersed in the air surrounding the machine. This takes places during sawing when the whole tool goes into the material piece. For this reason, there are problems with the direct removal of chips from the working zone and working tools. The dispersion of chips in all directions also occurs due to the high-speed rotation of those tools.

Wood working enterprises, as sources of air pollution, emit into the air wood dust classified as solid pollutants. Clean Air for Europe is the initiative taken by the EU Commission, by which one of its main aims set in 2002 was: "To reach such a quality of the environment where the level of pollutants coming from human activities does not cause any significant impacts and risks for human health" (EU Decision, 2002).

In this paper, experimental investigations of the wood chip removing system for sliding table saw were performed. The aim of the study was to examine chip suction system in the existing machine, commercially available on the market. Special attention was focused on its extraction hood without influence of fan parameters. The changes in a hood design have been proposed, causing higher efficiency of the chip removing system, which was confirmed by the results of experimental research.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

The sampling of pressure measurements was carried out during circular saw operation without machining. Table 1 shows the parameters of saw blades used during experiments.

The measurements were performed using the wide and narrow cover mounted in the hood of the suction-chip removing system and the saw blades of different diameter and rotational speed. For the saw blade No. 1, two of its maximum and minimum rotational speeds of 3500 min^{-1} and 6000 min^{-1}, and for saw blade No. 2, its nominal rotational speed of 3500 min^{-1} were considered, respectively. Variable fan speed was achieved by changing fan motor frequency. The relative static pressure was measured using a digital multi-function measuring instrument. The temperature, humidity and air flow meter Testo 480 (TESTO SE & Co., Germany) was applied. The results were averaged for 10 seconds at each measuring point. Measuring

Table 1 Parameters of woodworking machine saw blades during experiments
Tablica 1. Parametri listova pila na stroju za obradu drva proučavanih u eksperimentu

Woodworking machine *Stroj za obradu drva*	**Circular saw No. 1** *Kružna pila 1.*		**Circular saw No. 2** *Kružna pila 2.*
Tool diameter / *promjer alata*, *D* (mm)	∅ 300		∅ 450
Number of teeth / *broj zubi*, z	96		72
Tooth height / *visina zubi*, *h* (mm)	9.82		19.63
Overall set (kerf width) / širina *propiljka*, S_t (mm)	3.2		4.4
Thickness of saw blade / *debljina lista pile*, *a* (mm)	2.2		3.2
Rotational speed / *brzina vrtnje*, *n* (min^{-1})	3500	6000	3500

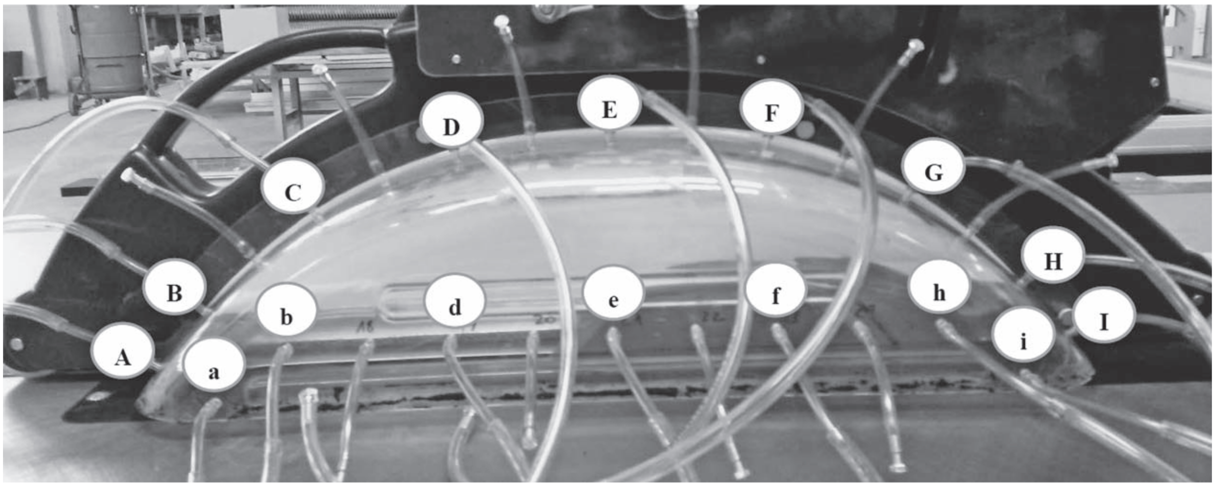


Figure 1 Location of measurement points on a wide cover of the hood
Slika 1. Raspored mjernih mjesta na širokom poklopcu usisnog ušća

range was from -10 to +10 kPa, resolution 0.01 kPa and accuracy ±0.3 Pa +1 % of the value measured in the lower range. Velocity at the entrance to the hood, as well as to the bottom shelter, was measured using the same instrument, with a hot wire probe. Measuring range was 0-20 m/s, resolution 0.01 m/s and accuracy ±0.03 m/s + 5 % of the measured value.

Experimental tests consisted of measuring the relative static pressure distribution zero-referenced against ambient air pressure at several points on the wide and narrow cover of suction-chip extraction hood (points “A”-“I” on the upper part and “a”-“i” on the side part of the wide cover and points “b*”-“h*” on the side of narrow cover). Locations of all measuring points are shown in Fig. 1 and Fig. 2. During preliminary measurements, more points were considered. However, it was found that there was a small pressure difference between the points situated close to each other.

The obtained results were analyzed and verified by the experiments performed using different shapes of the upper hood, Fig. 3.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

Results of relative static pressure measurements for the wide and narrow cover mounted in the hood of the existing system, further referred to as “base case”, showed that at most of the measurement points there was a vacuum pressure, as expected. However, some

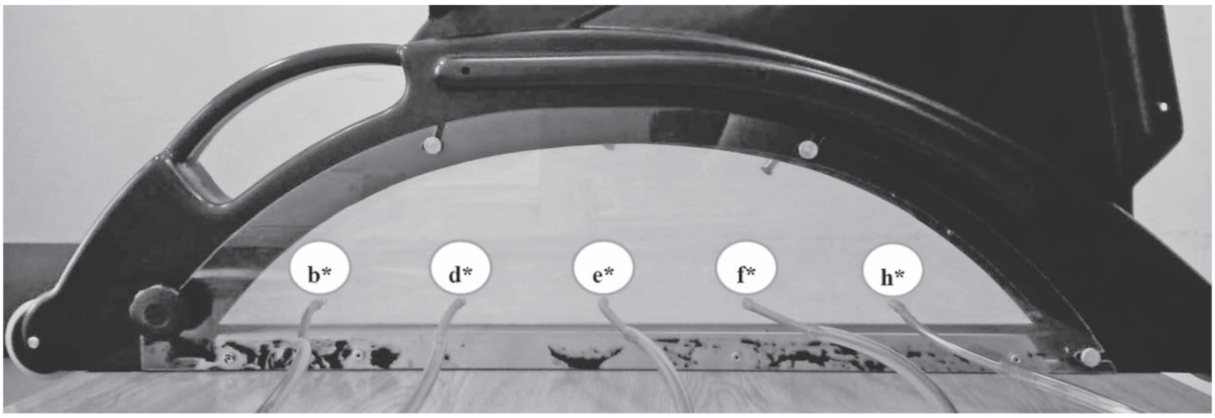


Figure 2 Location of measurement points on a narrow cover of the hood
Slika 2. Raspored mjernih mjesta na uskom poklopcu usisnog ušća

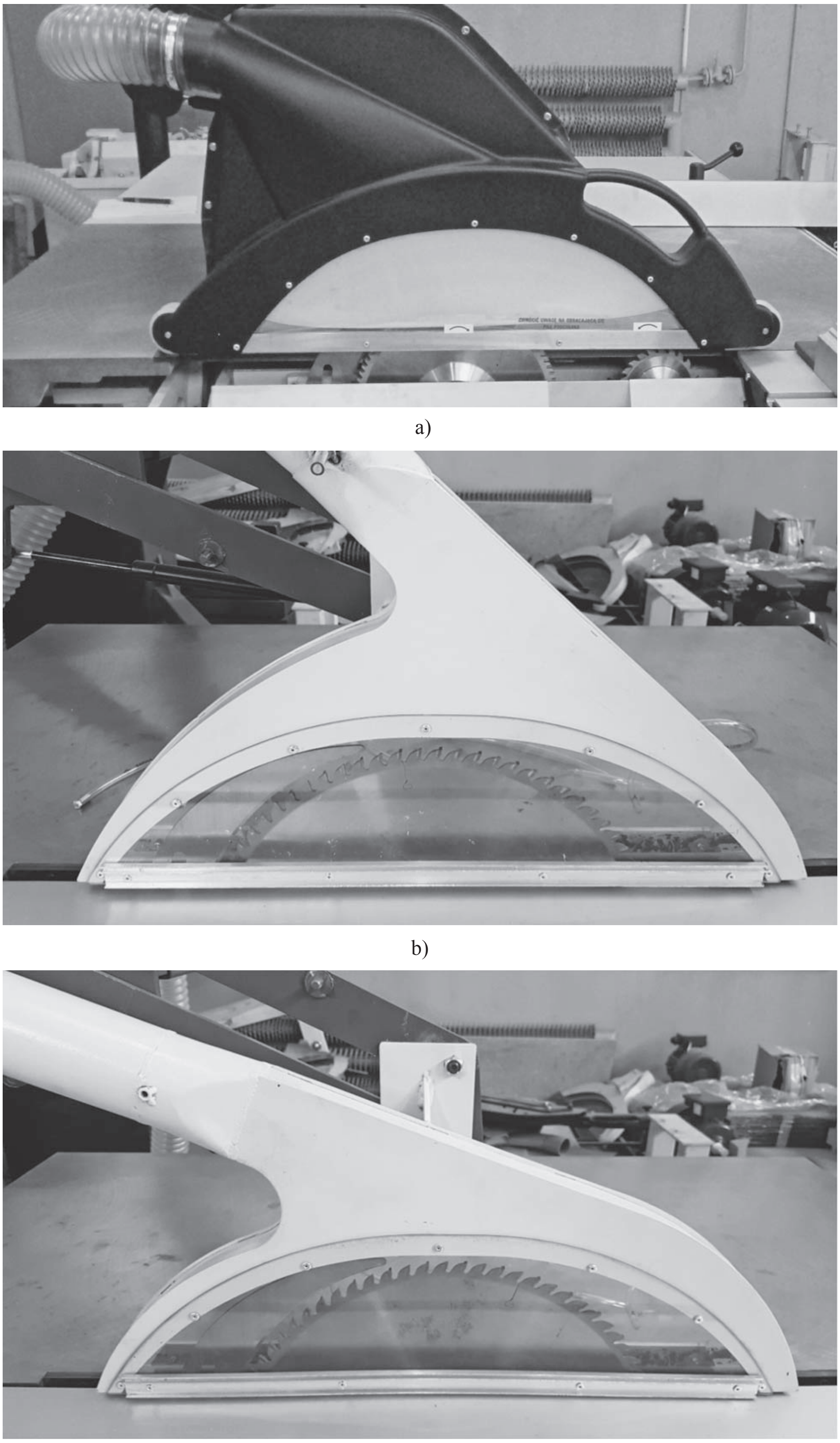


Figure 3 Chosen examples of the upper hood shape: a) base case, b) modified case, c) final case
Slika 3. Odabrani primjeri oblika gornjega usisnog ušća: a) početni oblik, b) modificirani oblik, c) konačni oblik

locations were observed with a very low vacuum pressure or even gauge pressure. These are points “A”-“B” and “a”-“b” for wide cover and “b*”-“d*” in case of the narrow cover. They are located in the zone of the highest influence of the air stream created by the kerf width and rotational speed of the saw blade. That influence at three of the critical points can be seen in Fig. 4 and Fig. 5. Saw blade rotational speed (Fig. 4) adversely affects the pressure distribution, causing disappearance of the desired vacuum pressure. The same result

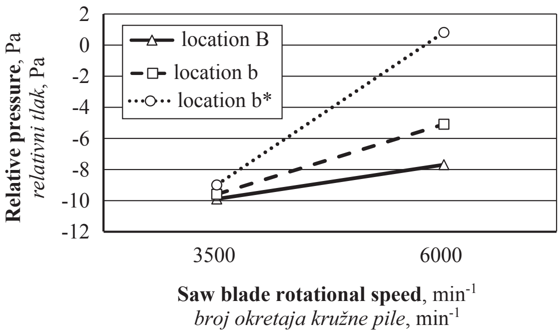


Figure 4 Relative static pressure as a function of saw blade rotational speed at different locations for wide and narrow cover of the hood; saw blade No. 1 (∅300 mm), fan motor frequency 50 Hz
Slika 4. Relativni statički tlak kao funkcija brzine vrtnje lista pile na različitim mjestima na širokom i uskom poklopcu usisnog ušća; list pile br. 1 (∅300 mm), frekvencija motora ventilatora 50 Hz

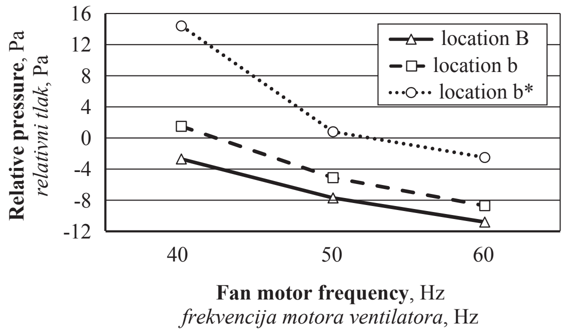


Figure 6 Relative static pressure as a function of fan motor frequency at different locations
for wide and narrow cover of the hood; saw blade No. 1 (∅300 mm), rotational speed 6000 min^{-1}
Slika 6. Relativni statički tlak kao funkcija frekvencije motora ventilatora na različitim mjestima na širokom i uskom poklopcu usisnog ušća; list pile br. 1 (∅300 mm), frekvencija vrtnje lista pile 6000 min^{-1}

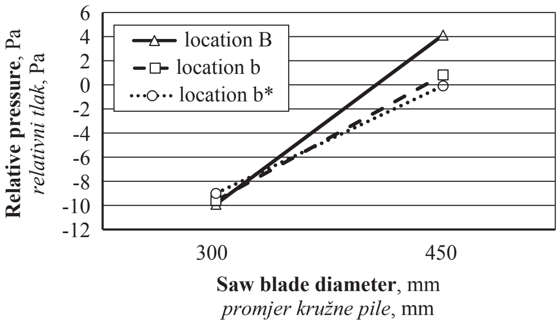


Figure 5 Relative static pressure as a function of saw blade diameter at different locations
for wide and narrow cover of the hood; saw blade rotational speed 3500 min^{-1}, fan motor frequency 50 Hz
Slika 5. Relativni statički tlak kao funkcija promjera lista pile na različitim mjestima na širokom i uskom poklopcu usisnog ušća; frekvencija vrtnje lista pile 3500 min^{-1}, frekvencija motora ventilatora 50 Hz

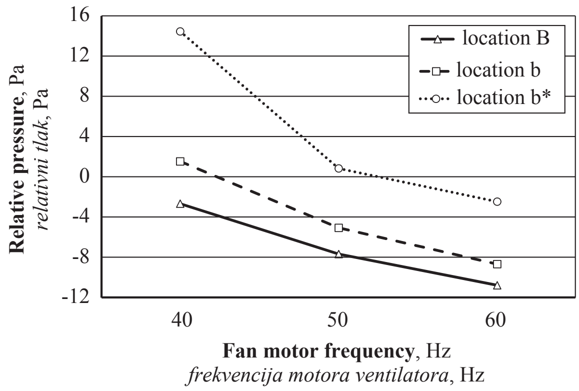


Figure 7 Velocity in outlet channel as a function of fan motor frequency at different saw blade diameters and rotational speed for the wide cover
Slika 7. Brzina u izlaznom kanalu kao funkcija frekvencije motora ventilatora pri različitim promjerima i brzinama vrtnje lista pile za široki poklopac

can be seen by increasing saw blade diameter (Fig. 5). Adverse effect occurs at all critical points.

As can be noticed, when the saw blade operated at the rotational speed of 3500 min^{-1}, there was a small vacuum pressure in locations B, b and b*. The value of relative static pressure ranged between - 9 Pa and - 10 Pa. On the other hand, when the saw blade speed was 6000 min^{-1}, the value of relative static pressure changed significanlty and even slight gauge pressure was measured on a narrow cover of the hood (location b*). For the wide cover of the hood, there was still vacuum pressure, but its value was lower than that for blade rotational speed of 3500 min^{-1}.

Changing saw blade diameter from ∅300 mm to ∅450 mm caused the transition from vacuum pressure of 9-10 Pa to gauge pressure of 1 Pa or 4 Pa for locations "B" and "b", respectively, and 0 pressure for location "b*". It is caused by higher linear velocities, occurred during the operation of larger saw blades.

In order to determine the effect of suction, fan speed on relative static pressure at critical locations of fan motor frequencies were changed ±20 %, from the initial value of 50 Hz without modification of the suction system. The measurement results for saw blade No. 1 (∅300 mm) and for fan motor frequencies of 40, 50 and 60 Hz are shown in Fig. 6. In case of reduced fan motor speed, a very large decrease in vacuum pressure and even the transition to gauge pressure was observed. The value of relative static pressure in locations "B", "b" and "b*" for that case was from +14 Pa to - 3 Pa. This can be explained by the influence of the main air flow in the hood, the scoring saw and the main saw blade rotational speed. On the other hand, increasing fan speed improved pressure distribution in all chosen measurement points and in consequence the performance of the chip removing system was improved.

Velocities in the outlet channel of the hood for both the wide and narrow cover were also measured. The results are shown in Fig. 7 and Fig. 8 for different saw blade diameters, rotational speeds and fan motor frequencies. During the operation of fan motor with the frequency of 50 Hz for saw blade diameter ∅300 mm at rotational speed of 3000 min^{-1} and 6000 min^{-1}, the velocity differences are small. Even for saw blade di-

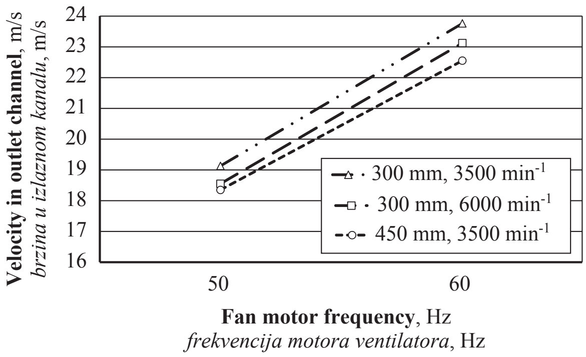


Figure 8 Velocity in outlet channel as a function of fan motor frequency at different saw blade diameters and rotational speed for the narrow cover
Slika 8. Brzina u izlaznom kanalu kao funkcija frekvencije motora ventilatora pri različitim promjerima i brzinama vrtnje lista pile za uski poklopac

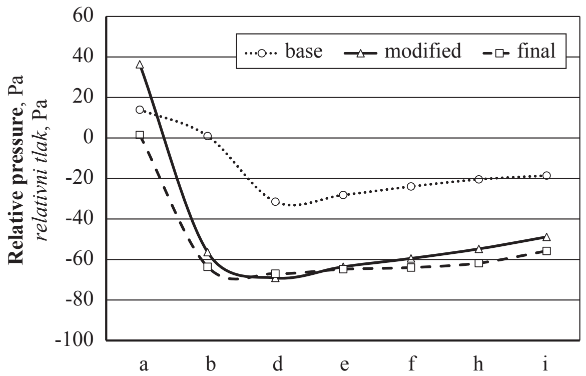


Figure 9 Relative static pressure distribution along the upper part of the wide cover
Slika 9. Raspodjela relativnoga statičkog tlaka duž gornjeg dijela širokog poklopca

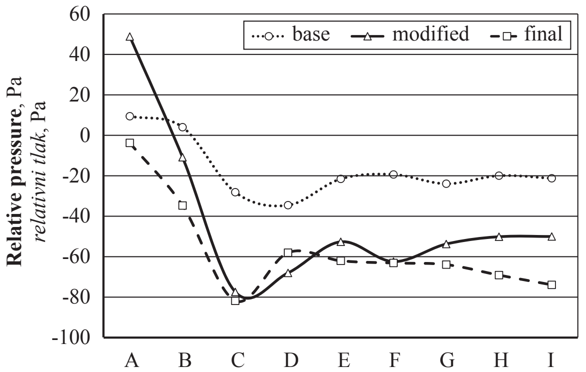


Figure 10 Relative static pressure distribution along the side part of the wide cover
Slika 10. Raspodjela relativnoga statičkog tlaka duž bočnog dijela širokog poklopca

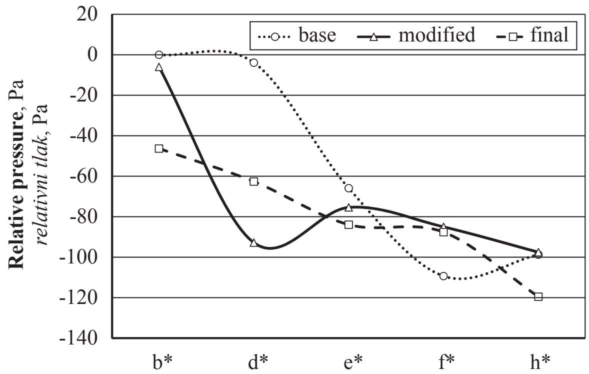


Figure 11 Relative static pressure distribution along the side of the narrow cover
Slika 11. Raspodjela relativnoga statičkog tlaka duž bočnog dijela uskog poklopca

ameter ∅450 mm, the velocity only slightly increases. Although these differences are due to the diameter and rotational speed of the saw blade, the fan motor frequency is still the most influencing factor. After changing frequency to 60 Hz, the value of velocity in the outlet channel of the hood significantly increased. Velocity improved by about 4 m/s in each case after frequency was increased by 20 %. However, the obtained velocity was still insufficient according to literature (Dzurenda, 2007).

In order to improve the performance of chip removing system without interfering with the fan structure, several modifications were carried out. The lower shelter shape was modified and changed to obtain smaller volume and, as a result, more efficient air flow and chip removal were achieved. Its leakages were minimized in critical places according to technological possibilities. The upper hood shape was also changed. The examples of its modifications are presented in Fig. 3b and 3c. In this element, the outlet channel angle and its inside passage for air flow were modified.

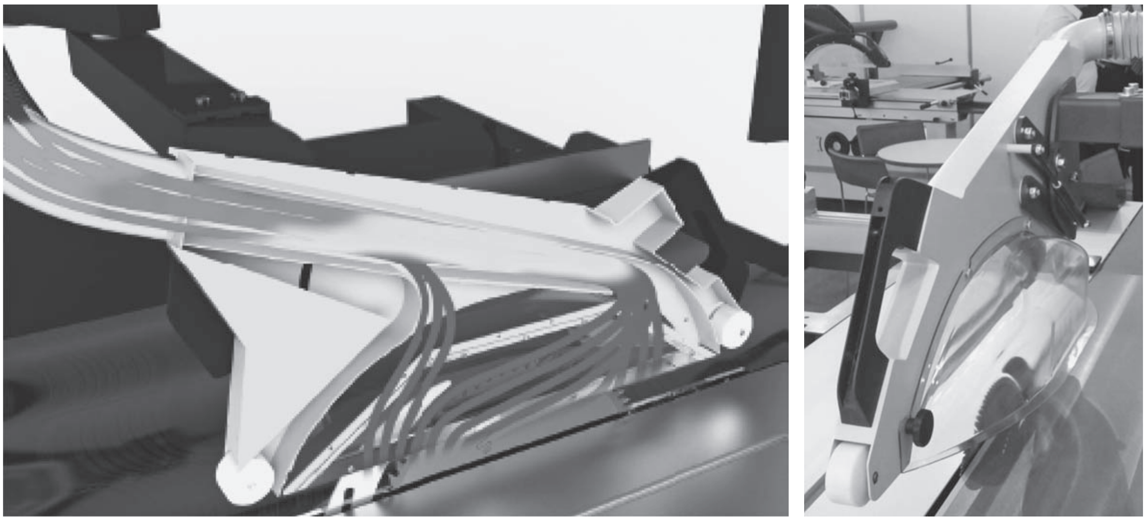
The results of pressure distribution after those modifications are shown for both wide and narrow cover in Fig. 9-11 as "modified" and "final" cases.

The results of measurement presented above show that blade shape, blade rotational speed and fan frequency have significant influence on the relative static pressure in chosen locations of the hood covers.

It can be emphasized that higher vacuum pressure in the modified and final hood shape was achieved in comparison with "base case", except for points "A" and "a" for modified case. When wide cover was used, gauge pressure was observed for "base case" and "modified case" in this location. For "final case", a little vacuum pressure was obtained in front of the hood. In the rest of the hood, the satisfactory pressure distribution was noticed without modification of the fan structure. Its final shape and inside construction is presented in Fig. 12.

4 CONCLUSIONS
4. ZAKLJUČAK

The existing chip removing system in the analyzed woodworking machine did not provide satisfactory chip extraction from the working area. The experiments proved that, in the area around the tool, insufficient vacuum pressure could hinder the organized transport of wood wastes. After several changes in the system, especially in the upper hood, all parts of the suction system were optimized and modified, except for the fan structure, which provided efficient perfor-



a) b)

Figure 12 Cross section a) and view b) of final design of the upper hood
Slika 12. Konačni dizajn gornjega usisnog ušća na stolnoj kružnoj pili: a) presjek i b) pogled sprijeda

mance. Eventually, a new design of the chip removing system was obtained. The final construction of the upper hood, which is part of the chip removing system, is shown in Fig. 12.

In order to achieve the most desirable results, however, it is strongly recommended that changes be made in the fan design or its motor resolution be optimized regardless of other modifications.

Acknowledgement – Zahvala

It is kindly acknowledged that this work has been carried out within the framework of the project POIR.01.01.01-00-05888/15, which has been financially supported by the European Regional Development Fund. The authors would also like to acknowledge the company REMA S. A. in Reszel (Poland), which is the beneficiary of the project, for helping out in the experimental part of this work. The data included in this paper was partially presented during the 23rd International Wood Machining Seminar, Warsaw, Poland. It could be emphasised that the sliding table saw Fx550, in which the presented solution of the suction system is applied, was awarded with the Gold Medal at the International Fair DREMA in Poznan, Poland in 2017.

5 REFERENCES
5. LITERATURA

1. Barański, J.; Jewartowski, M.; Wajs, J.; Pikała T., 2016: Experimental analysis of chip removing system in circular sawing machine. Trieskove a Beztrieskove Obrabanie Dreva, 10: 25-29.
2. Beljaková, A., Očkajová, A., 2007: Microscopic analyse of beech sanding dust. In: Proceedings of the 2nd ISC – Woodworking techniques. Zagreb, Croatia: Faculty of Forestry, Zagreb, Croatia, pp. 201-206.
3. Beljo Lučić, R.; Kos, A.; Antonović, A.; Vujasinović, E.; Šimičić, I., 2005: Svojstva usitnjenog materijala nastaloga pri mehaničkoj obradi drva. Drvna industrija, 56 (1): 11-19.
4. Dzurenda, L., 2007: Sypká drevná hmota, vzduchotechnická doprava a odlučovanie (Bulk wood mass, air transport and separation). 1st ed., 182 p. Technical University in Zvolen, Slovak Republic (in Slovak).
5. Fujimoto, K.; Takano, T., 2003: Mass concentration and particle size distribution of suspended during circular sawing. The Proceedings of the 16th International Wood Machining Seminar. Matsue, Japan, pp. 724-731.
6. Hemillä, P.; Gottlöber, C.; Weelling, I., 2003: Effect of cutting parameters to dust and noise in wood cutting, laboratory and industrial tests. The Proceedings of the 16th International Wood Machining Seminar. Matsue, Japan, pp. 375-384.
7. Klemet, I.; Detvaj, J., 2007: Technologia prvostupňového spracovania dreva (Technologies of processing of wood). 1st ed., 300 p. Technical University in Zvolen, Slovak Republic (in Slovak).
8. Kohler, B., 1995: Wood dust and cancer. National Report – Health, Safety and Environment, IARC, France.
9. Kopecký, Z.; Rousek, M., 2007: Dustiness in high-speed milling. Wood research, 52 (2): 65-76.
10. Kos, A.; Beljo Lučić, R., 2004: Factors influencing particle size distribution of oak sawdust developed during circular sawing. Trieskove a Beztrieskove Obrabanie Dreva. Technical University in Zvolen, Slovak Republic, 4: 131-137.
11. Očkajová, A., Beljaková, A., 2004: Motion of sanding mean versus granularity of sand wood dust. Trieskove a Beztrieskove Obrabanie Dreva, 4: 163-168.
12. Očkajová, A.; Beljo Lučić, R.; Čavlović, A.; Teraňová, J., 2006: Reduction of dustiness in sawing wood by universal circular saw. Drvna industrija, 57 (3): 119-126.
13. Orłowski, K., 2010: The fundamentals of narrow-kerf sawing: mechanics and quality of cutting. Technical University in Zvolen, Slovak Republic, 123 p.
14. Rogozinski, T.; Dolny, S., 2004: Influence of moisture content on the apparent densities of dust from sanding of alder wood. Trieskove a Beztrieskove Obrabanie Dreva, 4: 205-208.
15. Rončka, J.; Očkajová, A., 2007: The influence of sanding machine type and grit size on granularity of sanding wood dust. 2nd International Scientific Conference "Woodworking techniques". University of Zagreb. Zalesina, Croatia, pp. 289-294.

16. Wasielewski, R., 1999: Pilarki ramowe z eliptyczną trajektorią prowadzenia pil i hybrydowym wyrównoważonym układem napędu głównego (Frame sawing machines with elliptical saw blades movement and the system balanced). Gdańsk, Politechnika Gdańska, 106 p. (in Polish).
17. Wasielewski, R., Orłowski K., 2002: Hybrid dynamically balanced saw frame drive. Holz als Roh- und Werkstoff. 60 (3): 202-206. https://doi.org/10.1007/s00107-002-0290-4
18. Wieloch, G.; Osajda, M., 2007: Wymiary wiórów z drewna buka powstających przy toczeniu nożem samoobrotowym. International Conference "Wood – machine – tool – workpiece". Poznań, Poland, pp. 53-54 (in Polish).
19. *** 2002: Decision No 1600/2002/EC of the European Parliament and of the Council of laying down the Sixth Community Environment Action Programme. Official Journal of the European Communities, 10.9.2002: L 242/1 – L 242/15 http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32002D1600&from=EN (accessed on July 13, 2017).

Corresponding address:

Prof. KAZIMIERZ A. ORLOWSKI, Ph.D.

Gdansk University of Technology
Faculty of Mechanical Engineering
Department of Manufacturing Engineering
and Automation
G. Narutowicza 11/12
80-233 Gdansk, POLAND
e-mail: korlowsk@pg.gda.pl
ORCID iD: 0000-0003-1998-521X

Peter Rantuch, Jozef Martinka, Igor Wachter[1]

Effect of Thermal Treatment on Combustion Process of Spruce Wood (*Picea abies*)

Učinak toplinske obrade na proces izgaranja drva smreke (*Picea abies*)

Original scientific paper • Izvorni znanstveni rad
Received – prispjelo: 18. 9. 2017.
Accepted – prihvaćeno: 13. 6. 2018.
*UDK: 630*812.582; 674.032.13*
doi:10.5552/drind.2018.1752

ABSTRACT • *This paper deals with the effect of thermal treatment of spruce wood on its burning process. Samples of 100 mm x 100 mm were dried out and then heat-treated at 150 °C, 200 °C, 250 °C and 300 °C. Thus prepared samples were tested on a cone calorimeter at a heat flow of 50 kW·m^{-2}. The obtained results clearly show that with the increasing temperature of the treatment, the released heat from the surface unit decreases and the unit weight increases. The carbon dioxide concentration in the flue gas increases as well, however, the optical density of the smoke decreases substantially. It can be stated that the burning of spruce wood is considerably affected mainly by the thermal treatment at temperatures above 200 °C. From the point of view of the use of spruce wood as fuel, the most optimal treatment temperature is 250 °C.*

Key words: *torrefaction, Picea abies wood, heat flux, heat release*

SAŽETAK • *U radu se razmatra učinak toplinske obrade smrekova drva na proces njegova gorenja. Uzorci dimenzija 100 x 100 mm osušeni su i zatim toplinski obrađeni na 150, 200, 250 i 300 °C. Tako pripremljeni uzorci ispitani su na konusnom kalorimetru, pri toplinskom toku od 50 kW·m^{-2}. Iz dobivenih se rezultata može uočiti da se s povećanjem temperature toplinske obrade smanjuje oslobođena toplina površinske jedinice i povećava jedinična težina uzoraka od smrekovine. Koncentracija ugljikova dioksida u dimnom plinu također se povećava, ali se optička gustoća dima znatno smanjuje. Može se također zaključiti da na izgaranje smrekovine uglavnom znatno utječe toplinska obrada pri temperaturama višim od 200 °C. S gledišta upotrebe smrekovine kao ogrjeva, optimalna je temperatura toplinske obrade tog drva 250 °C.*

Ključne riječi: *torefakcija, drvo smreke, toplinski tok, otpuštanje topline*

1 INTRODUCTION
1. UVOD

The treatment of wood by thermal load can be divided into three basic areas on the basis of the required output raw material. Drying is intended to reduce wood moisture. It is usually performed at a temperature of up to 115 °C (Edvardsen and Sandland, 1999; Hansson and Antti, 2006; Zarea Hosseinabadi *et al.*, 2012; Sehlstedt-Persson, 1995). The second area is thermal modification.

Modern thermal modification processes are limited to temperatures no higher than 260 °C. As a result of thermally induced chemical changes to the macromolecular constituents, the physical and biological properties of wood are altered (Hill, 2007). Finally, wood is used for the preparation of torrefied wood. This semi refined material is an intermediate between

[1] Authors are assistants at Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology in Trnava, Slovak Republic.
[1] Autori su asistenti Slovačkoga tehnološkog sveučilišta u Bratislavi, Fakultet za znanost i tehnologiju materijala, Trnava, Slovačka.

wood and charcoal, which has undergone a mild pyrolysis in inert atmosphere, at temperatures from 200 °C to 300 °C and atmospheric pressure (Bourgois and Guyonnet, 1988).

Thermal decomposition of wood can be described using a five-reaction mechanism, consisting of three devolatilization reactions for the pseudo-components - hemicellulose, cellulose and lignin, and of two additional reactions in the air for char devolatilization and combustion (Broström *et al.*, 2012).

Heat-treatment affects the mechanical properties of wood, whereby hardwood species are more susceptible to this process than softwood. The decay resistance of heat-treatment may be achieved but at a high cost and with reduced mechanical properties (Kamdem *et al.*, 2002). Heat treatment mainly resulted in a darkening of wood tissues, improvement of the dimensional stability of wood and reduction of its mechanical properties (Bekhta and Niemz, 2003). Increased heat treatment and resulting weight loss reduce the modulus of rupture (MOR) and modulus of elasticity (MOE) (Mburu *et al.*, 2008). Živković *et al.* (2008) state that the results of laboratory tests show that the heat-treated wood, when compared to genuine wood, except of improvements in dimensional stability, also exhibits a lower equilibrium moisture content in room conditions. Results of Mburu *et al.* (2007) showed that resistance to fungi and termites was greatly improved by the treatment. The acidity and wood-water contact angle are higher and polar component of surface free energy is lower after thermal modification (Miklečić and Jirouš-Rajković, 2016).

A mild thermal treatment (modifying at 160 - 180 °C in oxygen-poor atmosphere) leads to clear changes of the measurable acoustic characteristics, such as Young's modulus, damping and sound velocity, so thermally modified wood is a material with favourable characteristics for making musical instruments (Pfriem, 2015).

As a solid energy carrier, biomass generally has a few disadvantages, which limits its use for coal replacement and as a feedstock for entrained flow gasification. The hydrophilic and fibrous nature, low calorific value and low bulk energy content imply high accumulated costs in the whole supply chain and severe challenges in more advanced conversion systems. By thermally pre-treating the biomass by torrefaction, these properties may be significantly improved (Strandberg *et al.*, 2015), so torrefaction is a promising technique for improving the biomass performance for energy utilization (Tapasvi *et al.*, 2012).

In contrast to fossil fuels, biomass has a unique potential for making positive environmental impact. In the plan of the sustainable biomass production and use, the carbon dioxide emitted would be absorbed by newly grown biomass. It can be burnt without emitting large amounts of nitrogen oxides, and with low emissions of sulphur dioxide (Quaak *et al.*, 1999).

During torrefaction, the main thermal decomposition reactions involve the hemicellulose polymers, resulting in improved fuel properties exhibited by the torrefied samples. Compared to raw samples, the composition of the torrefied samples is closer to that of coal, with higher carbon content and a lower volatile matter content, and with much higher hydrophobicity (Tapasvi *et al.*, 2012). The carbon contents of torrefied wood are greater than those of wood, but lower than those of charcoal. Carbon increases at the expense of oxygen and hydrogen, thus leading to decreases in both H/C and O/C ratios (Pentananunt *et al.*, 1990).

In comparison to non-thermally treated wood, torrefied biomass fuels contain a lower amount of volatile matter and a higher amount of fixed carbon (Ndibe *et al.*, 2015).

Both torrefaction temperature and reaction time have strong effects on the torrefaction process, but temperature effects are stronger than effects of reaction time (Tran *et al.*, 2013; Felfli *et al.*, 2005; Pimchuai *et al.*, 2010).

It was demonstrated that the weight loss of thermally modified wood is mostly the result of the reduction of the polysaccharide fraction, while hemicelluloses degraded faster than cellulose during heat exposure. The acid-insoluble lignin content increased with the severity of the treatment at the expense of the carbohydrate component. (González-Peña *et al.*, 2009) Similar results are described by Čabalová *et al.* (2013). Upon thermal decomposition of spruce wood with increasing temperature, the amount of lignin and the amount of extracts increased, but the abrasive layer had a decrease in extracts. At the same time, the polysaccharide fraction degraded significantly, the average polymerization degree of cellulose decreased where the crosslinking reactions occurred. The results of Calonego *et al.* (2016) show that the thermal modification of wood causes significant increases in the net calorific value, and the extractive content, and significant decreases in the holocellulose, galactose, xylose and glucose contents.

At higher temperatures, wood shrinks in the transversal plane, due to volatilization of wood constituents and due to a slight densification of the cell wall substance (González-Peña *et al.*, 2009).

The torrefaction process can also be applied to wood-based fuels. In terms of torrefied product properties, the torrefied samples absorb approximately one-third of the moisture compared to the raw fuels, and the total grinding energy decreases up to 40 - 88 % (Tapasvi *et al.*, 2012).

Degradation of hemicelluloses, cellulose and lignin and removing of moisture from the material, have a strong effect on the pelletizing properties of biomass. The friction in the press channel of a pellet mill increases, resulting in high pelletizing pressures that increase the energy uptake of the mill and might result in a decrease of capacity and in worst case in overheating of a blockage of the mill press channels (Stelte *et al.*, 2011). The common practice in pelletizing of thermally untreated biomass, using water to decrease energy consumption and to improve bonding properties, is not applicable in pelletizing of torrefied materials (Larsson *et al.*, 2013). The composition of torrefied briquettes at 220 °C does not undergo many changes.

However, at higher temperatures, changes in the composition are perceptible, with the briquette hemicellulose practically degraded and cellulose depolymerisation process initiated (Felfli *et al.*, 2005).

According to the report of the Ministry of Agriculture and Rural Development of the Slovak Republic and the National Forest Centre, in the year 2016, 9.3 mil. m^3 of wood was produced, of which 55.2 % was wood of coniferous trees. During this period, the production of spruce was 61.6 % of coniferous trees. A large amount of spruce timber was significantly affected by the activation of harmful biotic agents (Moravčík *et al.*, 2017). Usually such a contaminated wood is not suitable for construction or furniture purposes and it can be used for energy purposes. Therefore, this paper deals with the possibilities of thermal treatment of spruce and its influence on the burning of the resulting material.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

For the measurements, 5 sample pieces of tangentially split spruce wood (*Picea abies (L.) Karst.*) with dimensions of 100 mm x 100 mm and 20 mm thickness were used. The samples were first dried to zero humidity at 102 °C for 48 hours. Subsequently, four of them were further thermally treated at 150 °C, 200 °C, 250 °C and 300 °C in a preheated furnace. The heat treatment was carried out for 4 hours in a muffle furnace under an inert atmosphere (nitrogen flow rate of 200 ml·min^{-1}). Finally, the samples were transferred to an exsicator, where they cooled down to ambient temperature. The total time of procedure was approximately 55 hours (48 hours for drying, 4 hours of thermal treatment at appropriate temperature, approximately 3 hours for cooling). The percentage mass loss of samples due to their thermal treatment is shown in Figure 1. With the increase of treatment temperature, the weight loss of the sample also increases. Ramos-Carmona *et al.* (2017) attribute this phenomenon to hemicellulose and cellulose decomposition and to oxidation reactions. Barta-Rajnai *et al.* (2017) also describe strong decrease of the volatile extractive content. Since the spruce samples were thermally treated in a nitrogen atmosphere, the oxidation reactions did not occur and, therefore, it was possible to predict the effect of decomposition of the mentioned wood components.

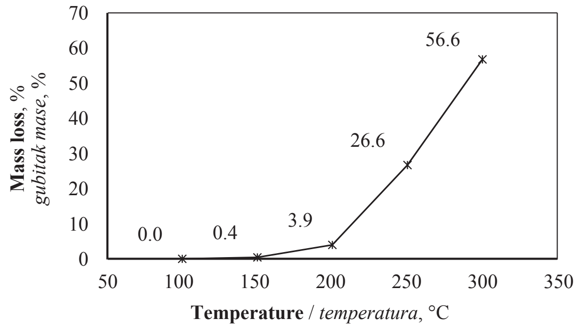


Figure 1 Dependence of the percentage mass loss on the temperature of thermal treatment
Slika 1. Ovisnost postotnoga gubitka mase o temperaturi toplinske obrade

The measurements were made on cone calorimeters meeting ISO standards 5660-1 (2015). Although a higher number of samples is required for the measurement of wood materials, due to the heterogeneous nature of wood, for cone calorimeter measurements the use of one sample for one heat flux is common, as evidenced by other authors. The samples were placed in the horizontal position under the emitter and initiation of the combustion was provided by an electric spark initiator. The measurement conditions are shown in Table 1. The time to ignition of the samples, the amount of heat released, the concentrations of carbon oxides in the flue gas and the amount of smoke released were observed.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

The rate of heat release (Figure 2) is very similar for most samples. There is almost no oxidation of the sample material before initiation of flame burning. Volatile flammable substances are released, while the concentration of these substances in the mixture with air does not reach the value required for their ignition. This first phase takes a relatively short time, which can be attributed in particular to high external heat flow. As soon as the rate of release of the flammable fuel is sufficient, initiation occurs. Due to rapid homogeneous burning, the rate of heat release increases sharply. Once the sharp peak has been reached, a hardened layer begins to form on the surface of the samples. This acts as an insulator and partially restricts the heating of the

Table 1 Measurement conditions for individual samples
Tablica 1. Uvjeti mjerenja za pojedine uzorke

Treatment temperature, °C / *Temperatura obrade,* °C	100	150	200	250	300
Ambient temperature, °C / *Temperatura okoline,* °C	23	23	23	23	23
Barometric pressure, Pa / *Barometarski tlak,* Pa	101 054	101 030	100 977	100 771	100 768
Relative air humidity, % / *Relativna vlažnost zraka,* %	21	20	20	20	20
External heat flux, kW·m^{-2} / *Vanjski toplinski tok,* kW·m^{-2}	50				
Nominal duct flow rate, dm^3·s^{-1} / *Nominalna brzina protoka,* dm^3·s^{-1}	24				
Sampling interval, s / *Interval uzorkovanja,* s	5				
Separation, mm / *Odvajanje,* mm	25				
C-factor / *C-faktor*	0.04296				

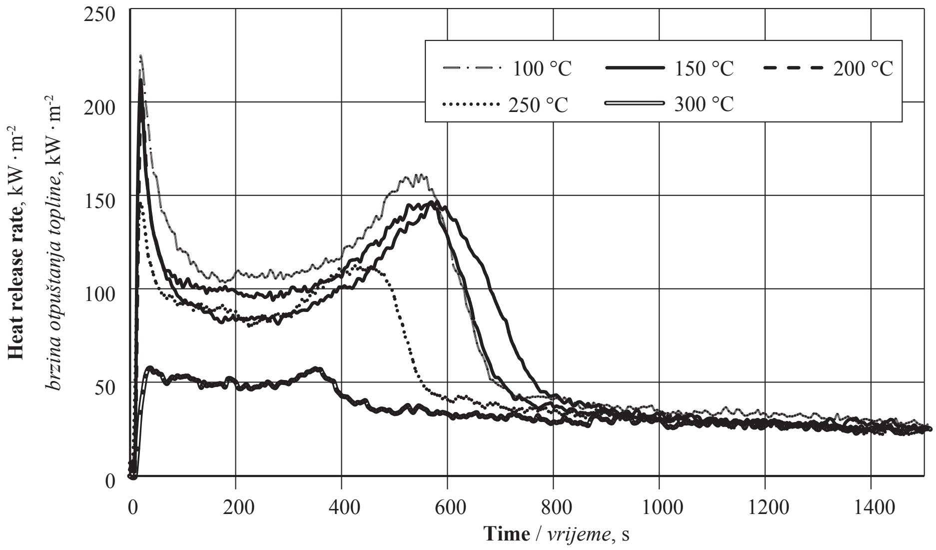


Figure 2 Time of heat release rate in combustion process of thermally-treated spruce wood
Slika 2. Vremenski tijek brzine otpuštanja topline u procesu izgaranja toplinski obrađene smrekovine

rest of the sample. At the same time, it partially prevents the penetration of volatile flammable substances into the burning area. Both of these mechanisms cause a decrease in the rate of heat release up to the phase of combustion stabilization. This area is visible in the graph in the form of a constant course. Then, it is followed by the second, considerably lower and wider peak. Hagen *et al.* (2009) state for the wood that the second peak occurs when the thermal wave reaches the back-insulating surface and the original material has already been pre-heated to the pyrolysis temperature, thereby effectively reducing the heat of the pyrolysis. After the flame burning, the rate of heat release decreases sharply. There are stages of smouldering and glowing, in which the heat is released mainly by the oxidation of carbon residues. The same course of burning in cone calorimetry testing has also been reported by Janssens (1991).

As the temperature of the thermal treatment increases, the value of both the first and the second peak decreases (Table 2). This decrease was also noted by Martinka *et al.* (2016) for spruce timber treated by different processes. Due to the high susceptibility of hemicelluloses to thermal degradation compared to lignin described by various authors (Mburu *et al.*, 2008; Mburu *et al.*, 2007; Calonego *et al.*, 2016), this phenomenon can be attributed to the gradual thermal decomposition of hemicelluloses and cellulose in wood during the preparation of samples. In this way, the proportion of volatile flammable fuel, which is a fuel for homogeneous combustion, is declining. Burning of the specimen heated at 300 °C has a specific course, where both the first and the second peak do not reach any sharp maximum and only slightly differ from the steady burning phase.

In the samples treated thermally at temperatures of 250 °C and 300 °C, relatively faster rate of combustion starts to show up, which has also been stated by Pentananunt *et al.* (1990) for wood treated at similar temperatures (250 °C - 270 °C).

In terms of the initiation phase, an important parameter is the average rate of heat release in the first 60 seconds. For a spruce panel measured on a cone calorimeter, Östman *et al.* (1985) indicate a value of 172 kW·m^{-2}. The dried spruce was measured with a very similar result at a level just above 166 kW·m^{-2} (Figure 3). It is clear from the other measurements that the first-minute average heat release rate decreases, with

Table 2 Results of thermally treated samples of spruce wood
Tablica 2. Rezultati toplinski obrađenih uzoraka smrekovine

Treatment temperature, °C / *Temperatura obrade,* °C	100	150	200	250	300
Time to ignition, s / *Vrijeme do zapaljenja,* s	9	8	8	8	12
First peak HRR*, kW·m^{-2} / *Prvi vrh HRR*,* kW·m^{-2}	223.76	210.17	196.49	145.44	57.25
Second peak HRR*, kW·m^{-2} / *Drugi vrh HRR*,* kW·m^{-2}	160,81	146,45	144,95	112,07	59,97
TSR**, m^2·m^{-2}	343.17	225.35	194.07	103.46	3.65
Mean HRR*, kW·m^{-2} / *Srednja vrijednost HRR*,* kW·m^{-2}	65.90	60.09	60.09	48.40	32.64
Mean EHC***, MJ·kg^{-1} / *Srednja vrijednost EHC***,* MJ·kg^{-1}	16.23	15.84	16.76	17.38	21.84
Mean MLR****, mg·s^{-1} / *Srednja vrijednost MLR****,* mg·s^{-1}	35.89	33.52	31.70	23.62	12.53
Mean CO yield, mg·g^{-1} / *Srednja vrijednost prinosa CO,* mg·g^{-1}	27.36	28.60	28.88	44.70	80.12
Mean CO_2 yield, g·g^{-1} / *Srednja vrijednost prinosa CO_2,* g·g^{-1}	1.35	1.34	1.43	1.52	1.81
THR*****, MJ·m^{-2}	118.57	108.07	108.07	87.15	58.67

*Heat Release Rate / *brzina oslobađanja topline*; **Total Smoke Release / *ukupno ispuštanje dima*; ***Effective Heat of Combustion / *učinkovita toplina izgaranja*; ****Mass Loss Rate / *brzina gubitka mase*; *****Total heat release / *ukupno oslobađanje topline*

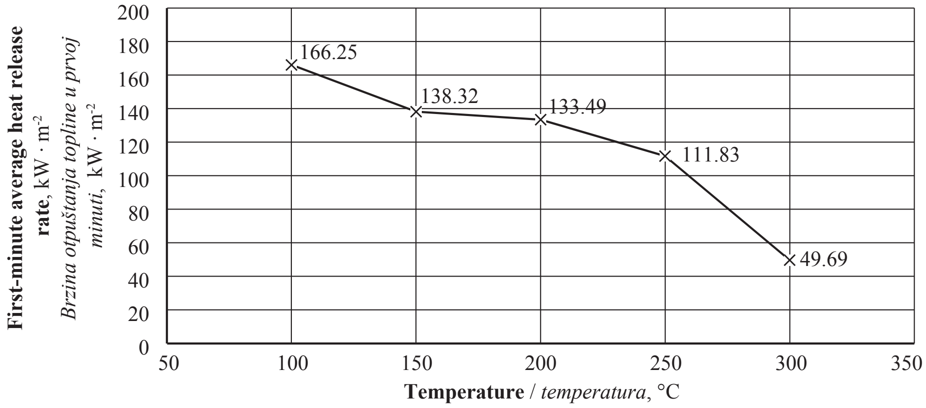


Figure 3 Influence of thermal treatment temperature on the first-minute average heat release rate in combustion of spruce wood
Slika 3. Utjecaj temperature toplinske obrade drva na brzinu otpuštanja topline u prvoj minuti izgaranja smrekovine

the temperature growth of the thermal spruce treatment, which is mainly due to the declining heat release rate. The decrease in the first peak of the heat release rate is also directly related to the decreasing maximum heat release energy (Table 2), which is an important indicator for the first phase of fire propagation.

The treatment temperature had a strong effect on total smoke release (Table 3). While dried wood released a smoke during the flame corresponding to an optical density of 345 $m^2 \cdot m^{-2}$, the wood torrefied at 300 °C no longer showed any smoke. Similar results were described by different authors. Pentananunt *et al.* (1990) indicate that the torrefied wood showed significantly less smoking during combustion compared to untreated wood. Felfi *et al.* (2005) state that, from the combustion point of view, decreases in O/C and H/C ratios are favorable since less smoke and water vapour are formed, improving the performance of briquettes and contributing to energy loss reduction. The release of less smoke can be attributed to a gradual change in the soot formation mechanism in samples undergoing the process of thermal treatment (Mitchell *et al.*, 2016).

Results of individual measurements are shown in Table 2. The time for sample ignition does not show a large diffusion in the specimens modified to 250 °C. The value of 8 s to 9 s is comparable to that reported for spruce by Östman *et al.* (1985) Initiation of the sample modified at 300 °C occurred slightly later than in the previous samples. Due to the very low peak of heat release rate and the visual observation at which the flame did not differ from other samples, it is clear that the amount of volatile combustible in the sample was small. Initiation of volatile flammable mixtures with air was, therefore, delayed.

Mean heat release rate per unit area and hence a total heat release does decrease with the increasing temperature of the treatment. However, since the heat treatment changes the weight of the samples, the mean effective heat of combustion increases. This result is consistent with the calorific value of wood due to thermal treatment (Calonego *et al.* 2016). At the same time, the yield of carbon dioxide and carbon monoxide increases. This is probably due to the higher carbon content of thermally modified wood compared to the original material described in the literature (Pentananunt *et al.*, 1990).

4 CONCLUSION
4. ZAKLJUČAK

The previous thermal treatment in an inert atmosphere has a notable influence on burning spruce wood. The influence occurs partly already before the sample initiation, which is higher compared to other specimens in the case of the sample modified at the temperature of 300 °C. The heat release rate reaches lower maximum values with the increasing adjustment temperature and its course is getting balanced. Intensity as well as flame burning time decrease as a result of decreasing flammable fuel content. However, in the case of thermal treatment, the weight of the sample also decreases, resulting in an increase in effective heat of combustion. The burning rate showed a sharp increase in samples treated at 250 °C or higher. In terms of flammability, the increase in the temperature of the heat treatment was confirmed by its decrease. In the case of torrefied wood, this is almost a hundredfold change, which can be considered very positive when used as a fuel. It can be concluded that the notable change in the burning of the treated wood is caused mainly by temperatures of thermal treatment above 200 °C. The highest amount of heat released per unit mass, substantially lower total smoke release, and the most uneven heat release during burning was observed in the sample thermally treated at the temperature of 300 °C. However, since the heat release rate in this sample reaches values very close to the external thermal flux applied to its surface, from the point of view of the use of spruce wood as a fuel, the preferred treatment temperature appears to be 250 °C.

Acknowledgments – Zahvala

This research was supported by the Slovak Research and Development Agency under the contract No. APVV-0057-12.

This work was supported by the KEGA under the contract No. 030UMB-4/2017 and under the contract No. 012TU Z-4/2016.

5 REFERENCES
5. LITERATURA

1. Barta-Rajnai, E.; Wang, L.; Sebestyén, Z.; Barta, Z.; Khalil, R.; Skreiberg, Ø.; Grønli, M.; Jakab, E.; Czégény, Z., 2017: Comparative study on the thermal behavior of untreated and various torrefied bark, stem wood, and stump of Norway spruce. Applied energy, 204: 1043-1054. https://doi.org/10.1016/j.apenergy.2017.05.057
2. Bekhta, P.; Niemz, P., 2003: Effect of high temperature on the change in color, dimensional stability and mechanical properties of spruce wood. Holzforschung, 57: 539-546. https://doi.org/10.1515/HF.2003.080
3. Bourgois, J.; Guyonnet, R., 1988: Characterization and analysis of torrefied wood. Wood science and Technology, 22: 143-155. https://doi.org/10.1007/BF00355850
4. Broström, M.; Nordin, A.; Pommer, L.; Branca, C.; Di Blasi, C., 2012: Influence of torrefaction on the devolatilization and oxidation kinetics of wood. Journal of analytical and applied pyrolysis, 96: 100-109. https://doi.org/10.1016/j.jaap.2012.03.011
5. Cabalová, I.; Kačík, F.; Kačíková, D.; Oravec, M., 2013: The influence of radiant heating on chemical changes of spruce wood. Acta Facultatis Xylologiae Zvolen, 55: 59-66.
6. Calonego, F. W.; Severo, E. T.; Sansígolo, C. A.; Rezende, M. A.; Bruder, E. M.; Costa, V. E., 2016: Calorific value and chemical properties in juvenile and mature wood of thermally-modified Eucalyptus Grandis. Drvna industrija, 67: 207-214. https://doi.org/10.5552/drind.2016.1522
7. Edvardsen, K.; Sandland, K. M., 1999: Increased drying temperature – Its influence on the dimensional stability of wood. European Journal of Wood and Wood Products, 57: 207-209. https://doi.org/10.1007/s001070050042
8. Felfli, F. F.; Luengo, C. A.; Suárez, J. A.; Beatón, P. A., 2005: Wood briquette torrefaction. Energy for Sustainable Development, 9: 19-22.
9. González-Peña, M. M.; Curling, S. F.; Hale, M. D., 2009: On the effect of heat on the chemical composition and dimensions of thermally-modified wood. Polymer Degradation and Stability, 94: 2184-2193. https://doi.org/10.1016/j.polymdegradstab.2009.09.003
10. Hagen, M.; Hereid, J.; Delichatsios, M. A.; Zhang, J.; Bakirtzis, D., 2009: Flammability assessment of fire-retarded Nordic Spruce wood using thermogravimetric analyses and cone calorimetry. Fire Safety Journal, 44: 1053-1066. https://doi.org/10.1016/j.firesaf.2009.07.004
11. Hansson, L.; Antti, A. L., 2006: The effect of drying method and temperature level on the hardness of wood. Journal of Materials Processing Technology, 171: 467-470. https://doi.org/10.1016/j.jmatprotec.2005.08.007
12. Hill, C. A., 2007: Wood modification: chemical, thermal and other processes. John Wiley & Sons.
13. ***ISO 5660-1: 2015: Reaction to fire tests, Heat release, smoke production and mass loss rate, Part 1: Heat release rate (cone calorimeter method) and smoke production rate (dynamic measurement).
14. Janssens, M., 1991: Rate of heat release of wood products. Fire safety journal, 17: 217-238. https://doi.org/10.1016/0379-7112(91)90003-H
15. Kamdem, D. P.; Pizzi, A.; Jermannaud, A., 2002: Durability of heat-treated wood. European Journal of Wood and Wood Products, 60: 1-6. https://doi.org/10.1007/s00107-001-0261-1
16. Larsson, S. H.; Rudolfsson, M.; Nordwaeger, M.; Olofsson, I.; Samuelsson, R., 2013: Effects of moisture content, torrefaction temperature, and die temperature in pilot scale pelletizing of torrefied Norway spruce. Applied energy, 102: 827-832. https://doi.org/10.1016/j.apenergy.2012.08.046
17. Martinka, J.; Kacíková, D.; Rantuch, P.; Balog, K., 2016: Investigation of the influence of spruce and oak wood heat treatment upon heat release rate and propensity for fire propagation in the flashover phase. Acta Facultatis Xylologiae Zvolen res Publica Slovaca, 58: 5-14.
18. Mburu, F.; Dumarçay, S.; Bocquet, J. F.; Petrissans, M.; Gérardin, P., 2008: Effect of chemical modifications caused by heat treatment on mechanical properties of Grevillea robusta wood. Polymer degradation and stability, 93: 401-405. https://doi.org/10.1016/j.polymdegradstab.2007.11.017
19. Mburu, F.; Dumarçay, S.; Huber, F.; Petrissans, M.; Gérardin, P., 2007: Evaluation of thermally modified Grevillea robusta heartwood as an alternative to shortage of wood resource in Kenya: characterisation of physicochemical properties and improvement of bio-resistance. Bioresource Technology, 98: 3478-3486. https://doi.org/10.1016/j.biortech.2006.11.006
20. Miklečić, J.; Jirouš-Rajković, V., 2016: Influence of Thermal Modification on Surface Properties and Chemical Composition of Beech Wood (*Fagus sylvatica* L.). Drvna industrija, 67: 65-71. https://doi.org/10.5552/drind.2016.1520
21. Mitchell, E. J. S.; Lea-Langton, A. R.; Jones, J. M.; Williams, A.; Layden, P.; Johnson, R., 2016: The impact of fuel properties on the emissions from the combustion of biomass and other solid fuels in a fixed bed domestic stove. Fuel processing technology, 142: 115-123. https://doi.org/10.1016/j.fuproc.2015.09.031
22. Moravčík, M.; Kovalčík, M.; Bednárová, D.; Halvoň, L.; Kaštier, P.; Kunca, A.; Longauerová, V.; Miková, A.; Oravec, M.; Pajtík, J.; Pavlenda, P.; Sarvašová, Z.; Schwarz, M., 2017: Report on Forestry in the Slovak Republic for 2016. Ministry of Agriculture and Rural Development of the Slovak Republic; National Forest Centre, 68 p.
23. Ndibe, C.; Maier, J.; Scheffknecht, G., 2015: Combustion, cofiring and emissions characteristics of torrefied biomass in a drop tube reactor. Biomass and bioenergy, 79: 105-115. https://doi.org/10.1016/j.biombioe.2015.05.010
24. Östman, B.; Svensson, I. G.; Blomqvist, J., 1985: Comparison of three test methods for measuring rate of heat release. Fire and Materials, 9: 176-184. https://doi.org/10.1002/fam.810090406
25. Pentananunt, R.; Rahman, A. M.; Bhattacharya, S. C., 1990: Upgrading of biomass by means of torrefaction. Energy, 15: 1175-1179. https://doi.org/10.1016/0360-5442(90)90109-F
26. Pfriem, A., 2015: Thermally modified wood for use in musical instruments. Drvna industrija, 66: 251-253. https://doi.org/10.5552/drind.2015.1426
27. Pimchuai, A.; Dutta, A.; Basu, P., 2010: Torrefaction of agriculture residue to enhance combustible properties. Energy & Fuels, 24: 4638-4645. https://doi.org/10.1021/ef901168f
28. Quaak, P.; Knoef, H.; Stassen, H. E., 1999: Energy from biomass: a review of combustion and gasification technologies. World Bank technical paper no. WTP 422, Energy series, Washington, D.C.: The World Bank. https://doi.org/10.1596/0-8213-4335-1
29. Ramos-Carmona, S.; Delado-Balcázar, S.; Perez, J. F., 2017: Physicochemical characterization of torrefied wood biomass under air as oxidizing atmosphere. BioResources, 12: 5428-5448. https://doi.org/10.15376/biores.12.3.5428-5448
30. Sehlstedt-Persson, S. M., 1995: High-temperature drying of Scots pine, A comparison between HT-and LT-drying.

European Journal of Wood and Wood Products, 53: 95-99. https://doi.org/10.1007/BF02716400
31. Stelte, W.; Clemons, C.; Holm, J. K.; Sanadi, A. R.; Ahrenfeldt, J.; Shang, L.; Henriksen, U. B., 2011: Pelletizing properties of torrefied spruce. Biomass and Bioenergy, 35: 4690-4698. https://doi.org/10.1016/j.biombioe.2011.09.025
32. Strandberg, M.; Olofsson, I.; Pommer, L.; Wiklund-Lindström, S.; Åberg, K.; Nordin, A., 2015: Effects of temperature and residence time on continuous torrefaction of spruce wood. Fuel Processing Technology, 134: 387-398. https://doi.org/10.1016/j.fuproc.2015.02.021
33. Tapasvi, D.; Khalil, R.; Skreiberg, Ø.; Tran, K. Q.; Grønli, M., 2012: Torrefaction of Norwegian birch and spruce: an experimental study using macro-TGA. Energy & Fuels, 26: 5232-5240. https://doi.org/10.1021/ef300993q
34. Tran, K. Q.; Luo, X.; Seisenbaeva, G.; Jirjis, R., 2013: Stump torrefaction for bioenergy application. Applied Energy, 112: 539-546. https://doi.org/10.1016/j.apenergy.2012.12.053
35. Zarea Hosseinabadi, H.; Doosthoseini, K.; Layeghi, M., 2012: Drying kinetics of poplar (*Populus deltoides*) wood particles by a convective thin layer dryer. Drvna industrija, 63: 169-176. https://doi.org/10.5552/drind.2012.1201
36. Živković, V.; Prša, I.; Turkulin, H.; Sinković, T.; Jirouš-Rajković, V., 2008: Dimensional stability of heat treated wood floorings. Drvna industrija, 59: 69-73.

Corresponding address:

Ing. PETER RANTUCH, Ph.D.

Department of Integrated Safety
Faculty of Materials Science and Technology in Trnava
Slovak University of Technology in Bratislava,
Botanická 49
917 24 Trnava, SLOVAKIA
e-mail: peter.rantuch@stuba.sk

Samim Yasar, Abdullah Beram, Gurcan Guler[1]

Effect of Extraction Technique on Composition of Volatile Constituents of Oleoresin from *Pinus Brutia* Ten.

Utjecaj tehnike ekstrakcije na sastav hlapljivih sastojaka oleoresina iz drva *Pinus brutia* Ten.

Original scientific paper • Izvorni znanstveni rad
Received – prispjelo: 28. 9. 2017.
Accepted – prihvaćeno: 13. 6. 2018.
*UDK:630*813.4; 630*874.1; 674.032.475.4*
doi:10.5552/drind.2018.1754

ABSTRACT • *In this study, volatile constituents of oleoresin from Pinus brutia Ten. were extracted by solid phase microextraction (SPME) and hydrodistillation. Gas chromatography-mass spectroscopy (GC/MS) was performed to determine volatile constituents of turpentine oil (obtained by hydrodistillation) and extract from oleoresin (obtained by SPME). Eleven volatile compounds constituted the total of turpentine oil obtained by hydrodistillation, whereas SPME extract contained 32 volatile compounds. Three distinctive volatile constituents in the turpentine oil were α-pinene (49.12 %), β-pinene (19.12 %) and* Δ^3*-carene (15.33 %). They were represented in the amount of 44.35 %, 18.59 % and 14.58 % in the SPME extract. The volatile constituents of turpentine oil were monoterpenes and sesquiterpenes. Monoterpenes, sesquiterpenes, terpene oxides, alcohols, aldehydes, esters and ethers were identified as main groups in the SPME extract by GC/MS. The results of chromatographic analysis showed that solid phase microextraction was a more effective extraction technique than hydrodistillation for isolating volatile constituents from oleoresin.*

Keywords: *volatile constituents, oleoresin, hydrodistillation, solid phase microextraction (SPME), GC/MS*

SAŽETAK • *Za ovu su studiju hlapljivi sastojci oleoresina iz drva Pinus brutia Ten. izdvojeni mikroekstrakcijom čvrste faze (SPME) i hidrodestilacijom. Radi određivanja hlapljivih sastojaka terpentinskog ulja (dobivenoga hidrodestilacijom) i ekstrakta oleoresina (dobivenoga SPME-om), provedena je plinska kromatografija i masena spektrometrija (GC/MS). Jedanaest hlapljivih spojeva sadržavalo je terpentinsko ulje dobiveno hidrodestilacijom, dok je ekstrakt dobiven SPME-om sadržavao 32 hlapljiva spoja. Tri karakteristična hlapljiva sastojka u terpentinskom ulju bila su α-pinene (49,12 %), β-pinene (19,12 %) i* Δ^3*-karen (15,33 %). Ti su spojevi u ekstraktu SPME-a bili zastupljeni u udjelu od 44,35, 18,59 i 14,58 %. Hlapljivi sastojci terpentinskog ulja bili su monoterpeni i seskviterpeni, a kao glavne skupine u ekstraktu SPME-a uz pomoć GC/MS metode identificirani su monoterpeni, seskviterpeni, terpenski oksidi, alkoholi, aldehidi, esteri i eteri. Rezultati kromatografske analize pokazali su da je za izolaciju hlapljivih sastojaka oleoresina mikroekstrakcija čvrste faze učinkovitija tehnika ekstrakcije od hidrodestilacije.*

Ključne riječi: *hlapljivi sastojci, oleoresin, hidrodestilacija, mikroekstrakcija čvrste faze (SPME), GC/MS*

[1] Authors are professor and research assistants at Department of Forest Products Engineering, Faculty of Forestry, Isparta University of Applied Sciences, Isparta, Turkey.
[1] Autori su profesor i znanstveni asistenti Odjela za tehnologiju proizvoda od drva, Šumarski fakultet, Isparta University of Applied Sciences, Isparta, Turska.

1 INTRODUCTION
1. UVOD

Oleoresin is obtained as exudates from pine trees by tapping the bark (bark chipping). Turpentine, essential oil, is produced by steam/hydro distillation from oleoresin. Turpentine is also known commercially as the "spirits of turpentine", "pine tree terpenic", "pine oleoresin", "gum turpentine", "terpenes oil", "turpentine from Bordeaux" or "oil of turpentine". α-pinene and β-pinene are the major constituents of turpentine. Pinenes are mostly used as starting materials to produce more valuable components (Jantam and Ahmad, 1999; McMorn *et al.*, 2000; Rezzi *et al.*, 2005; Wang *et al.*, 2006; Limberger *et al.*, 2007; Mercier *et al.*, 2009). Besides pinenes, turpentine contains other terpenes such as camphene, Δ^3-carene, tricyclene, myrcene, *p*-cymene, limonene, β-caryophyllene and aromadendrene. Moreover, turpentine compounds are useful raw material for the production of pharmaceuticals, plasticizers, repellents, insecticides, solvents, perfumery, food additives, antiviral, antimicrobial and antioxidant compounds (Roberge *et al.*, 2001; Macchioni *et al.*, 2003; Sun, 2007; Burdock and Carabin, 2008; Mayekiso *et al.*, 2008; Behr and Johnen, 2009; Zulak and Bohlmann, 2010; Adams *et al.*, 2011; Teshome, 2011; Back *et al.*, 2012; Rudback *et al.*, 2012; Gillette *et al.*, 2012; Limberger *et al.*, 2012).

Brutian pine *(Pinus brutia* Ten.) is especially used for the production of oleoresin in Turkey (Oz *et al.*, 2012; Deniz, 2013; Oz *et al.*, 2015). It grows widely in the Mediterranean region, Aegean region, Marmara region and also in some localities of the western Black Sea region in a total area of about 5.8 million ha in Turkey (OGM, 2015).

Solid phase microextraction (SPME) is a sampling technique, whereby a constituent is adsorbed onto the surface of the coated silica fiber. Afterwards, constituents are desorbed into a suitable chromatography instrument coupled with an appropriate detector for identification and quantification. SPME is usually performed by gas chromatography (GC) in the applications. In SPME-GC analysis, the fiber is introduced into the injection port of GC device and constituents are thermally desorbed from the coating for chromatographically determination (Malik *et al.*, 2006). SPME was especially applied in environmental chemistry (Fattore *et al.*, 1996; Abalos *et al.*, 2002; Mousavi *et al.*, 2007), for example for determining organic pollutants in environmental samples (Penalver *et al.*, 1999) and phthalate esters in environmental waters (Polo *et al.*, 2005). It was regularly used to isolate volatile and semivolatile components (Zhang and Pawliszyn, 1993; James and Stack, 1996), for example for determining volatile components of some medicinal and aromatic plants (Bicchi *et al.*, 2007; Yasar *et al.*, 2016) and semivolatile organics in environmental solids (Hageman *et al.*, 1999).

The determination of volatile constituents of oleoresin, after isolation of turpentine oil by hydrodistillation, is a commonly used procedure (Rezzi *et al.*, 2005; Wang *et al.*, 2006; Tümen and Reunanen, 2010; Oz *et al.*, 2015). Besides hydrodistillation technique, the volatile constituents of oleoresin were isolated from brutian pine using SPME in this study. This was followed by determination of volatile constituents of turpentine oil (obtained by hydrodistillation) and extract (obtained by SPME) by gas chromatography-mass spectroscopy (GC/MS). Finally, both applications were compared to reveal which extraction technique is more effective for isolating the volatile constituents of oleoresin.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Materials
2.1. Materijali

Oleoresin of brutian pine *(Pinus brutia* Ten.) was obtained from Karaisali-Adana (37°17'40.0"N 35°09'15.0"E) in Turkey. Tapping was applied using an acid paste method after bark chipping. The bark of each tree was chipped 10 cm in width and 5 cm in height using a wounding apparatus at 1m height above ground. Afterwards, a collector was placed under the wound for gathering flowed oleoresin and the chemical stimulant. The acid paste was applied as chemical stimulant using plastic injectors. Acid paste contained 65 % solution of sulphuric acid, coal, dust, barley-rice bran and dyotamide soil. Sample trees were aged 35, 35 and 37 years, and they were 16, 17 and 18 meters in height and 30, 35 and 38 cm in diameter.

2.2 SPME and GC/MS analysis
2.2. SPME i GC/MS analiza

The solid phase microextraction (SPME) apparatus, equipped with a fiber coated and a 75 μm-thick layer of Carboxen/Polydimethylsiloxane (CAR/PDMS), was used for the isolation of volatile constituents from oleoresin. 2 g of oleoresin were used in the experiment. Firstly, oleoresin was placed in a 10 mL vial, which was sealed with a silicone septum and a crimp cap and heated at 60 °C for 15 min. Secondly, SPME fiber was pushed through the headspace of a sample vial. The volatile constituents were adsorbed at 60 °C for 30 min. Then fiber was inserted directly into the injection port of the Shimadzu 2010 Plus GC/MS. GC/MS device was equipped with a Restek Rx-5Sil MS capillary column (30 m x 0.25 mm i.d., 0.25 μm film thickness) coupled to a mass spectrometer with an ion trap detector in full scan under electron impact ionization (70 eV). Helium was used as carrier gas with a flow rate of 1.61 mL/min. The injection and detection were performed at the temperature of 250 °C. Quadrupole temperature was also 250 °C. Mass range was between 35 and 450 m/z. The temperature of column was kept at 40 °C for 2 min, subsequently raised to 250 °C at a rate of 4 °C/min and then held at 250 °C for 5 min. The software used was LabSolutions GCMSsolution Version 2.7.

2.3. Isolation of turpentine oil and GC/MS analysis
2.3. Izolacija terpentinskog ulja i GC/MS analiza

For the isolation of turpentine oil, 100 g of oleoresin were submitted to hydrodistillation for 5 h using

Table 1 Extraction parameters for hydrodistillation and SPME
Tablica 1. Parametri ekstrakcije za hidrodestilaciju i SPME analizu

Extraction type *Vrsta ekstrakcije*	**Time** *Vrijeme* min	**Sample weight** *Masa uzorka* g	**Solvent** *Otapalo*
Hydrodistillation / *hidrodestilacija*	300	100	Distilled water / *Destilirana voda*
SPME Sampling / *SPME uzorkovanje*	45	2	-

a Clevenger-type apparatus. Hydrodistillation yielded 30.4 % (w/w) turpentine oil from oleoresin. 30 μL turpentine oil were added to 970 μL hexane (GC grade) and 1 μL of this solution was submitted to injection port of GC/MS. GC/MS was performed under the same conditions as described above.

2.4 Identification of constituents
2.4. Identifikacija sastojaka

Retention indices of volatile constituents were determined using a series of saturated *n*-alkanes. *n*-alkanes were injected after each sample at the same chromatographic conditions as described above for GC/MS. The volatile constituents were identified by comparison of their mass spectra with the Wiley, NIST, Tutor and FF-NSC libraries or with data already available in the literature (Adams, 2007). Percentage amounts were calculated based on peak areas from the GC/MS chromatogram by the computer software described above.

2.5 Statistical analysis
2.5. Statistička analiza

MiniTab 16 software was used for statistical analyses. Independent samples *t* test analysis was applied to determine the statistical significance. For each variable, independent samples *t* test was separately done.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

SPME was definitely a more efficient sample preparation technique as compared to classical hydrodistillation, and it could be performed with a much smaller amount of oleoresin than hydrodistillation (Table 1). For this reason, SPME technique offers more advantages than conventional hydrodistillation for extraction.

GC/MS chromatograms of volatile constituents of turpentine oil obtained by hydrodistillation and extract obtained by SPME from oleoresin of *Pinus brutia* Ten. are demonstrated in Figure 1 and 2.

Identified volatile constituents of turpentine oil and SPME extract of oleoresin from *Pinus brutia* Ten. are given in Table 2. Through the application of SPME for the extraction of volatile compounds from oleoresin, it was possible to determine a total of 32 compounds by direct injection on GC/MS. α-pinene, β-pinene and Δ^3-carene were the major constituents (44.35 %, 18.59 % and 14.58 %, respectively) of oleoresin. According to GC/MS analysis of the hydrodistilled turpentine oil, a total of 11 volatile constituents were characterized. At the highest percentage of monoterpenes, they were represented by α-pinene (49.12 %), β-pinene (19.2 %) and Δ^3-carene (15.33 %).

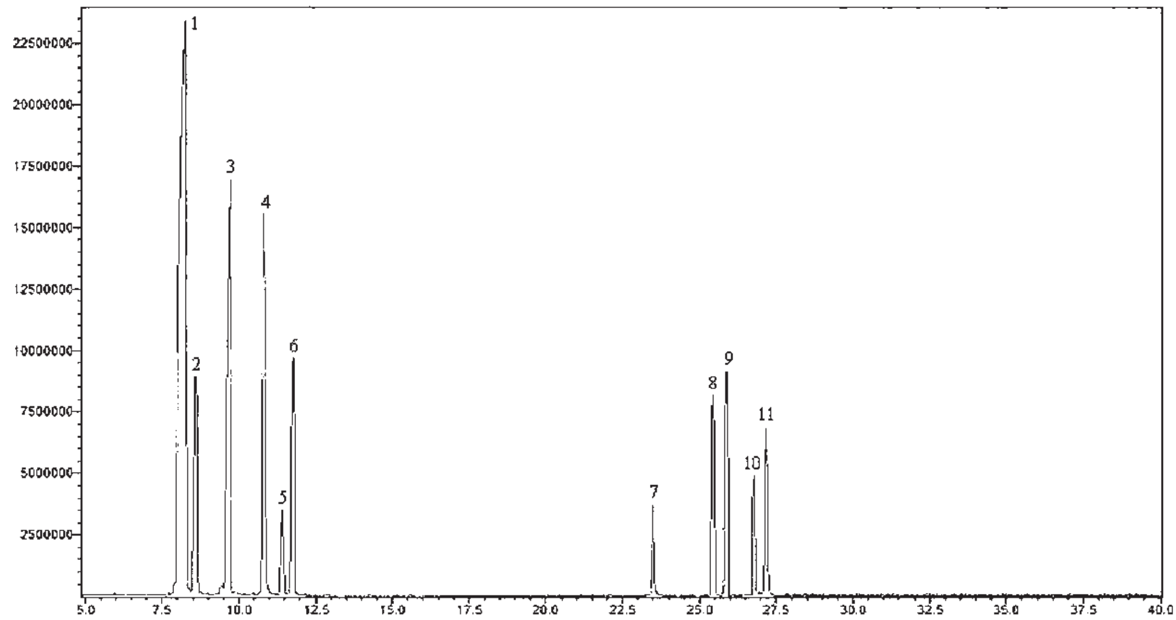


Figure 1 GC/MS chromatogram of turpentine oil obtained by hydrodistillation of oleoresin from *Pinus brutia* Ten. (1: α-pinene, 2: camphene, 3: β-pinene, 4: Δ^3-carene, 5: *p*-cymene, 6: limonene, 7: α-cubebene, 8: α-gurjunene, 9: β-caryophyllene, 10: aromadendrene, 11: α-humulene)
Slika 1. GC/MS kromatogram terpentinskog ulja dobivenoga hidrodestilacijom oleoresina iz drva *Pinus brutia* Ten. (1: α-pinen, 2: camfen, 3: β-pinen, 4: Δ^3-karen, 5: *p*-cimen, 6: limonen, 7: α-kubeben, 8: α-gurjunen, 9: β-kariofilen, 10: aromadendren, 11: α-humulen)

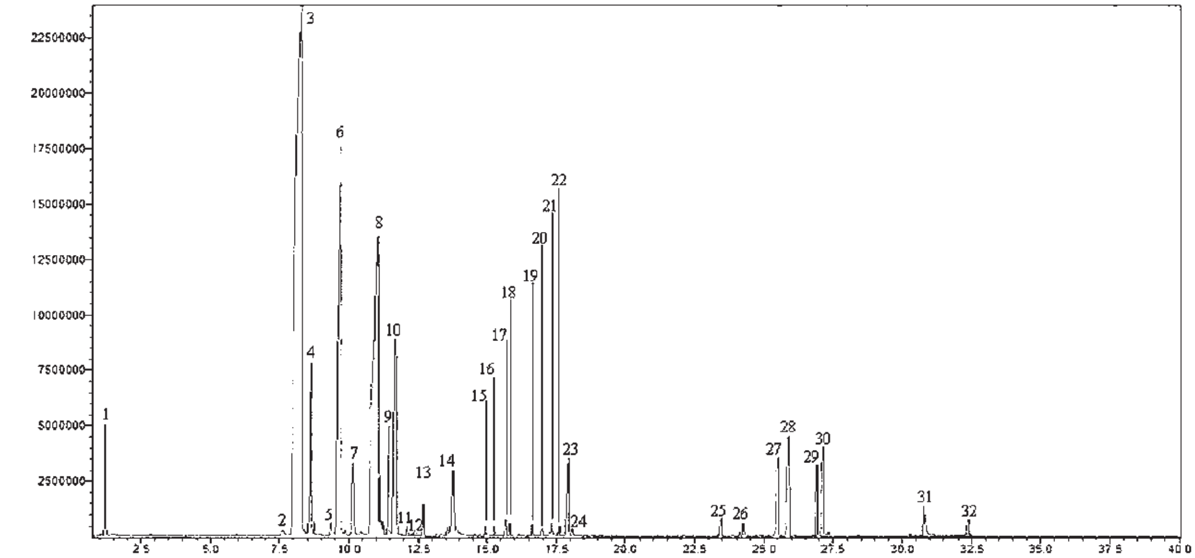


Figure 2 GC/MS chromatogram of SPME extract of oleoresin from *Pinus brutia* Ten. (1: isopropyl acetate, 2: tricyclene, 3: α-pinene, 4: camphene, 5: benzaldehyde, 6: β-pinene, 7: myrcene, 8: Δ^3-carene, 9: *p*-cymene, 10: limonene, 11: butyl 2-methylbutyrate, 12: (E)-β-ocimene, 13: γ-terpinene, 14: *p*-α-dimethylstyrene, 15: 2.4-dimethylanisole, 16: α-campholene aldehyde, 17: terpin-3-en-1-ol, 18: trans-β-terpineol, 19: trans-limonene oxide, 20: isoborneol, 21: terpinen-4-ol, 22: *p*-cymen-8-ol, 23: α-terpineol, 24: verbenone, 25: α-cubebene, 26: cyclosativene, 27: α-gurjunene, 28: β-caryophyllene, 29: aromadendrene, 30: α-humulene, 31: caryophyllene oxide, 32: humulene oxide)

Slika 2. GC/MS kromatogram SPME ekstrakta oleoresina iz drva *Pinus brutia* Ten. (1: izopropil acetat, 2: triciklen, 3: α-pinen, 4: kamfen, 5: benzaldehid, 6: β-pinen, 7: mircen, 8: Δ^3-karen, 9: *p*-cimen, 10: limonen, 11: butil 2-metilbutirat, 12: (E)-β-ocimen, 13: γ-terpinen, 14: *p-a*-dimetilstiren, 15: 2,4-dimetilanisol, 16: a-kamfolen aldehid, 17: terpin-3-en-1-ol, 18: trans- β -terpineol, 19: trans-limonen oksid, 20: izoborneol, 21: terpinen-4-ol, 22: *p*-cimen-8-ol, 23: *a*-terpineol, 24: verbenon, 25: *a*-kuben, 26: ciklosativen, 27: *a*-gurjunen, 28: β-kariofilen, 29: aromadendren, 30: *a*-humulen, 31: kariofilen oksid, 32: humulen oksid)

α-pinene, camphene, β-pinene, Δ^3-carene, *p*-cymene, limonene, α-cubebene, α-gurjunene, β-caryophyllene, aromadendrene and α-humulene constituted the total of turpentine oil by hydrodistillation, whereas these compounds appeared as 90.25 % in the extract by SPME. The present findings show that 9.75 % of volatile constituents cannot be extracted by hydrodistillation of oleoresin from *Pinus brutia* Ten.

According to independent samples *t* test, a significant difference was found between hydrodistillation and SPME sampling for α-pinene, camphene, *p*-cymene, α-cubebene, α-gurjunene, β-caryophyllene and aromadendrene ($p<0.05$). However, there was no significant variance between hydrodistillation and SPME sampling for β-pinene, Δ^3-carene, limonene and α-humulene ($p>0.05$) (Table 2).

The present chemical composition of volatile compounds in the turpentine oil sample from *Pinus brutia* Ten. [α-pinene (49.12 %), β-pinene (19.12%), Δ^3-carene (15.33 %), other monoterpenes (6.79 %) and sesquiterpenes (9.56 %)] is higher than findings by Papajannopoulos *et al.* (2001), who determined α-pinene (13.7 %), β-pinene (5.1 %), and other terpenes (4.5 %) using GC/MS and α-pinene (8.47 %), β-pinene (2.99 %), Δ^3-carene (3.37 %) and other terpenes (1.49 %) using GC.

The findings by Ulukanli *et al.* (2014) were comparable with this study. They found α-pinene (25.4 %), β-pinene (9.69 %) and Δ^3-carene (0.16 %) in the turpentine oil sample from *Pinus brutia* Ten.

Oz *et al.* (2015) determined, as major compounds, α-pinene, β-pinene and γ-terpinene with quantities of 19.7 %, 13.3 % and 10.2 % in the turpentine oil of oleoresin from *Pinus brutia* Ten. These results support the present findings except for γ-terpinene and Δ^3-carene. γ-terpinene was not obtained in the turpentine oil of this study. Δ^3-carene was presented as 3.7 % in the work by Oz *et al.* (2015), whereas Δ^3-carene was determined as a major compound in the turpentine oil of this study.

The main groups of determined volatile constituents of turpentine oil and SPME extract from oleoresin of *Pinus brutia* Ten. are listed in Table 3. Monoterpenes and sesquiterpenes were identified in the turpentine oil, whereas monoterpenes, sesquiterpenes, terpene oxides, alcohols, aldehydes, esters and ethers were characterized in the extract by SPME. Based on independent samples *t* test, a significant difference was found between hydrodistillation and SPME sampling for monoterpenes and sesquiterpenes ($p<0.05$).

4 CONCLUSIONS
4. ZAKLJUČAK

Using SPME for the extraction from oleoresin, 32 volatile constituents were determined by direct injection in GC/MS, whereas 11 volatile constituents were identified in the turpentine oil by GC/MS after hydrodistillation of oleoresin from *Pinus brutia* Ten. Three major volatile constituents in the turpentine oil were α-pinene

Table 2 Volatile constituents of turpentine oil and SPME extract from oleoresin of *Pinus brutia* Ten.
Tablica 2. Hlapljivi sastojci terpentinskog ulja i SPME ekstrakta iz oleoresina iz drva *Pinus brutia* Ten.

No	RI[A]	**Compound** *Sastojak*	**Hydrodistillation** *Hidrodestilacija* %[B]	**SPME Sampling** *SPME uzorkovanje* %[B]	***t*-test results** *Rezultati t-testa*		
					F	***t***	***p***
1	635	isopropyl acetate	-	1.72 (0.06)*	-	-	-
2	918	tricyclene	-	0.26 (0.04)	-	-	-
3	937	α-pinene	49.12[a] (0.65)	44.35[b] (1.09)	0.466	5.323	0.0060
4	947	camphene	2.74[c] (0.18)	2.17[d] (0.12)	0.276	3.708	0.0207
5	956	benzaldehyde	-	0.17 (0.03)	-	-	-
6	975	β-pinene	19.12[e] (0.52)	18.59[e] (0.13)	2.118	1.392	0.2365
7	989	myrcene	-	1.45 (0.05)	-	-	-
8	1010	Δ^3-carene	15.33[f] (0.44)	14.58[f] (0.35)	0.102	1.882	0.1330
9	1023	*p*-cymene	1.10[g] (0.11)	1.47[h] (0.12)	0.041	-3.229	0.0320
10	1029	limonene	3.03[i] (0.20)	3.11[i] (0.16)	0.066	-0.444	0.6803
11	1040	butyl 2-methylbutyrate	-	0.15 (0.03)	-	-	-
12	1045	(E)-β-ocimene	-	0.03 (0.01)	-	-	-
13	1056	γ-terpinene	-	0.53 (0.05)	-	-	-
14	1088	*p*-α-dimethylstyrene	-	1.11 (0.03)	-	-	-
15	1113	2.4-dimethylanisole	-	0.16 (0.03)	-	-	-
16	1121	α-campholene aldehyde	-	0.19 (0.03)	-	-	-
17	1133	terpin-3-en-1-ol	-	0.39 (0.07)	-	-	-
18	1136	trans-β-terpineol	-	0.25 (0.02)	-	-	-
19	1159	trans-limonene oxide	-	0.17 (0.02)	-	-	-
20	1168	isoborneol	-	0.14 (0.03)	-	-	-
21	1177	terpinen-4-ol	-	0.21 (0.03)	-	-	-
22	1184	*p*-cymen-8-ol	-	0.17 (0.05)	-	-	-
23	1193	α-terpineol	-	1.51 (0.07)	-	-	-
24	1202	verbenone	-	0.14 (0.01)	-	-	-
25	1347	α-cubebene	1.24[j] (0.19)	0.32[k] (0.14)	0.176	5.571	0.0051
26	1370	cyclosativene	-	0.26 (0.04)	-	-	-
27	1406	α-gurjunene	2.39[l] (0.23)	1.15[m] (0.16)	0.283	6.347	0.0032
28	1418	β-caryophyllene	2.80[n] (0.09)	1.73[o] (0.05)	0.637	14.791	0.0001
29	1444	aromadendrene	1.42[p] (0.12)	1.11[r] (0.05)	1.241	3.324	0.0293
30	1452	α-humulene	1.71[s] (0.10)	1.67[s] (0.12)	0.098	0.361	0.7366
31	1581	caryophyllene oxide	-	0.45 (0.07)	-	-	-
32	1604	humulene oxide	-	0.29 (0.02)	-	-	-

A – Retention indices calculated against *n*-alkanes / *indeksi zadržavanja izračunani prema n-alkanima*; B – Percentages calculated from GC/MS data. / *postotci izračunani iz GC/MS podataka*; a-s – Variances according to *t* test / *varijance prema t-testu*; * Standard deviations / *standardne devijacije*

(49.12%), β-pinene (19.12%) and Δ^3-carene (15.33%). They were represented by the amounts of 44.35%, 18.59% and 14.58% in oleoresin volatiles isolated by SPME. Monoterpenes and sesquiterpenes were determined in the turpentine oil, while monoterpenes, sesquiterpenes, terpene oxides, alcohols, aldehydes, esters and

Table 3 Main groups of determined constituents of turpentine oil and SPME extract from oleoresin of *Pinus brutia* Ten.
Tablica 3. Glavne skupine određenih sastojaka terpentinskog ulja i SPME ekstrakta iz oleoresina drva *Pinus brutia* Ten.

No	**Main group** *Glavna skupina*	**Hydrodistillation** *Hidrodestilacija* %	**SPME Sampling** *SPME uzorkovanje* %	***t*-test results** *Rezultati t-testa*		
				F	***t***	***p***
1	Monoterpene *monoterpen*	90.44[a] (1.08)*	87.79[b] (0.22)	2.429	3.407	0.0271
2	Sesquiterpene *seskviterpen*	9.56[c] (0.56)	6.24[d] (0.35)	0.386	7.147	0.0020
3	Terpene oxide *terpen oksid*	-	0.91 (0.05)	-	-	-
4	Alcohol / *alkohol*	-	2.67 (0.09)	-	-	-
5	Aldehyde / *aldehid*	-	0.36 (0.03)	-	-	-
6	Ester / *ester*	-	1.87 (0.06)	-	-	-
7	Ether / *eter*	-	0.16 (0.04)	-	-	-

a-d – Variances according to *t* test / *varijance prema t-testu*; * Standard deviations / *standardne devijacije* ethers were identified as main groups in the extract by SPME. Regarding the quantities of identified volatile compounds occurring in resin of *Pinus brutia* Ten., SPME has been shown as a more appropriate extraction technique than conventional hydrodistillation.

5 REFERENCES
5. LITERATURA

1. Abalos, M.; Prieto, X.; Bayona, J. M., 2002: Determination of volatile alkyl sulfides in wastewater by headspace solid-phase microextraction followed by gas chromatography-mass spectrometry. J. Chromatogr. A, 963: 249-257. https://doi.org/10.1016/s0021-9673(02)00543-5
2. Adams, R. P., 2007: Identification of essential oil components by gas chromatography/mass spectroscopy. IL, USA: Allured Publishing Corporation: Carol Stream. https://doi.org/10.1016/s1044-0305(97)00026-3
3. Adams, T. B.; Gavin, C. L.; McGowen, M. M.; Waddell, W. J.; Cohen, S. M.; Feron, V. J.; Marnett, L. J.; Munro, I. C.; Portoghese, P. S.; Rietjens, I. M.; Smith, R. L., 2011: The FEMA GRAS assessment of aliphatic and aromatic terpene hydrocarbons used as flavor ingredients. Food Chem. Toxicol., 49: 2471-2494. https://doi.org/10.1016/j.fct.2011.06.011
4. Back, J.; Aalto, J.; Henriksson, M.; Hakola, H.; He, Q.; Boy, M., 2012: Chemodiversity of a Scots pine stand and implications for terpene air concentrations. Biogeosciences, 9: 689-702. https://doi.org/10.5194/bg-9-689-2012
5. Behr, A., Johnen, L., 2009: Myrcene as a natural base chemical in sustainable chemistry: a critical review. ChemSus Chem., 2: 1072-1095. https://doi.org/10.1002/cssc.200900186
6. Bicchi, C.; Cordero, C.; Liberto, E.; Sgorbini, B.; Rubiolo, P. 2007: Reliability of fibres in solid-phase microextraction for routine analysis of the headspace of aromatic and medicinal plants. J. Chromatogr. A, 1152(1-2): 138-149. https://doi.org/10.1016/j.chroma.2007.02.011
7. Burdock, G. A.; Carabin, I. G., 2008: Safety assessment of Ylang-Ylang (*Cananga* spp.) as a food ingredient. Food Chem. Toxicol., 46: 433-445. https://doi.org/10.1016/j.fct.2007.09.105
8. Deniz, I., 2013: Nonwood products industry (in Turkish), Lecture note. Karadeniz Technical University, Faculty of Forestry. Trabzon.
9. Fattore, E.; Benfenati, E.; Fanelli, R., 1996: Analysis of chlorinated 1,3-butadienes by solid-phase microextraction and gas chromatography-mass spectrometry. J. Chromatogr. A, (737): 85-91. https://doi.org/10.1016/0021-9673(95)01338-5
10. Gillette, N. E.; Hansen, E. M.; Mehmel, C. J.; Mori, S. R.; Webster, J. N.; Erbilgin N.; Wood, D. L., 2012. Area-wide application of verbenone-releasing flakes reduces mortality of whitebark pine *Pinus albicaulis* caused by the mountain pine beetle *Dendroctonus ponderosae*. Agric. For. Entomol., 14: 367-375. https://doi.org/10.1111/j.1461-9563.2012.00577.x
11. Hageman, K. J.; Mazeas, L.; Grabanski, C. B.; Miller, D. J.; Hawthorne, S. B., 1996: Coupled subcritical water extraction with solid-phase microextraction for determining semivolatile organics in environmental solids. Anal. Chem., 68 (22): 3892-3898. https://doi.org/10.1021/ac960751c
12. James, K. J.; Stack, M. A., 1996: The determination of volatile organic compounds in soils using solid phase microextraction with gas chromatography. J. High Resolut. Chromatogr., 19: 515-519. https://doi.org/10.1002/jhrc.1240190908
13. Jantam, I.; Ahmad, A. S., 1999: Oleoresins of three Pinus species from Malaysian pine plantations. ASEAN Review of Biodiversity and Environmental Conservation, 1-9.
14. Limberger, R. P.; Aleixo, A. M.; Fett-Neto, A. G.; Henriques, A. T., 2007: Bioconversion of (+)- and (-)-alphapinene to (+)- and (-)-verbenone by plant cell cultures of *Psychotria brachyceras* and *Rauvolfia sellowii*. Electron. J. Biotechnol., 10: 500-507. https://doi.org/10.2225/vol10-issue4-fulltext-8
15. Limberger, R. P.; Schuh, R. S.; Henriques, A. T., 2012: Pine terpene biotransformation. pp. 107-126; in: A. G. Fett-Neto; Rodrigues-Correa, K. C. S., eds. Pine resin: biology, chemistry and applications. Research Signpost, Kerala, India. ISBN: 978-81-308-0493-4.
16. Macchioni, F., Cioni, P. L.; Flamini, G.; Morelli, I.; Maccioni, S.; Ansaldi, M., 2003: Chemical composition of essential oils from needles, branches and cones of *Pinus pinea, P. halepensis, P. pinaster* and *P. nigra* from central Italy. Flavour Fragr. J., 18: 139-143. https://doi.org/10.1002/ffj.1178
17. Malik, A. K.; Kaur, V.; Verma, N., 2006: A review on solid phase microextraction – high performance liquid chromatography as a novel tool for the analysis of toxic metal ions. Talanta, 68 (3): 842-849. https://doi.org/10.1016/j.talanta.2005.06.005
18. Mayekiso, B.; Magwa, M. L.; Coopoosamy, R. M., 2008: The chemical composition and antibacterial activity of the leaf extract of *Salvia repens* Burch. Ex Benth. J. Med. Plant Res., 2: 159-162. https://doi.org/10.5897/ajb2007.000-2377
19. McMorn, P.; Roberts, G.; Hutchings G. J., 2000: Oxidation of α-pinene to verbenone using silica-titania co-gel catalyst. Catal. Lett., 67: 203-206. https://doi.org/10.1023/a:1019009403820
20. Mercier, B.; Prost, J.; Prost, M., 2009: The essential oil of turpentine and its major volatile fraction (α and β-pinenes): a review. International Journal of Occupational Medicine and Environmental Health, 22 (4): 331-342. https://doi.org/10.2478/v10001-009-0032-5
21. Mousavi, M.; Noroozian, E.; Jalali-Heravi, M.; Mollahosseini, A., 2007: Optimization of solid-phase microextraction of volatile phenols in water by a polyaniline-coated Pt-fiber using experimental design. Anal. Chim. Acta., 581: 71-77. https://doi.org/10.1016/j.aca.2006.08.001
22. Oz, M.; Deniz, I.; Komut, O.; Fidan, M. S., 2012: Resin butterfly (*Dioryctria sylvestrella* Ratz.) at red pine (*Pinus brutia* Ten.) and amounts of essential oils in stalk resins. KSU J. Nat. Sci., Special Issue: 89-95.
23. Oz, M.; Deniz, I.; Komut, O.; Fidan, M. S., 2015: Chemical composition of oleoresin and larvae gallery resin of *Pinus brutia* attacked by *Dioryctria sylvestrella* Ratz. Drvna industrija, 66 (3): 179-188. https://doi.org/10.5552/drind.2015.1408
24. Papajannopoulos, A. D.; Song, Z. Q.; Liang, Z. Q.; Spanos, J. A., 2001: GC-MS analysis of oleoresin of three Greek pine species. Eur. J. Wood Wood Prod., 59 (6): 443-446. https://doi.org/10.1007/s00107-001-0249-x
25. Penalver, A.; Pocurull, E.; Borrull, F.; Marce, R. M., 1999: Trends in solid-phase microextraction for determining organic pollutants in environmental samples. TrAC, Trends Anal. Chem., 18 (8): 557-568. https://doi.org/10.1016/s0165-9936(99)00145-4

26. Polo, M.; Llompart, M.; Garcia-Jares, C.; Cela, R., 2005: Multivariate optimization of a solid-phase microextraction method for the analysis of phthalate esters in environmental waters. J. Chromatogr. A, 1072 (1): 63-72. https://doi.org/10.1016/j.chroma.2004.12.040
27. Rezzi, S.; Bighelli, A.; Castola, V.; Casanova, J., 2005: Composition and chemical variability of the oleoresin of *Pinus nigra* ssp. *laricio* from Corsica. Ind. Crops Prod., 21: 71-79. https://doi.org/10.1016/j.indcrop.2003.12.008
28. Roberge, D. M.; Buhl, D.; Niederer, J. P. M.; Holderich, W. F., 2001: Catalytic aspects in the transformation of pinenes to *p*-cymene. Appl. Catal. A, 215: 111-124. https://doi.org/10.1016/s0926-860x(01)00514-2
29. Rudback, J.; Bergstrom, M. A.; Borje, A.; Nilsson, U.; Karlberg, A. T., 2012: α-Terpinene, an antioxidant in tea tree oil, autoxidizes rapidly to skin allergens on air exposure. Chem. Res. Toxicol., 25: 713-721. https://doi.org/10.1021/tx200486f
30. Sun, J., 2007: D-Limonene: safety and clinical applications. Altern. Med. Rev., 12: 259-264.
31. Teshome, T., 2011: Analysis of resin and turpentine oil constituents of *Pinus patula* grown in Ethiopia. Ee-JRIF, 3 (1): 38-48.
32. Tümen, I.; Reunanen, M., 2010: A comparative study on turpentine oils of oleoresins of *Pinus sylvestris* L. from three districts of Denizli. Records of Natural Products, 4 (4): 224.
33. Ulukanli, Z.; Karabörklü, S.; Bozok, F.; Burhan, A.; Erdogan, S.; Cenet, M.; Karaaslan, M. G., 2014: Chemical composition, antimicrobial, insecticidal, phytotoxic and antioxidant activities of Mediterranean *Pinus brutia* and *Pinus pinea* resin essential oils. Chin J Nat Med., 12 (12): 901-910. https://doi.org/10.1016/s1875-5364(14)60133-3
34. Wang, Z.; Calderon, M. M.; Carandang, M. G., 2006: Effects of resin tapping on optimal rotation age of pine plantation. J. Forest Eco., 11: 245-260. https://doi.org/10.1016/j.jfe.2005.10.001
35. Yasar, S.; Disli, M.; Sonkaya, Y., 2016: Comparison of volatile components of *Thymus zygioides Griseb*. var. *lycaonicus* (Celak.) Ronniger due to reaping time. Turk J For, 17 (2): 94-98. https://doi.org/10.18182/tjf.37096
36. Zhang, Z.; Pawliszyn, J., 1993: Headspace solid phase microextraction. Anal. Chem., 65: 1843-1852. https://doi.org/10.1021/ac00062a008
37. Zulak, K. G.; Bohlmann, J., 2010: Terpenoid biosynthesis and specialized vascular cells of conifer defense. J. Integr. Plant Biol., 52: 86-97. https://doi.org/10.1111/j.1744-7909.2010.00910.x
38. *** 2015: OGM Forest atlas (In Turkish). Ankara: General Directorate of Forestry.

Corresponding address:

Prof. SAMIM YASAR, Ph.D.

Department of Forest Products Engineering
Faculty of Forestry, Isparta University
of Applied Sciences
32260 Isparta, TURKEY
e-mail: samimyasar@isparta.edu.tr

Timuçin Bardak[1], Eser Sozen[2], Kadir Kayahan[1], Selahattin Bardak[3]

The Impact of Nanoparticles and Moisture Content on Bonding Strength of Urea Formaldehyde Resin Adhesive

Utjecaj nanočestica i sadržaja vode u drvu na čvrstoću lijepljenja urea-formaldehidnim ljepilom

Original scientific paper • Izvorni znanstveni rad
Received – prispjelo: 29. 9. 2017.
Accepted – prihvaćeno: 13. 6. 2018.
*UDK: 630*812.222; 630*.824.328; 630*824.43*
doi:10.5552/drind.2018.1755

ABSTRACT • *Wood and wood products have been used in different environmental conditions. Moisture content (MC) and relative humidity (RH) are key parameters for these conditions and bonding strength. Nanotechnology has paved the way to more durable adhesives. An experimental study was conducted to examine the effects of various nanoparticles and moisture content on bonding strength of urea formaldehyde (UF) resin adhesive. In this study, nanosilicon dioxide (SiO_2) and titanium dioxide (TiO_2) were blended with UF. Nanoparticle reinforced adhesives were processed at different nano fillers concentrations (0.5 % and 1 %) and each adhesive was tested at the moisture content of 0 %, 12 %, 18 % and 25 %. According to the results of bonding strength tests, contained nano-SiO_2 adhesives showed better bonding strengths as compared to the control (pure UF) and contained nano-TiO_2 adhesives. The highest bonding strength has been determined at 12 % wood moisture in all specimens. Increasing the moisture content has decreased bonding strength of all samples including control samples. This study showed that nano (SiO_2 and TiO_2) particles have improved the bonding strength of pure UF. Besides, the addition of nano-SiO_2 and nano-TiO_2 changed the physicochemical properties of UF adhesive by XRD test. The novelty of this study was to demonstrate that nanoparticles (SiO_2 and TiO_2) could be beneficial for the bonding strength of UF adhesive in harsh environmental conditions.*

Keywords: *nanoparticles, urea formaldehyde, moisture content, lap joint shear strength, bonding strength*

SAŽETAK • *Drvo i drvni proizvodi upotrebljavaju se u različitim okolišnim uvjetima. Sadržaj vode u drvu (MC) i relativna vlažnost zraka (RH) ključni su parametri koji utječu na čvrstoću lijepljenja drva u određenim okolišnim*

[1] Authors are Ph.D. and lecturer at Department of Furniture and Decoration, Vocational Schools, Bartin University, Turkey. [2]Author is research assistant at Department of Forest Industrial Engineering, Faculty of Forestry, Bartin University, 74100, Turkey. [3]Author is assistant professor at Department of Industrial Engineering, Faculty of Engineering and Architecture, Sinop University, Turkey.
[1] Autori su doktor znanosti i predavač Odjela za namještaj i opremanje, Stručna škola, Sveučilište u Bartinu, Bartin, Turska. [2]Autor je znanstveni asistent Odjela za industrije na bazi šuma, Šumarski fakultet, Sveučilište u Bartinu, Bartin, Turska. [3]Autor je docent Odjela za industrijski inženjering, Fakultet inženjerstva i arhitekture, Sveučilište u Sinopu, Turska.

uvjetima. Nanotehnologija je otvorila put za proizvodnju postojanijih ljepila. U radu su prikazani rezultati eksperimentalnog istraživanja utjecaja različitih nanočestica i sadržaja vode u drvu na čvrstoću lijepljenja urea-formaldehidnim ljepilom (UF). U istraživanju su nanosilikonski dioksid (SiO_2) i titanijev dioksid (TiO_2) pomiješani s UF ljepilom. Ljepila ojačana nanočesticama pripremljena su uz dodatak različitih koncentracija nanopunila (0,5 i 1 %), a svako je ljepilo ispitano na drvu različitog sadržaja vode u njemu: 0, 12, 18 i 25 %. Iz rezultata ispitivanja čvrstoće lijepljenja može se uočiti da su ljepila s nanočesticama SiO_2 pokazala veću čvrstoću lijepljenja u usporedbi s kontrolnim uzorcima (lijepljenih čistim UF ljepilom) i s uzorcima lijepljenim ljepilom ojačanim nanočesticama TiO_2. Najveća čvrstoća lijepljenja postignuta je na uzorcima sa sadržajem vode od 12 %. Uz povećan sadržaj vode smanjila se čvrstoća lijepljenja svih uzoraka, uključujući i kontrolne. Na temelju rezultata istraživanja može se zaključiti da se dodavanjem nanočestica (SiO_2 i TiO_2) ljepilu poboljšava čvrstoća zalijepljenog spoja odnosno da se tim ljepilom postiže čvršće lijepljenje nego čistim UF ljepilom. Osim toga, uz pomoć XRD testa utvrđeno je da su se dodavanjem nanočestica SiO_2 i TiO_2 promijenila fizikalno-kemijska svojstva UF ljepila. Istraživanje je potvrdilo da nanočestice (SiO_2 i TiO_2) mogu biti korisne za čvrstoću lijepljenja drva UF ljepilom u nepovoljnim okolišnim uvjetima.

Ključne riječi: *nanočestice, urea-formaldehid, sadržaj vode, smicajna čvrstoća spoja, čvrstoća lijepljenja*

1 INTRODUCTION
1. UVOD

The application of nanotechnology in wood industry is on the rise. Adhesive bonding is generally used in various applications due to its several benefits such as the large area of bonding, possibility of joining different materials (Katnam *et al*., 2011; Ghosh *et al*. 2016). Bonding technology has been developing for a long time. Urea-formaldehyde (UF) resins are the most generally used adhesives in the forest industry (Lubis *et al.,* 2017). UF resin adhesive has a lot of advantages such as good performance in the panel, solubility in water and lower cost. However, there are disadvantages to using UF resin adhesives as well; they have lower resistance to excess moisture and formaldehyde emission from the panels (Park *et al.,* 2009). Moisture absorption is indicated as one of the important causes of impairing the mechanical properties of polymers because physical changes occur at microscopic levels in composites (Mieloszyk and Ostachowicz, 2017).

For many years, nanomaterials have received much interest for application in adhesives due to high specific surface areas and unique mechanical properties (Heon Kwon *et al.,*2015). Nanocomposites are formed by the dispersion of nanoparticles into the polymer. They have unique properties, such as high heat resistance, toughness and stiffness (Bauer and Mehnert, 2005; Salla *et al.,* 2012). Scientific and industrial interest has focused on polymer nanocomposites (Dorigato and Pegoretti, 2011). There are many studies that considered the development of nanocomposites (Yang *et al.,* 2006; Wang *et al.,* 2011). However, studies on the assessment of nanoparticles in the adhesive industry are limited. Adhesives have an important place in wood industry. The quality and durability of a wooden product primarily depend on the quality of its adhesive bonding. Nanoparticles can help to produce enhanced wood products (Bardak *et al.,* 2017).

Many difficulties in applying wood as an engineering material arise from variations in moisture content. This situation also has a negative effect on the adhesive performance. In this study, bonding performances of urea formaldehyde adhesive at different equilibrium moisture contents (EMC) of wood were determined.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

Urea formaldehyde adhesive was obtained from SFC Integrated Forestry Products Company (Turkey). It has a solid content of 60 %, pH 8.0, and density 1.260 g/cm^3. Nano-SiO_2 and nano-TiO_2 were supplied by MkNANO (Canada). Properties of nanoparticles used in the research are presented in Table 1. In the study, oak (*Quercus robur*), with the specific gravity of 0.65 g/cm^3, was used as wood material. Modulus of rapture (*MOR*) and modulus of elasticity (*MOE*) were determined in bending test according to the procedures described in TS 2474 (1976). *MOR* and *MOE* values of wood material were found to be 87 MPa and 12350 MPa, respectively.

Table 1 Properties of nanoparticles used in the research
Tablica 1. Svojstva nanočestica upotrijebljenih u istraživanju

Properties / *Svojstvo*	**SiO_2**	**TiO_2**
Nanoparticle size *Veličina nanočestice*	15 nm	50 nm
Specific surface area *Specifična površina*	650 m^2/g	150 m^2/g
Purity / *Čistoća,* %	99	99
Dissociation / *Disocijacija*	Hydrophilic *hidrofilna*	Hydrophilic *hidrofilna*

2.1 Preparation of adhesives
2.1. Priprema ljepila

Nano-SiO_2 and nano-TiO_2 were added to urea formaldehyde adhesive at the rate of 0.5 % and 1 % (according to solid content), separately. The UF resins reinforced with nanoparticles were mixed with a 30 min mechanical stirrer. Then, 1.5 % ammonium chloride was added as a hardener to UF resins reinforced with nanoparticles. Sample codes, nanoparticle types and rates are given in Table 2.

Table 2 Sample codes, nanoparticle types and rates used in the study
Tablica 2. Oznake uzoraka te vrsta i udio nanočestica u ljepilu

Sample codes *Oznaka uzorka*	**Nanoparticle type** *Vrsta nanočestica*	**Nanoparticle rate** *Udio nanočestica* %
Pure UF	-	-
0.5 % SiO_2+UF	SiO_2	0.5
1 % SiO_2+UF	SiO_2	1
0.5 % TiO_2+UF	TiO_2	0.5
1 % TiO_2+UF	TiO_2	1

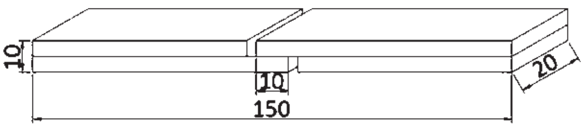


Figure 1 Dimensions of shear strength test sample (mm)
Slika 1. Dimenzije uzorka za ispitivanje smicajne čvrstoće

2.2 Bonding strength
2.2. Čvrstoća lijepljenja

The obtained UF mixings were applied in the amount of 180–190 g/m^2 to one surface of the samples with the dimensions of 200 x 50 x 5 mm. Then, samples were pressed at 115±5 ºC temperature and 1 N/mm^2 pressure for 7 minutes by using a hydraulic test machine. Specimens were then removed from press, and they were cut to dimensions of 150 x 20 x 5 mm according to EN 302-1 Norm. Figure 1 shows the dimensions of shear test samples.

Samples were kept at four different EMC air conditions (0 %, 12 %, 18 %, and 25 %) by using conditioning chamber. To determine EMC, moisture control samples (MCSs) were placed to conditioning cabinet for every different moisture content. Table 3 shows air conditions for 0 %, 12 %, 18 %, and 25 % EMCs.

The samples were tested in a device with maximum load capacity of 100 kN. Shear strength was calculated from Equation (1).

$$\tau = \frac{F\max}{A} \tag{1}$$

Where τ is shear strength (N/mm^2), Fmax is maximum load, and A is bonding surface of sample (10 x 20=200 mm^2). All shear strength data were analyzed by using SPSS software. ANOVA was used for establishing the differences between the groups.

XRD graph was made on a Rigaku Smartlab (Chech Republic) with Ni-filtered Cu Ka (1.540562 Å) radiation source operated at 45 kV voltage and 40 mA electric current. The viscosities of the adhesive were measured by Brookfield CAP 2000 + viscometer, according to the ASTM D2256-11 standard. All gel-time measurements were made at a temperature of 100 °C in a trace of water.

Table 3 Air conditions and reached EMCs
Tablica 3. Svojstva zraka i postignuti ravnotežni sadržaji vode u drvu

Temperature *Temperatura* ºC	**Relative humidity** *Relativna vlažnost zraka* %	**Time** *Vrijeme* days *dani*	**Moisture content** *Sadržaj vode u drvu* %
103±2	0 (in oven)	3	0 (Oven dry)
20±2	65	2	12
15±2	80	4	18
10±2	90	10	25

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

Table 4 shows that the addition of nanoparticles to UF adhesive generally yields a significant change in bonding strength at different moisture contents.

The results clearly show that the value of the bonding strength of UF adhesive increases with nanoparticles - 0.5 % and 1 % SiO_2 at different moisture content of 0, 12, 18 and 25 %. For example, the highest bonding strength value (8.01 N/mm^2) was acquired from the samples with wood moisture of 12 % at 0.5 % SiO_2. At the same time, the addition of 0.5 % TiO_2 was determined to have a good effect on adhesion strength for wood moisture of 12, 18 and 25%. On the other hand, 1 % TiO_2 nanoparticles did not provide significant changes in adhesion strength for wood moisture of 0 % and 25 %. It was reported that the poly(vinyl acetate) adhesive with 0.3 and 1.0 % nanoparticles content

Table 4 Average and standard deviation values of bonding strength
Tablica 4. Prosječna vrijednost i standardna devijacija čvrstoće lijepljenja

Sample codes *Oznaka uzorka*	**Moisture content** *Sadržaj vode u drvu* %	**Bonding strength** *Čvrstoća lijepljenja* N/mm^2
Pure UF	0	5.89 (0.75)[a]
	12	6.17 (0.89)
	18	5.75 (1.12)
	25	4.99 (0.89)
0.5 % SiO_2+UF	0	6.99 (1.09)
	12	8.01 (0.81)
	18	7.86 (1.19)
	25	7.72 (1.32)
1 % SiO_2+UF	0	6.44 (0.65)
	12	7.99 (1.45)
	18	7.91 (1.30)
	25	7.19 (1.27)
0.5 % TiO_2+UF	0	5.37 (0.99)
	12	7.07 (1.35)
	18	6.67 (1.20)
	25	6.34 (1.15)
1 % TiO_2+UF	0	5.09 (0.67)
	12	7.83 (0.95)
	18	7.23 (1.08)
	25	5.15 (0.50)

[a] Values in parentheses are sample standard deviations. / *Vrijednosti u zagradama standardne su devijacije.*

Table 5 Result of Duncan test
Tablica 5. Rezultati Duncanova testa

Sample codes *Oznaka uzorka*	**Moisture content** *Sadržaj vode u drvu* %	**Number of samples** *Broj uzoraka*	**Shear strength** *Smicajna čvrstoća* N/mm²
Pure UF	25	15	4.99 A
1 % TiO_2+UF	0	15	5.09 AB
1 % TiO_2+UF	25	15	5.15 AB
0.5 % TiO_2+UF	0	15	5.37 ABC
Pure UF	18	15	5.75 ABCD
Pure UF	0	15	5.89 BCDE
Pure UF	12	15	6.17 CDEF
0.5 % TiO_2+UF	25	15	6.34 DEFG
1 % SiO_2+UF	0	15	6.44 DEFGH
0.5 % TiO_2+UF	18	15	6.67 EFGH
0.5 % SiO_2+UF	0	15	6.99 FGHI
0.5 % TiO_2+UF	12	15	7.07 GHIJ
1 % SiO_2+UF	25	15	7.19 GHIJK
1 % TiO_2+UF	18	15	7,23 HIJK
0.5 % SiO_2+UF	25	15	7.72 IJK
1 % TiO_2+UF	12	15	7.83 IJK
0.5 % SiO_2+UF	18	15	7.86 IJK
1 % SiO_2+UF	18	15	7.91 JK
1 % SiO_2+UF	12	15	7.99 K
0.5 % SiO_2+UF	12	15	8.01 K

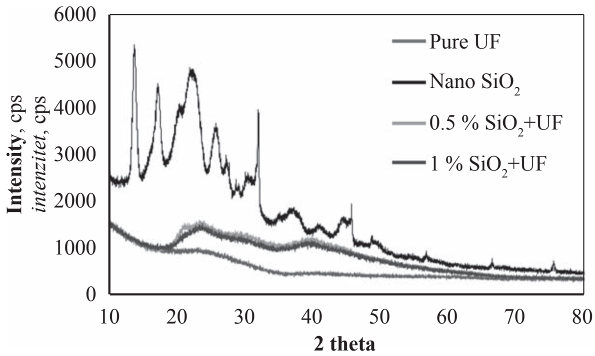


Figure 4 XRD curves of neat UF and nano-SiO_2 filled nanocomposites
Slika 4. XRD krivulje čistog urea-formaldehida i nanokompozita s punilom od nanočestica SiO_2

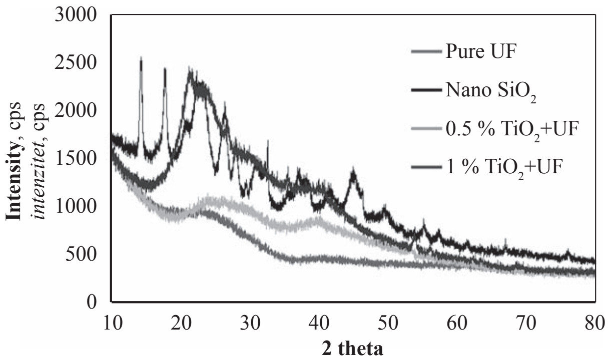


Figure 5 XRD curves of neat UF and nano-TiO_2 filled nanocomposites
Slika 5. XRD krivulje čistoga urea-formaldehida i nanokompozita s punilom od nanočestica TiO_2

showed a higher bonding strength compared to that with pure adhesive in dry state (Peruzzo *et al.,*2014). The high surface area of nanoparticles increases the contact surface area with the adhesive resulting in strong adhesion between matrix and nanomaterial (Younesi-Kordkheili, 2017). Duncan test results obtained with the SPSS program are showed in Table 5.

With the rise of moisture content, the bonding strength of all adhesives increased to certain moisture content (12 %) and then started to decrease. Urea formaldehyde absorbs moisture when exposed to harsh environmental conditions (Biswas *et al.,* 2011). Generally, the XRD analysis is used to determine the distribution of nanoparticles in the polymer matrix (Kaboorani and Riedl, 2011). Figures 4 and 5 show the XRD outcomes of UF resins reinforced with nanoparticles and nanoparticles (TiO_2, SiO_2) prepared in this study.

Nanocomposites have three types of morphology: immiscible (conventional or micro composite), intercalated and exfoliated or miscible (Paul and Robeson, 2008). Exfoliated nanocomposites - In an exfoliated system, the individual nano-material layers are separated in a continuous polymer matrix by an average distance that depends on nanomaterial loading (Sinha Ray and Okamoto, 2003; Silvestre *et al.,* 2016). Nano-SiO_2 and nano-TiO_2 significant peaks are reduced in intensity or even disappeare, showing a high degree of intercalation and/or exfoliation of the nanoparticle layers in UF polymer matrix (Hedayati and Arefazar, 2009; Zabarjad Shiraz *et al.,* 2013). According to XRD test results, the nanoparticles dispersed in the polymer. This dispersion can be the reason for the increase in bonding strength of UF (Bardak *et al.,* 2017).

Table 6 shows the effect of nanoparticles content on the viscosity of UF adhesives. Nano-SiO_2 and nano-TiO_2 rise the viscosity of the UF adhesive in contrast with the pure UF adhesive. This can be explained by strong agglomeration tendency of nanomaterials (Veigel *et al.,* 2011).

Studies have shown that, as the viscosity of UF adhesive increases, so does the adhesion bonding strength. This situation is explained by the increase of molecular weight and crosslink density of the nano/UF (Osemeohan *et al*., 2010).

Table 6 Effect of nanoparticles content on the viscosity of UF adhesives
Tablica 6. Utjecaj sadržaja nanočestica na viskoznost UF ljepila

Sample codes *Oznaka uzorka*	**Viscosity** *Viskoznost*
Pure UF	178 cP
0.5 % SiO_2+UF	183 cP
1 % SiO_2+UF	191 cP
0.5 % TiO_2+UF	184 cP
1 % TiO_2+UF	185 cP

Table 7 Variation of gel time with nanoparticles
Tablica 7. Promjena vremena geliranja ljepila s nanočesticama

Sample codes *Oznaka uzorka*	**Gel time** *Vrijeme geliranja*
Pure UF	94 sn
0.5 % SiO_2+UF	90 sn
1 % SiO_2+UF	94 sn
0.5 % TiO_2+UF	92 sn
1 % TiO_2+UF	96 sn

Table 7 shows the variation of the gel time with nanoparticles. It is clear that the gel time values of the UF adhesive did not change significantly with nano-SiO_2 and nano-TiO_2. This is in accordance with the literature (Dukarska and Czarnecki, 2016).

4 CONCLUSIONS
4. ZAKLJUČAK

The purpose of this study was to investigate the bonding performance of UF adhesives reinforced with nanoparticles. The results showed that the bonding strength of UF adhesive with 0.5-1 % nano-SiO_2 and 0.5 % nano-TiO_2 increase significantly when compared to that of pure UF adhesive at all moisture contents. On the other hand, there was no significant difference in 1 % nano-TiO2 in 0 % and 25 % moisture contents.

All samples with moisture content of 12 % resulted in the highest bonding strength. Besides, the viscosity of UF adhesive increased with the nano-SiO_2 and nano-TiO_2 content. However, the addition of nanoparticles did not change gel time of the UF adhesive significantly. Consequently, it can be stated that nanoparticles could be beneficial in the development of more moisture-resistant UF adhesives.

5 REFERENCES
5. LITERATURA

1. Bardak, T.; Tankut, A. N.; Tankut, N.; Aydemir, D.; Sozen, E., 2017: The bending and tension strength of furniture joints bonded with polyvinyl acetate nanocomposites. Maderas. Ciencia y tecnología, 19 (1): 51-62. http://dx.doi.org/10.4067/S0718-221X2017005000005.
2. Bauer, F.; Mehnert, R., 2005: Uv curable acrylate nanocomposites: properties and applications. Journal of Polymer Research, 12: 483-491. http://dx.doi.org/ 10.1007/s10965-005-4339-z.
3. Biswas, D.; Bose, K. S.; Hossain, M. M., 2011: Physical and mechanical properties of urea formaldehyde-bonded particleboard made from bamboo waste. International Journal of Adhesion & Adhesives, 31: 84-87. http://dx.doi.org/ 10.1016/j.ijadhadh.2010.11.006.
4. Dorigato, A.; Pegoretti, A., 2011: The role of alumina nanoparticles in epoxy adhesives. Journal of Nanoparticle Research, 13: 2429-2441. http://dx.doi.org/ 10.1007/s11051-010-0130-0.
5. Dukarska, D.; Czarnecki, R., 2016: Fumed silica as a filler for MUPF resin in the process of manufacturing water-resistant plywood. European of Journal of Wood and Wood Product, 74: 5-14. http://dx.doi.org/10.1007/s00107-015-0955-4.
6. Ghosh, P. K.; Patel, A.; Kumar, K., 2016: Adhesive joining of copper using nano-filler composite adhesive. Polymer, 87: 159-169. https://doi.org/10.1016/j.polymer.2016.02.006.
7. Hedayati, A.; Arefazar, A., 2009: Multi-scale analysis of polypropylene based organoclay containing composites, Part 1: Morphology. Polymer Testing, 28: 128-138. https://doi.org/10.1016/j.polymertesting.2008.10.007.
8. Kwon, H. J.; Lee, S.-H.; Ayrilmis, N.; Han T. H., 2015: Tensile shear strength of wood bonded with urea–formaldehyde with different amounts of microfibrillated cellulose. International journal of Adhesion and Adhesives, 60: 88-91. https://doi.org/10.1016/j.ijadhadh.2015.04.002.
9. Kaboorani, A.; Riedl, B., 2011: Effects of adding nanoclay on performance of polyvinyl acetate (PVA) as a wood adhesive. Composites Part A: Applied Science and Manufacturing, 42: 1031-1039. https://doi.org/10.1016/j.compositesa.2011.04.007.
10. Katnam, K. B.; Comer, A. J.; Stanley W. F.; Buggy, M.; Ellingboe A. R.; Young, T. M., 2011: Characterising prepreg and non-crimp-fabric composite single lap bonded joints. International Journal of Adhesion & Adhesives, 31: 679-686. https://doi.org/10.1016/j.ijadhadh.2011.06.013.
11. Lubis M. A. R.; Park B.-D.; Lee S.-M., 2017: Modification of urea-formaldehyde resin adhesives with blocked isocyanates using sodium bisulfite. International Journal of Adhesion & Adhesives, 73: 118-124. https://doi.org/10.1016/j.ijadhadh.2016.12.001.
12. Mieloszyk, M.; Ostachowicz, W., 2017: Moisture contamination detection in adhesive bond using embedded FBG sensors. Mechanical Systems and Signal Processing, 84: 1-14. https://doi.org/10.1016/j.ymssp.2016.07.006.
13. Osemeahon, S. A.; Nkafamiya, I. I.; Milam, C.; Modibbo, U. U., 2010: Utilization of amino resin for emulsion paint formulation: Effect of urea formaldehyde viscosity on urea formaldehyde and soybean oil copolymer composite. African Journal of Pure and Applied Chemistry, 4(1): 1-6.
14. Park, B.-D.; Lee S.-M.; Roh J.-K., 2009: Effects of formaldehyde/urea mole ratio and melamine content on the hydrolytic stability of cured urea-melamine-formaldehyde resin. European Journal of Wood and Wood Product, 67: 121-123. https://doi.org/10.1007/s00107-008-0277-x.
15. Paul. D. R.; Robeson, L. M., 2008: Polymer nanotechnology: Nanocomposites. Polymer (Guildf), 49: 3187-3204. https://doi.org/10.1016/j.polymer.2008.04.017.
16. Peruzzo, P. J.; Bonnefond, A.; Reyes, Y.; Fernandez, M.; Fare, J.; Ronne, E.; Paulis, M.; Leiza, J. R., 2014: Beneficial in-situ incorporation of nanoclay to waterborne PVAc/PVOH dispersion adhesives for wood applications. International Journal of Adhesion and Adhesives, 48: 295-302. https://doi.org/10.1016/j.ijadhadh.2013.09.042.
17. Salla, J.; Pandey, K. K.; Srinivas, K., 2012: Improvement of UV resistance of wood surfaces by using ZnO nanoparticles. Polymer Degradation and Stability, 97: 592-596. https://doi.org/10.1016/j.polymdegradstab.2012.01.013.
18. Silvestre, J.; Silvestre, N.; Brito, J. D., 2016: Polymer nanocomposites for structural applications: Recent trends and new perspectives. Mechanicsof Advanced Materials and Structures, 23: 1263-1277. htpp://dx.doi.org./10.1080/15376494.2015.1068406.
19. Ray S. S.; Okamoto, M., 2003: Polymer/layered silicate nanocomposites: a review from preparation to processing. Progress in Polymer Science, 28: 1539-1641. https://doi.org/10.1016/j.progpolymsci.2003.08.002.

20. ***TS 2474, 1976: Wood-determination of ultimate strength in static bending. Turkish Standards Institution, Ankara, Turkey (in Turkish).
21. Veigel, S.; Muller, U.; Keckes, J.; Obersriebnig, M.; Gindl-Altmutter, W., 2011: Cellulose nanofibrils as filler for adhesives: effect on specific fracture energy of solid wood-adhesive bonds. Cellulose, 18: 1227-1237. https://doi.org/10.1007/s10570-011-9576-1.
22. Wang, Z.; Gu, Z.; Hong, Y.; Cheng, L.; Li, Z., 2011: Bonding strength and water resistance of starch-based wood adhesive improved by silica nanoparticles. Carbohydrate Polymers, 86: 72-76. https://doi.org/10.1016/j.carbpol.2011.04.003.
23. Yang, H.; Zhang, Q.; Guo, M.; Wang, C.; Du, C.; Fu, Q., 2006: Study on the phase structures and toughening mechanism in PP/EPDM/SiO2 ternary composites. Polymer, 47: 2106-2115. https://doi.org/10.1016/j.polymer.2006.01.076.
24. Younesi-Kordkheili, H., 2017: Improving physical and mechanical properties of new lignin- urea-glyoxal resin by nanoclay. European Journal of Wood and Wood Products, 1-7. https://doi.org/10.1007/s10570-011-9576-1.
25. Zabarjad Shiraz, N.; Enferad, E.; Monfared, A.; Mojarrad, M. A., 2013: Preparation of Nanocomposite Based on Exfoliation of Montmorillonite in Acrylamide Thermosensitive Polymer. ISRN Polymer Science, 1-5. http://dx.doi.org/10.1155/2013/280897.

Corresponding address:

Research Assistant ESER SÖZEN

Bartin University
Faculty of Forestry
Department of Forest Industrial Engineering
74100 Bartin, TURKEY
e-mail: esozen@bartin.edu.tr

Agnieszka Laskowska[1]

Susceptibility of Thermo-Mechanically Modified Scots Pine (*Pinus Sylvestris* L.) Sapwood and Heartwood to Colour Change under the Influence of Ultraviolet Radiation

Osjetljivost termo-mehanički modificiranog drva srži i bjeljike običnog bora (*Pinus sylvestris* L.) na promjenu boje pod utjecajem ultraljubičastog zračenja

Original scientific paper • Izvorni znanstveni rad
Received – prispjelo: 29. 8. 2017.
Accepted – prihvaćeno: 13. 6. 2018.
*UDK: 630*812.111; 630*812.463; 674.032.475.4*
doi:10.5552/drind.2018.1756

ABSTRACT • *The impact of ultraviolet radiation on the colour of thermo-mechanically modified sapwood and heartwood of pine (Pinus sylvestris L.) was examined in the study. Samples of wood were densified in a hydraulic press at unit pressure of 80 MPa, at three levels of temperature of the press platens: 100 °C, 150 °C and 200 °C, for 360 s. The parameters of wood colour were determined using the mathematical colour space models CIE L*a*b* and L*C*h. As a result of the modification of pine sapwood at the temperature of 200 °C, the change in wood colour ΔE was twice as substantial as the change in wood colour after modifications at lower temperatures. The total colour difference for pine heartwood, irrespective of the modification temperature, was at least twice as substantial as the change in the colour of pine sapwood. The most substantial changes in sapwood and heartwood lightness occurred after 20 h exposure to UV radiation. Changes in lightness occurring within 20 h, irrespective of the temperature of treatment, accounted for about 30 - 60 % of the total change. After 300 h of irradiation, the value of ΔE for sapwood densified at temperatures of 100 °C, 150 °C and 200 °C was, respectively, 15 %, 27 % and 34 % higher than the value of ΔE for heartwood densified at the same temperatures.*

Keywords: *colour, densification, heartwood, sapwood, Scots pine, thermo-mechanical modification*

SAŽETAK • *U studiji je istražen utjecaj ultraljubičastog (UV) zračenja na boju termo-mehanički modificiranog drva bjeljike i srži običnog bora (Pinus sylvestris L.). Uzorci drva izloženi su procesu ugušćivanja u hidrauličkoj*

[1]Author is an assistant professor at Faculty of Wood Technology, Warsaw University of Life Sciences – SGGW, Warsaw, Poland.
[1]Autorica je docentica Fakulteta drvne tehnologije, Sveučilište bioloških znanosti u Varšavi (SGGW), Varšava, Poljska.

*preši jediničnog tlaka 80 MPa i pri tri različite temperature: 100, 150 i 200 °C tijekom 360 sekunda. Parametri boje drva određeni su uz pomoć matematičkih modela prostora boja CIE L*a*b* i L*C*h. Kao posljedica modifikacije drva bjeljike običnog bora pri temperaturi 200 °C promjena boje drva bila je dvostruko veća nego pri modifikaciji na nižim temperaturama. Ukupna razlika u boji uzoraka od srži običnog bora, bez obzira na temperaturu modifikacije, bila je dva puta veća od promjene boje na uzorcima od drva bjeljike. Najveće promjene svjetline uzoraka od drva srži i bjeljike običnog bora nastale su nakon 20 sati izlaganja UV zračenju. Promjene svjetline koje se pojavljuju nakon 20 sati izlaganja UV zračenju, bez obzira na temperaturu modifikacije, činile su oko 30 – 60 % ukupne promjene svjetline. Nakon 300 sati UV zračenja vrijednost ΔE za uzorke od drva bjeljike podvrgnute procesu ugušćivanja pri temperaturama 100, 150 i 200° C bila je 15, 27 i 34 % veća od vrijednosti ΔE za uzorke od drva srži podvrgnute ugušćivanju pri jednakim temperaturama.*

Ključne riječi: *boja, proces ugušćivanja, srž, bjeljika, obični bor, termo-mehanička modifikacija*

1 INTRODUCTION
1. UVOD

The colour of wood is an effect of the selective reflection and diffusion of light rays with wavelength characteristic of a given material. A material has a colour corresponding to the spectral composition of reflected and diffused rays. It absorbs the remaining rays forming part of the spectral composition, so they do not reach the eye and do not give the impressions of colour. One of the characteristic features of wood is the changeability of colour. The colour of wood depends on a number of external factors, among which climatic conditions play the most significant role (Hon and Minemura, 1991; Sharratt *et al.*, 2009; Tolvaj and Mitsui, 2010). Tolvaj and Mitsui (2010) found that colour alteration of black locust wood can be seen by the naked eye after 2-3 h of solar irradiation. Sharratt *et al.* (2009) showed that the majority of colour changes of Scots pine (*Pinus sylvestris* L.) occurred within the first 24 h after simulated accelerated sunlight exposure. The colour of wood also depends on habitat conditions. Depending on the type and content of extractives, particular wood species show different susceptibility to colour change under the influence of ultraviolet radiation (Pandey, 2005; Persze and Tolvaj, 2012; Moya, *et al.* 2012).

Some wood species are capable of forming coloured heartwood. The oldest annual growth rings, located most closely to the pith, change their chemical composition and have limited water permeability. Heartwood is often darker in colour compared to sapwood, which makes it possible to distinguish it with the naked eye. Heartwood only fulfils a mechanical role. It strengthens the trunk, and this part of the trunk becomes naturally impregnated during the life of the tree and it is more resistant to microorganisms and insects than sapwood. Sapwood, in addition to strengthening the trunk, participates in the plant's vital functions, *e.g.* water transmission and accumulation of nutrients, and for this reason it is definitely more susceptible to rots and insects feeding. In extreme cases, *e.g.* in the case of common oak wood, sapwood, which is usually narrow, is treated as waste, a part of the trunk that is not suitable for processing. Pine wood is a heartwood species with coloured heartwood. The sapwood component in pine wood is considerable and may reach up to 1/3 of the trunk width. Similarly to heartwood, pine sapwood is used for industrial purposes. Pine sapwood is light yellow, whereas heartwood is red-brown. The darker colour of heartwood is caused by the presence of gum, tannins, dye substances and other extractives (Wagenführ, 2007).

Thermo-mechanical modification is one of the methods enabling the improvement of physical and mechanical properties of wood without the use of chemicals (Ülker *et al.*, 2012; Rautkari *et al.*, 2013; Laskowska, 2017). The following features are most frequently described as quality indicators of densified wood: density, hardness, dimensional stability (Ülker *et al.*, 2012; Laine *et al.*, 2013, 2016; Rautkari *et al.*, 2013; Tu *et al.*, 2014). There is no comprehensive data on the impact of abiotic factors, *i.e.* ultraviolet radiation, on the colour of wood subjected to densification. Neither is there comprehensive data concerning colour changes in densified wood broken down into sapwood and heartwood areas. Wood colour stability is an important feature, since it is among the primary factors determining the usability of wood. Moreover, it may constitute an indirect indicator of wood quality and strength (Bekhta and Niemz, 2003; Johansson and Morén, 2006; González-Peña and Hale, 2009).

The purpose of the study was to determine the impact of ultraviolet radiation on the colour of thermo-mechanically modified sapwood and heartwood of pine (*Pinus sylvestris* L.). A particularly important aspect was to determine the change in the colour parameters of wood in time. Another important aspect was to verify the differences in the susceptibility of pine sapwood and heartwood to colour change under the influence of ultraviolet radiation.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

Pine (*Pinus sylvestris* L.) sapwood (S) and heartwood (H) from a forest in the central Poland, managed by the State Forests National Forest Holding, were used for the study. The samples used for the study had the dimensions of 120 mm (longitudinal), 60 mm (radial) x 5 mm (tangential). 20 samples were used for each variant of thermo-mechanical modification and exposed to light irradiation. The surface of samples was finished by planing. The samples were conditioned for three months in a normal climate (temperature 20 °C ± 2 °C, relative humidity 65 % ± 5 %).

The thermo-mechanical modification of wood was conducted in a laboratory hydraulic press. The temperature of the press platens was 100 °C, 150 °C and 200 °C, while the unit pressure was 80 MPa. The thermo-mechanical modification of wood included three stages: (1) heating wood samples for 180 s with the closed press platens without exerting pressure, (2) pressing at the assumed pressure for 180 s, (3) cooling wood samples in an unheated hydraulic press without exerting pressure. The cooling process was carried out until wood achieved the temperature of approximately 70 °C.

Four fluorescent lamps were used for ultraviolet radiation, each with a capacity of 100W (model 100R, LIGHTECH company, Poland). Wood samples were subjected to ultraviolet radiation within a spectrum range of 340 - 360 nm. The used source of radiation was imitating the solar radiation, in particular the UVA component. In studies by other authors, a strong UV light emitter, *i.e.* a mercury vapour lamp with total light emission of 320W, was used for wood light irradiation (Tolvaj and Mitsui, 2010). Wood samples were subjected to ultraviolet radiation within a spectrum range of 300 - 400 nm. Wood samples were light irradiated for 300 h, and colour parameters were determined after each subsequent 20 h of irradiation. 20 samples were used for studying colour for each variant of non-densified and densified wood. Colour parameters were examined at three measurement points for each sample.

Wood moisture was determined in accordance with ISO 13061-1 (2014) requirements, and density in accordance with ISO 13061-2 (2014). Wood moisture was 7.82 % (±0.13). The compression ratio (*CR*) was calculated according to Eq. 1, where t_0 is the original thickness (mm), and t_d is wood thickness after densification (mm).

$$CR = \frac{t_0 - t_d}{t_0} \cdot 100\ (\%) \qquad (1)$$

The following colour parameters were determined: lightness (L^*), chromatic coordinate on the red-green axis (a^*), chromatic coordinate on the yellow-blue axis (b^*), saturation (C^*) and hue angle (h). The total colour difference ΔE was determined according to ISO 7724-3 (1984). SP60 spectrophotometer made by X-Rite Europe GmbH (Regensdorf, Switzerland) was used to examine the colour parameters. The sensor head was 8 mm in diameter. Measurements were made using a D65 illuminant.

Statistical analysis of the results was performed using STATISTICA Version-12 software of StatSoft, Inc. (Tulsa, USA). The statistical analysis of the results was performed at a significance level of 0.05. The trend lines were determined, and parameters of the curve equation (y) were specified along with the coefficients of determination R^2 for correlations describing the change in pine wood colour parameters in time.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

The influence of the area of wood (sapwood, heartwood) and of densification temperature (based on ANOVA, Fischer's F - test) on the parameters of densified wood was shown in Table 1. It was also specified to what extent the factors under analysis affected the wood colour parameters immediately after the modification (parameters identified by the symbol M, *e.g.* L^*_M) and after 300 h of light irradiation of wood (parameters identified by the symbol R, *e.g.* L^*_R). The influence of the area of wood and temperature of treatment on the colour change ΔE after 20 h and 300 h of light irradiation was analysed (marked as ΔE_20R and ΔE_300R, respectively).

The wood area (sapwood, heartwood) demonstrated a significant influence on all the pine properties under study except for density. The degree of densification of sapwood was so high that comparable densities were achieved for sapwood and heartwood as a result of modification. The temperature of thermo-mechanical modification showed a significant influence on all pine wood properties under study ($p < 0.05$). The interaction between the area of densified wood and the temperature of treatment, which shaped the wood parameters under study except for a^* and h after light irradiation, was also significant. When analysing the percentage impact of factors on the properties of densified pine wood under study, considerable differences in the effect of these factors could be noted. The temperature of treatment influenced the values of *CR* and density (influence at a level of 98 %), b^* and ΔE (influence at a level of 44 - 63 %) to a much greater extent than the area of the densified wood. The differences between sapwood and heartwood determined primarily the values of L^*, a^*, h, both immediately after densification, and after light irradiation (influence at a level of 50 - 84 %). The level of influence of the factors under analysis on colour parameters was different after light irradiation than immediately after densification. When the influence of the wood area increased, the influence of the temperature decreased and *vice versa*. For example, the wood area influenced the differences in the lightness of wood to a greater extent after light irradiation than immediately after densification (the influence of this factor increased from 50 % to 76 %), whereas the influence of the temperature of treatment on the lightness of wood after light irradiation (12 %) was smaller than after densification (32 %).

The present studies show that the higher the temperature of the press platen, the higher degree of compression of pine sapwood and heartwood and, consequently, the higher density, was achieved. Pine heartwood was compressed to a lesser degree than sapwood (Figure 1a). This was due to the lesser susceptibility of latewood zones in heartwood to densification. Heartwood latewood is characterised by greater density and it is often saturated with resin which, by filling the interior of cells, makes their densification difficult. Pine heartwood may contain even five times as much resin as sapwood (Sandermann and Augustin, 1963).

As a result of greater compression, the density of sapwood became comparable to the density of heartwood (Figure 1b). The density of non-densified pine sapwood and heartwood was 466 kg·m^{-3} (±17) and 558 kg·m^{-3} (±9), respectively. This value was comparable to values cited in the literature. According to Wagen-

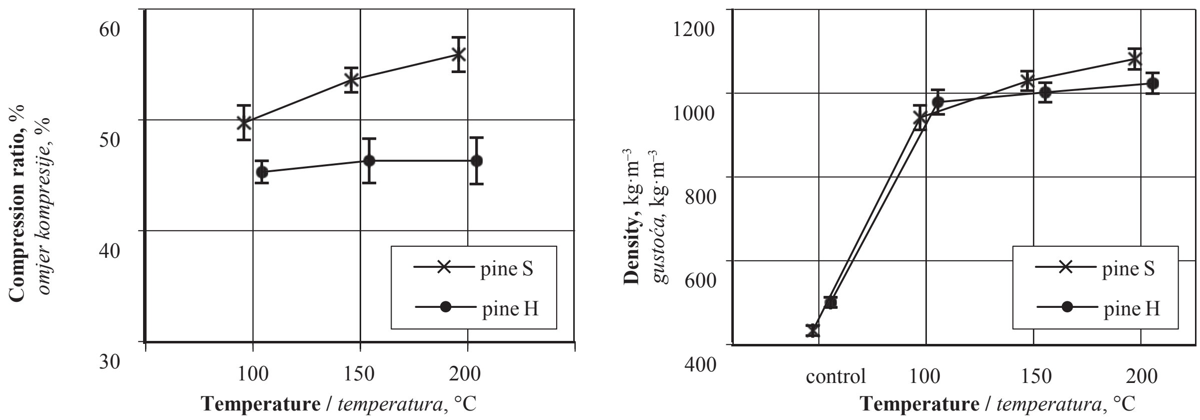
Table 1 Statistical evaluation of factors influencing parameters of thermo-mechanically densified pine wood
Tablica 1. Statistička procjena čimbenika koji utječu na svojstva termo-mehanički ugušćenog drva običnog bora

Factor Čimbenik	**Properties** / *Svojstva*					
	Compression ratio / *Omjer kompresije*			**Density** / *Gustoća*		
	Fisher's F-test *Fisherov F-test*	Significance level *Razina značajnosti*	Factor Influence *Utjecaj čimbenika* %	Fisher's F-test *Fisherov F-test*	Significance level *Razina značajnosti*	Factor Influence *Utjecaj čimbenika* %
	F	p	X	F	p	X
Wood area (1)	357.62	0.000000	1	1.1	0.295394	0
Temp. (2)	9264.44	0.000000	98	3455.5	0.000000	98
(1) × (2)	54.38	0.000000	1	38.3	0.000000	1
Error			0			1
	***L**_M**			***L**_R**		
	F	p	X	F	p	X
Wood area (1)	341.1	0.000000	50	581.2	0.000000	76
Temp. (2)	72.7	0.000000	32	31.6	0.000000	12
(1) × (2)	14.9	0.000000	7	4.8	0.004187	2
Error			11			10
	***a**_M**			***a**_R**		
	F	p	X	F	p	X
Wood area (1)	631.420	0.000000	69	448.06	0.000000	83
Temp. (2)	58.979	0.000000	19	5.21	0.002590	3
(1) × (2)	10.743	0.000006	4	1.24	0.299904	1
Error			8			13
	***b**_M**			***b**_R**		
	F	p	X	F	p	X
Wood area (1)	273.47	0.000000	36	13.0	0.000571	5
Temp. (2)	114.11	0.000000	46	57.4	0.000000	63
(1) × (2)	20.84	0.000000	8	4.7	0.004495	5
Error			10			27
	Δ*E*_20R			**Δ*E*_300R**		
	F	p	X	F	p	X
Wood area (1)	6.799	0.011080	3	34.871	0.000000	10
Temp. (2)	38.806	0.000000	44	67.734	0.000000	60
(1) × (2)	23.156	0.000000	26	9.315	0.000028	8
Error			27			22
	***C**_M**			***C**_R**		
	F	p	X	F	p	X
Wood area (1)	345.01	0.000000	42	19.8	0.000031	8
Temp. (2)	115.38	0.000000	42	47.9	0.000000	58
(1) × (2)	21.23	0.000000	8	3.6	0.017797	4
Error			8			30
	***h*_M**			***h*_R**		
	F	p	X	F	p	X
Wood area (1)	522.0	0.000000	77	521.4	0.000000	84
Temp. (2)	24.5	0.000000	11	7.6	0.000167	4
(1) × (2)	4.1	0.010082	2	1.2	0.300333	1
Error			10			11

führ (2007), pine wood (*Pinus sylvestris* L.) density in an air-dry condition ranges from 330 kg·m^{-3} to 890 kg·m^{-3}, with the mean value of 510 kg·m^{-3}. The mean density after thermo-mechanical modification ranged from 986 kg·m^{-3} to 1126 kg·m^{-3} for sapwood and from 1023 kg·m^{-3} to 1068 kg·m^{-3} for heartwood. Generally, it can be concluded that thermo-mechanical modification resulted in twice as high density of pine sapwood and heartwood. Laine *et al.* (2016) densified Scots pine (*Pinus sylvestris* L.) sapwood at 150 °C for 1h. The highest density they obtained by densifying 12.5 mm thick samples was 915 ± 25.7 kg·m^{-3} (the densification ratio was 50 %).

3.1 Pine wood colour parameters after thermo-mechanical modification
3.1. Parametri boje drva bora nakon termo-mehaničke modifikacije

The thermo-mechanical modification of pine sapwood and heartwood at temperatures of 100 °C and 150 °C caused slight changes in the colour lightness of wood, only just noticeable to the naked eye. Only treatment at a temperature of 200 °C resulted in a clear



a) b)

Figure 1 Compression ratio (a) and density (b) of densified pine wood

Slika 1. a) Omjer kompresije, b) gustoća ugušćenog drva bora u ovisnosti o temperaturi tijekom procesa ugušćivanja

change in colour. Similar correlations were found by Bekhta *et al*. (2014), who examined the effect of short-term thermo-mechanical (STTM) densification temperature and pressure on the surface colour of veneer of alder, beech, birch and pine. The authors do not specify whether they examined pine sapwood or heartwood. A decrease in the lightness of wood, as a result of treatment, is caused by the degradation of hemicelluloses, whereby the greater the degradation of hemicelluloses, the higher is the temperature of heat treatment. As a result, the lignin content in wood increases, giving wood a darker colour (Diouf *et al.*, 2011; Bekhta *et al.*, 2014).

The densification of pine sapwood at temperatures of 100 °C and 150 °C did not influence, to a significant extent, the values of *a** and *b** and, consequently, did not contribute to the total colour difference Δ*E*. As a result, the changes in the value of Δ*E* (at a level of ca. 3.5) were comparable for pine sapwood densified at temperatures of 100 °C and 150 °C (Table 2). The most significant changes in wood colour towards red occurred at a modification temperature of 200 °C, both in case of sapwood and heartwood. As the modification temperature of sapwood and heartwood increased, the saturation of colour *C** increased and the value of h decreased. A change in colour towards red may be due to the presence of extractives in wood (Bekhta *et al.*, 2014). As heartwood contains more extractives, it was more susceptible to colour change towards red than sapwood. According to Waliszewska *et al*. (2015), as obtained by Soxhlet extraction with ethanol, the extractive content in the sapwood of a 75-year old pine tree ranges from 2.3 to 2.7 %, and in its heartwood from 6.8 % to 13.3 %. An increase in the yellow component could also be observed with the increase of modification temperature in case of heartwood that contained more lignin. The factors accountable for the wood becoming yellow include primarily lignin and its derivatives, *i.e.* quinones and stilbenes (Hon and Glasser, 1979). The value of *b** for sapwood and heartwood modified at a

Table 2 Pine wood colour parameters after thermo-mechanical modification (standard deviations in parentheses)

Tablica 2. Parametri boje drva bora nakon termo-mehaničke modifikacije (u zagradama su standardna odstupanja)

Area *Površina*	**Densification temperature** *Temperatura u procesu ugušćivanja* °C	**Parameters** / *Parametri*					
		*L**	*a**	*b**	ΔE	*C**	*h*
pine sapwood *bjeljika drva bora*	Control *kontrolni uzorak*	81.32 (±2.04)	4.48 (±0.82)	23.91 (±0.44)	-	24.34 (±0.50)	79.41 (±1.85)
	100	80.96 (±0.67)	4.52 (±0.37)	26.41 (±0.86)	3.35 (±0.42)	27.16 (±0.90)	80.90 (±0.54)
	150	80.45 (±0.54)	4.65 (±0.32)	26.58 (±0.99)	3.56 (±0.38)	27.93 (±1.02)	80.79 (±0.41)
	200	77.15 (±1.50)	6.47 (±0.56)	28.83 (±1.55)	6.91 (±1.05)	29.55 (±1.57)	77.33 (±0.98)
pine heartwood *srž drva bora*	Control *kontrolni uzorak*	77.66 (±1.48)	7.37 (±0.88)	25.56 (±0.62)	-	26.61 (±0.77)	73.96 (±1.64)
	100	74.78 (±1.87)	9.46 (±0.92)	30.71 (±2.00)	6.60 (±0.45)	32.14 (±2.16)	72.89 (±0.78)
	150	73.11 (±1.93)	9.88 (±0.95)	33.93 (±2.27)	10.63 (±1.36)	35.22 (±2.37)	72.49 (±1.03)
	200	65.36 (±3.84)	12.09 (±1.35)	36.12 (±1.02)	16.39 (±2.37)	38.10 (±1.17)	71.52 (±1.83)

temperature of 200 °C was, respectively, 21 % and 41 % higher than for non-modified sapwood and heartwood. The modification of pine sapwood at a temperature of 200 °C resulted in a change in wood colour ΔE that was twice as substantial as the change in wood colour after modifications at lower temperatures. The densification of pine heartwood resulted in a greater difference in wood colour. The higher the modification temperature, the more substantial was the total colour difference for pine heartwood. In general, it can be concluded that the total colour difference for pine heartwood, irrespective of the modification temperature, was twice as substantial as the change in the colour of pine sapwood.

3.2 Colour parameters of thermo-mechanically modified pine wood after light irradiation
3.2. Parametri boje termo-mehanički modificiranog drva bora nakon izlaganja UV zračenju

Significant changes in the colour of wood under the influence of ultraviolet radiation were observed. The below analysis, based on the CIE *L*a*b** and *L*C*h* systems, provides the detailed characteristics of wood colour.

Pine sapwood was characterised by lesser susceptibility to a change in lightness *L** under the influence of ultraviolet radiation than heartwood. The difference between *L** before and after light irradiation of pine sapwood was ca. 8, whereas in the case of pine heartwood it ranged from ca. 7 to 12. The above correlations were caused by differences in the chemical composition of wood. The factor accountable for wood darkening is lignin (Hon and Glasser, 1979; Diouf *et al*., 2011; Bekhta *et al*., 2014). Pine heartwood contains more lignin than sapwood (Waliszewska *et al*., 2015). Moreover, as the densification temperature increased, the degradation of hemicelluloses became more intense, which additionally contributed to the increase in the lignin percentage content in wood. As a result, the colour of pine sapwood and heartwood densified at a temperature of 200 °C was much darker than in the case of the same wood densified at temperatures of 100 °C and 150 °C. This confirms mechanisms involved in the thermal decomposition of wood components. Kollmann and Fengel (1965) heated oak and pine wood at different temperatures. The authors found that pine lost weight at about 100 °C, whilst oak remained stable to about 130 °C. Additionally, it should be noted that wood densified at a higher temperature changed its *L** under the influence of light irradiation to a lesser extent. Within 300 h, the value of *L** for pine sapwood and heartwood densified at temperatures of 100 °C and 150 °C decreased by 12 %, whereas pine sapwood and heartwood densified at a temperature of 200 °C recorded a decrease of 9 %. The study showed that the most substantial changes in wood lightness occurred after 20 h exposure to UV radiation, both for

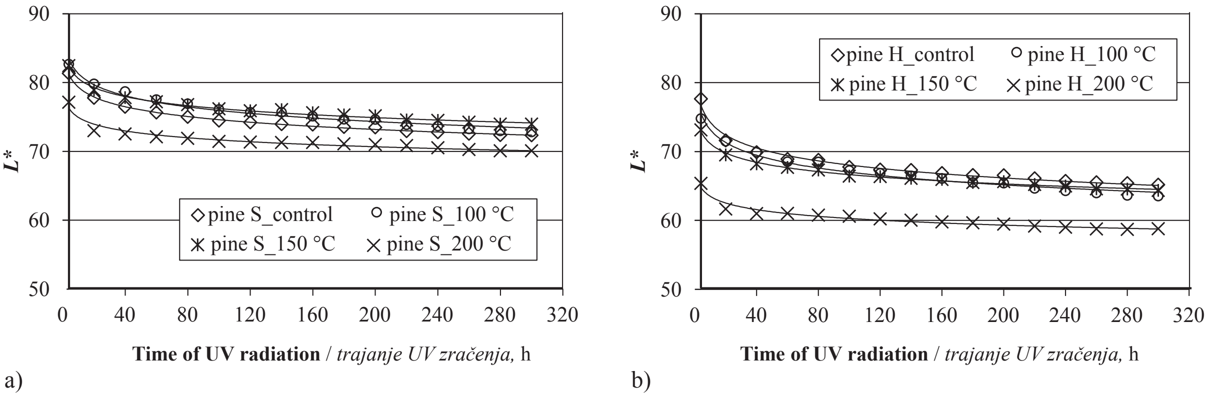


Figure 2 Change of lightness (*L**) of pine sapwood (a) and heartwood (b) after exposure to UV radiation
Slika 2. Promjena svjetline (*L**): a) bjeljike, b) srži drva bora nakon izlaganja UV zračenju

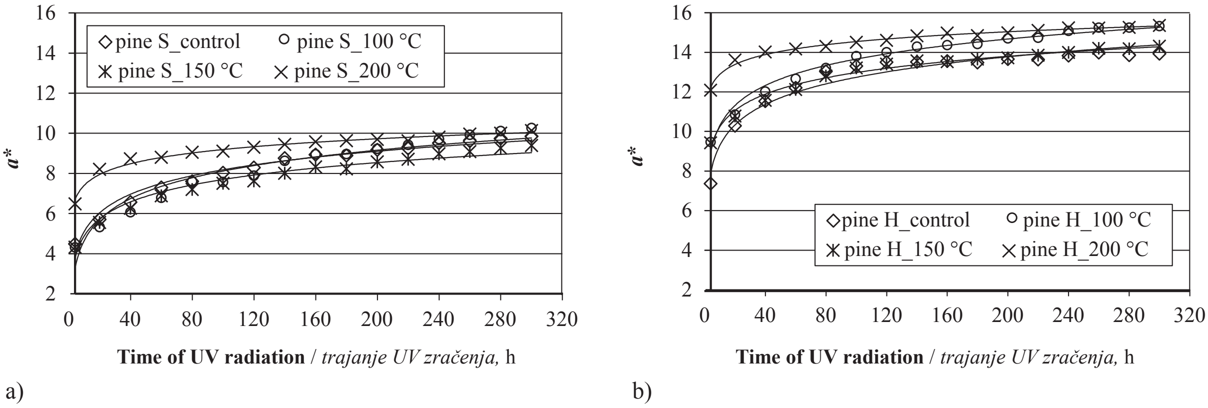
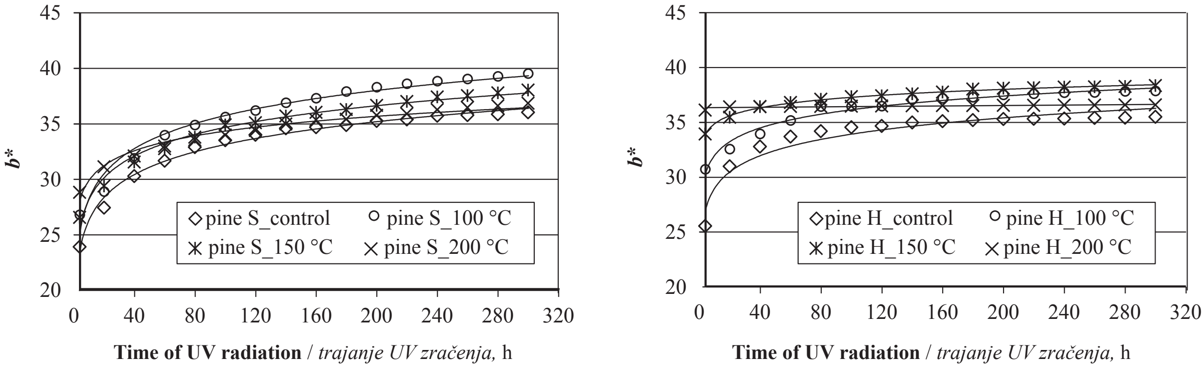


Figure 3 Change in *a** parameter of pine sapwood (a) and heartwood (b) after exposure to UV radiation
Slika 3. Promjena parametra *a**: a) bjeljike, b) srži drva bora nakon izlaganja UV zračenju



a) b)

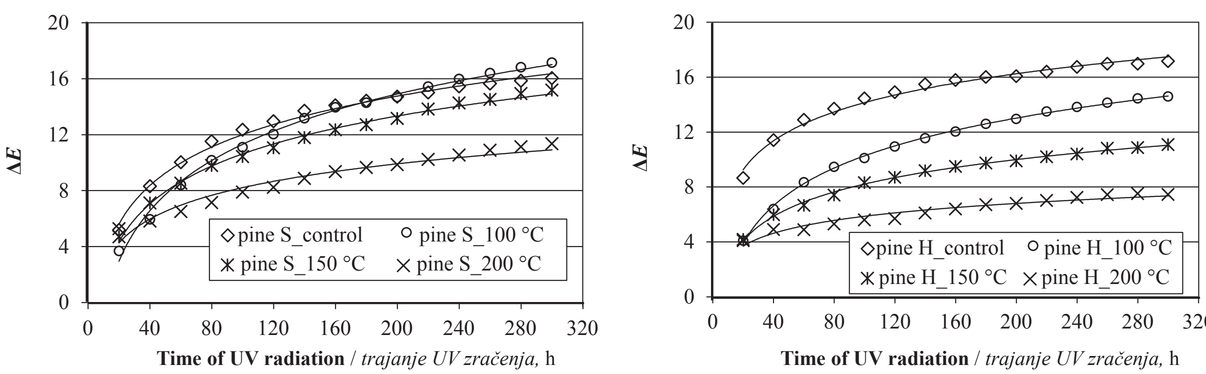
Figure 4 Change in b^* parameter of pine sapwood (a) and heartwood (b) after exposure to UV radiation
Slika 4. Promjena parametra b^*: a) bjeljike, b) srži drva bora nakon izlaganja UV zračenju

sapwood and heartwood (Figure 2). Changes in lightness occurring within 20 h, irrespective of the temperature of treatment, accounted for about 30 - 60 % of the total change in pine sapwood and heartwood. Tolvaj and Mitsui (2010) also found that the most substantial changes in the lightness of black locust, beech, Japanese cedar and spruce wood occurred during the first 20 h of sun light irradiation.

As a result of light irradiation, pine wood changed colour towards red (Figure 3). The value of a^*, after 300 h of light irradiation, was double for non-densified sapwood and heartwood compared with its value before light irradiation. After 300 h of light irradiation, the value of a^* was 1.5 times higher for heartwood (non-densified and densified) than for sapwood. Heartwood changed its parameter a^* under the influence of light irradiation to a lesser extent than sapwood. Sapwood and heartwood, densified at a temperature of 200 °C, changed their parameter a^* under the influence of light irradiation to a considerably lesser extent than sapwood and heartwood densified at a lower temperature. After 300 h of light irradiation, the value of a^* for sapwood, depending on the modification temperature, was from 60 % to 140 % higher than before irradiation. On the other hand, the value of a^* for heartwood, after 300 h of light irradiation, was from 30 % to 60 % higher than before light irradiation, depending on the modification temperature. A change in colour towards red may be due to the presence of extractives in the wood (Yazaki *et al*., 1994; Gierlinger *et al*., 2004; Persze and Tolvaj, 2012; Bekhta *et al*., 2014). The values of a^* show a trend in the colour change of sapwood and heartwood towards red, due to a decrease in the hue angle, as shown in Figure 8c, d.

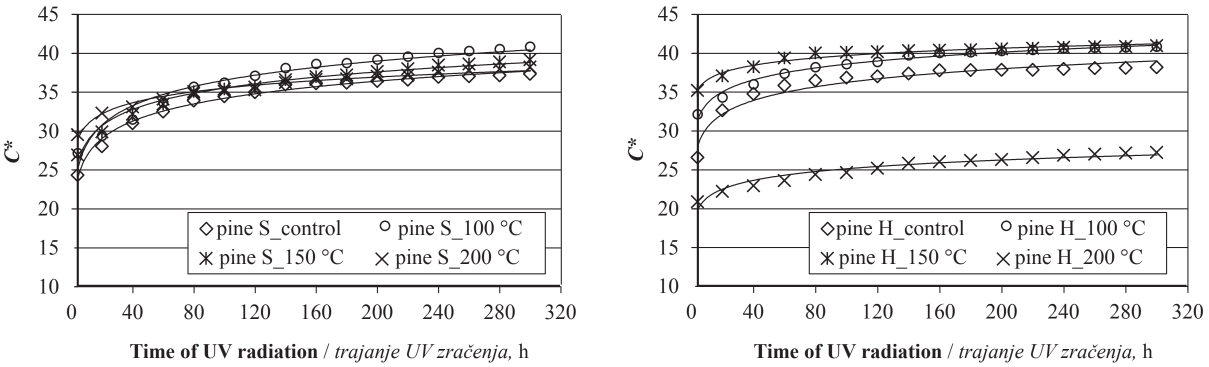
The colour of sapwood changed towards yellow under the influence of light irradiation to a greater extent than the colour of heartwood (Figure 4). After 300 h of light irradiation, the value of a^* for sapwood, depending on the modification temperature, was from 30 % to 50 % higher than before light irradiation. The value of a^* for heartwood after 300 h of light irradiation, on the other hand, was from 2 % to 25 % higher than before light irradiation, depending on the modification temperature. The higher the modification temperature, the smaller was the change in the value of b^* of the wood under the influence of light irradiation. Heartwood modified at 200 °C did not show a significant change in the value of b^* under the influence of light irradiation. The values of b^* show a trend in the colour change of sapwood and heartwood towards yellow, caused by an increased colour saturation (Figure 8a, b). Yellowing is the main colour change of wood, this being an effect of the photodegradation of lignin (Nimz 1973; Hon and Glasser, 1979; Yazaki *et al*., 1994; Huang *et al*., 2012; Persze and Tolvaj, 2012).

Sapwood showed greater dynamics of colour change under the influence of light irradiation than heartwood (Figure 5). The value of ΔE after 300 h of light irradiation of non-densified sapwood was three times as high as after 20 h of light irradiation. The value of



a) b)

Figure 5 Total colour difference (ΔE) of pine sapwood (a) and heartwood (b)
Slika 5. Ukupna promjena boje (ΔE): a) bjeljike, b) srži drva bora



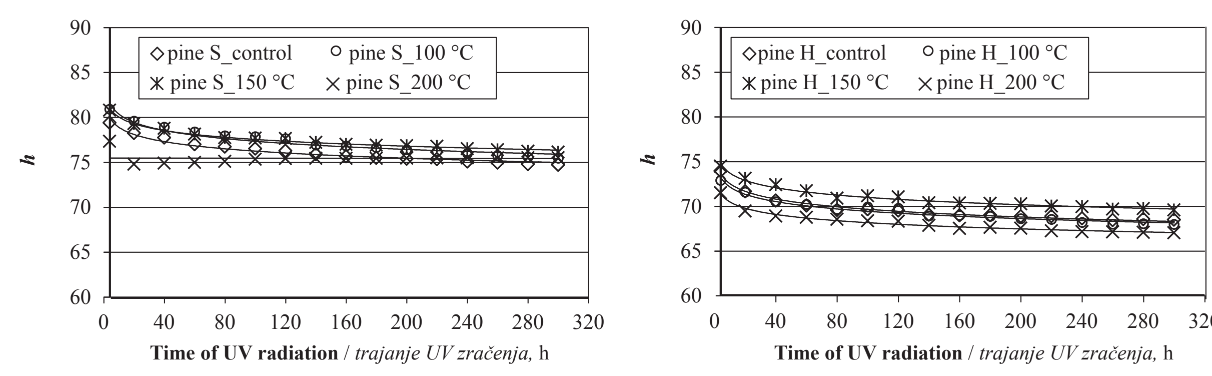
a) b)

Figure 6 Change in C* parameter of pine sapwood (a) and heartwood (b) after exposure to UV radiation
Slika 6. Promjena parametra *C**: a) bjeljike, b) srži drva bora nakon izlaganja UV zračenju

ΔE after 300 h of light irradiation of non-densified heartwood was double compared with its value after 20 h of light irradiation. The value of ΔE of non-densified sapwood after 300 h of light irradiation was 7 % lower than in the case of non-densified heartwood and the differences were statistically significant ($p < 0.05$). The total colour difference for sapwood densified at a temperature of 100 °C, 150 °C and 200 °C was, respectively, 15 %, 27 % and 34 % more substantial than the value of ΔE for heartwood densified at the same temperatures. This is due to the fact that thermo-mechanically modified pine sapwood is characterised by greater susceptibility to colour change under the influence of light irradiation than thermo-mechanically modified heartwood.

The most substantial changes in the colour of wood occurred after 20 h of light irradiation. A change in colour within 20 h accounted for about 20 %, 30 % and 45 % of the total colour change in densified sapwood at temperatures of 100 °C, 150 °C and 200 °C. Changes in colour within 20 h accounted for about 30 %, 40 % and 55 % of the total colour difference for densified heartwood at temperatures of 100 °C, 150 °C and 200 °C. The higher the temperature of thermo-mechanical modification, the smaller were the values of ΔE after 300 h of light irradiation. An exception was pine sapwood densified at 100 °C and 150 °C, which was characterised by the value of ΔE similar to that of non-densified pine sapwood. Tolvaj and Mitsui (2010) noted that the differences in wood colour under the influence of light irradiation are due to the differences in extractive content. Pine heartwood contains more extractives than sapwood (Waliszewska *et al*., 2015). Ultraviolet radiation causes degradation of extractives and then also quick oxidation of degradation products, leading to a sudden drop in lightness. The modified chromophores act as an energy trap, which slows down the process of photodegradation of the main wood components (Németh *et al*., 1992). Therefore, the colour change of heartwood is slower than that of sapwood.

No significant differences were found between the values of *C** for non-densified and densified pine sapwood under the influence of ultraviolet radiation (Figure 6). Similar correlations were found for pine heartwood. An exception was pine heartwood densified at 200 °C. After 300 h of light irradiation, the value of *C** for that heartwood was 30 % lower than for non-densified heartwood. It should be noted that, after 300 h of light irradiation, the value of *C** for sapwood densified at temperatures of 100 °C, 150 °C and 200 °C was, respectively, 50 %, 45 % and 30 % higher than the value of C* for sapwood before densification. The value of *C** for heartwood densified at temperatures of 100 °C, 150 °C and 200 °C, after 300 h of light irradiation, was, respectively, 30 %, 15 % and 30 % higher than the value of *C** for heartwood before densification. Significant differences between the values of *C** for sapwood and heartwood were only found when wood was densified at 200 °C.



a) b)

Figure 7 Change in *h* parameter of pine sapwood (a) and heartwood (b) after exposure to UV radiation
Slika 7. Promjena parametra *h*: a) bjeljike, b) srži drva bora nakon izlaganja UV zračenju

Table 3 Curve equations describing relations between L^*, a^*, b^*, C^*, h, ΔE and time (t) of UV exposure (a – directional factor, b – absolute term) and R^2 – coefficient of determination)
Tablica 3. Jednadžbe krivulja koje opisuju odnose između L^*, a^*, b^*, C^*, h, ΔE i vremena (t) UV zračenja (a – koeficijent smjera, b – odsječak na osi y, R^2 – koeficijent determinacije)

Wood species *Vrsta drva*	**Temperature of densification** *Temperatura procesa ugušćivanja* °C	**Parameters** / *Parametri*			
		$a^* = a \cdot \ln(t) + b$	R^2	$b^* = a \cdot \ln(t) + b$	R^2
pine sapwood *bjeljika drva bora*	control	$a^* = 1.57 \cdot \ln(t) + 0.88$	0.99	$b^* = 3.07 \cdot \ln(t) + 18.98$	0.98
	100	$a^* = 1.91 \cdot \ln(t) - 0.85$	0.98	$b^* = 3.86 \cdot \ln(t) + 17.73$	0.99
	150	$a^* = 1.43 \cdot \ln(t) + 1.01$	0.98	$b^* = 3.20 \cdot \ln(t) + 19.82$	0.99
	200	$a^* = 0.68 \cdot \ln(t) + 6.10$	0.98	$b^* = 2.19 \cdot \ln(t) + 24.13$	0.99
pine heartwood *srž drva bora*	control	$a^* = 1.27 \cdot \ln(t) + 6.99$	0.92	$b^* = 1.54 \cdot \ln(t) + 27.09$	0.94
	100	$a^* = 1.66 \cdot \ln(t) + 5.94$	0.99	$b^* = 1.95 \cdot \ln(t) + 27.10$	0.96
	150	$a^* = 1.30 \cdot \ln(t) + 6.94$	0.98	$b^* = 1.05 \cdot \ln(t) + 32.47$	0.99
	200	$a^* = 0.66 \cdot \ln(t) + 11.54$	0.98	$b^* = 0.01 \cdot \ln(t) + 36.40$	0.98
		$L^* = a \cdot \ln(t) + b$	R^2	$\Delta E = a \cdot \ln(t) - b$	R^2
pine sapwood *bjeljika drva bora*	control	$L^* = -2.01 \cdot \ln(t) + 83.85$	0.99	$\Delta E = 3.97 \cdot \ln(t) - 6.27$	0.98
	100	$L^* = -2.65 \cdot \ln(t) + 88.28$	0.98	$\Delta E = 5.19 \cdot \ln(t) - 12.57$	0.99
	150	$L^* = -1.85 \cdot \ln(t) + 84.74$	0.97	$\Delta E = 3.90 \cdot \ln(t) - 7.34$	0.99
	200	$L^* = -1.07 \cdot \ln(t) + 76.44$	0.95	$\Delta E = 2.46 \cdot \ln(t) - 3.09$	0.96
pine heartwood *srž drva bora*	control	$L^* = -2.32 \cdot \ln(t) + 78.58$	0.99	$\Delta E = 3.04 \cdot \ln(t) + 0.17$	0.99
	100	$L^* = -3.01 \cdot \ln(t) + 80.99$	0.98	$\Delta E = 3.97 \cdot \ln(t) - 7.99$	0.99
	150	$L^* = -1.88 \cdot \ln(t) + 75.27$	0.99	$\Delta E = 2.57 \cdot \ln(t) - 3.63$	0.99
	200	$L^* = -1.16 \cdot \ln(t) + 65.54$	0.92	$\Delta E = 1.35 \cdot \ln(t) - 0.35$	0.95
		$C^* = a \cdot \ln(t) + b$	R^2	$h = a \cdot \ln(t) + b$	R^2
pine sapwood *bjeljika drva bora*	control	$C^* = 3.36 \cdot \ln(t) + 18.69$	0.98	$h = -1.37 \cdot \ln(t) + 82.64$	0.99
	100	$C^* = 4.39 \cdot \ln(t) + 15.98$	0.99	$h = -1.59 \cdot \ln(t) + 84.78$	0.96
	150	$C^* = 3.41 \cdot \ln(t) + 19.66$	0.99	$h = -1.18 \cdot \ln(t) + 83.01$	0.98
	200	$C^* = 2.30 \cdot \ln(t) + 24.85$	0.98	$h = a \cdot t + b$	
				$h = 0.01 \cdot t + 74.94$	0.76
				$h = a \cdot \ln(t) + b$	R^2
pine heartwood *srž drva bora*	control	$C^* = 1.91 \cdot \ln(t) + 27.69$	0.95	$h = -1.24 \cdot \ln(t) + 75.40$	0.98
	100	$C^* = 2.46 \cdot \ln(t) + 27.16$	0.99	$h = -1.18 \cdot \ln(t) + 74.89$	0.97
	150	$C^* = 1.32 \cdot \ln(t) + 33.63$	0.92	$h = -1.18 \cdot \ln(t) + 76.43$	0.98
	200	$C^* = 2.06 \cdot \ln(t) + 15.70$	0.98	$h = -1.01 \cdot \ln(t) + 72.81$	0.98

Changes in the value of h under the influence of light irradiation for sapwood and heartwood were logarithmic. An exception was pine sapwood densified at 200 °C (Figure 7). After 300 h of light irradiation of non-densified sapwood and sapwood densified at 100 °C and 150 °C, a 6 % decrease in the value of h was recorded as compared to the wood before light irradiation. In the case of non-densified and densified heartwood, a 7 % decrease in the value of h was recorded after 300 h of light irradiation as compared to the wood before light irradiation. The differences were statistically significant ($p < 0.05$). In general, it can be concluded that, after 300 h of light irradiation, the value of h for sapwood was 10 % higher than the value of h recorded for heartwood, irrespective of the modification temperature.

Table 3 presents a summary of equations of the straight lines showing the correlations between the wood colour parameters and the values of the coefficient of determination R^2. The high values of R^2, close to "1", indicate the usefulness of the regression equation for anticipating the value of the dependent variable L^*, a^*, b^*, C^*, h and ΔE using the independent variable t, which is the wood light irradiation time.

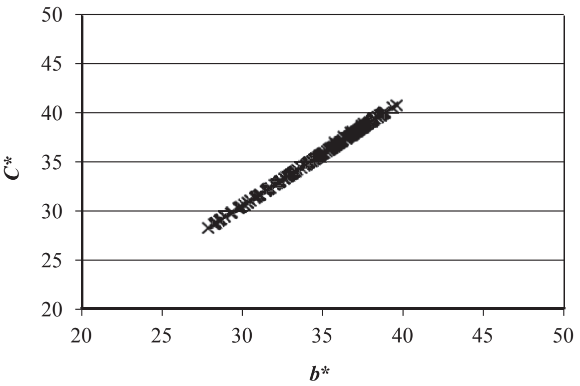
Regression equations of colour parameters for pine wood densified throughout the range of temperatures and light irradiation is presented in Table 4. The R^2 values show that a change in colour parameters is much more pronounced for pine sapwood than pine heartwood. In the case of pine heartwood, the coefficient of determination R^2 was less than 0.50 for four out of nine determined correlations. The correlations between the colour parameters of pine sapwood were found to have the value of R^2 greater than 0.61. The best linear correlation was found between C^* and b^* for pine sapwood ($R^2 = 0.99$) as well as heartwood ($R^2 = 0.93$). A high correlation was also found between h and a^* for pine sapwood ($R^2 = 0.97$) and heartwood ($R^2 = 0.92$). This means that only the values of b^* and a^* can be used to determine the values of C^* and h, respectively, (Figure 8).

4 CONCLUSIONS
4. ZAKLJUČAK

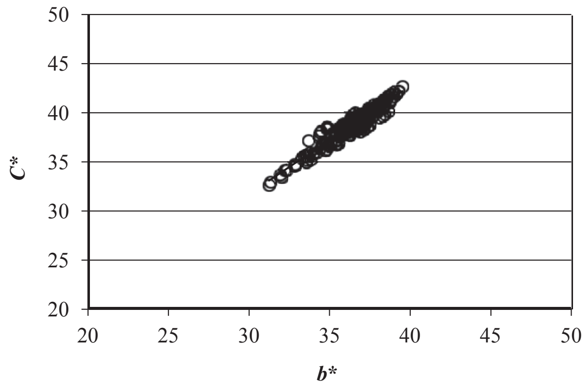
On the basis of the present study, it has been found that ultraviolet radiation has a significant influence on the colour of thermo-mechanically modified

Table 4 Regression equations of colour parameters for pine sapwood and heartwood samples densified at all investigated ranges of temperature and light irradiation
Tablica 4. Regresijske jednadžbe parametara boje uzoraka od bjeljike i srži drva bora nakon procesa ugušćivanja pri svim istraživanim temperaturama i UV zračenjima

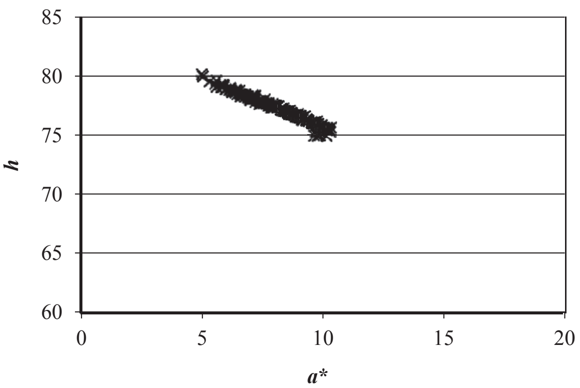
Area of pine wood / *Dio drva bora*			
Sapwood / *Bjeljika*		**Heartwood** / *Srž*	
Function	R^2	Function	R^2
$a^* = -0.62 \cdot L^* + 54.96$	0.88	$a^* = -0.46 \cdot L^* + 43.98$	0.66
$b^* = -1.18 \cdot L^* + 124.64$	0.75	$b^* = -0.23 \cdot L^* + 51.83$	0.23
$\Delta E = -1.33 \cdot L^* + 111.98$	0.61	$\Delta E = -0.30 \cdot L^* + 29.54$	0.09
$C^* = -1.29 \cdot L^* + 133.78$	0.77	$C^* = -0.37 \cdot L^* + 63.70$	0.41
$C^* = 2.19 \cdot a^* + 18.66$	0.95	$C^* = 0.77 \cdot a^* + 28.90$	0.57
$C^* = 1.08 \cdot b^* - 1.82$	0.99	$C^* = 1.17 \cdot b^* - 3.71$	0.93
$h = 0.56 \cdot L^* + 35.04$	0.94	$h = 0.52 \cdot L^* + 35.36$	0.60
$h = -0.87 \cdot a^* + 84.24$	0.97	$h = -1.15 \cdot a^* + 85.36$	0.92
$h = -0.39 \cdot b^* + 90.90$	0.84	$h = -0.41 \cdot b^* + 84,87$	0.08



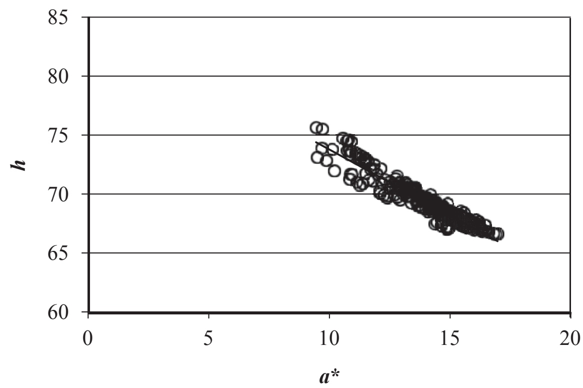
a) pine sapwood $C^*(b^*)$ / *bjeljika drva bora*



b) pine heartwood $C^*(b^*)$ / *srž drva bora*



c) pine sapwood $h(a^*)$ / *bjeljika drva bora*



d) pine heartwood $h(a^*)$ / *srž drva bora*

Figure 8 Correlation between colour parameters for pine sapwood and heartwood samples densified at all investigated ranges of temperature and light irradiation
Slika 8. Korelacija između parametara boje uzoraka od bjeljike i srži drva bora nakon procesa ugušćivanja pri svim istraživanim temperaturama i UV zračenjima

pine sapwood and heartwood. The higher the temperature of thermo-mechanical modification, the smaller was the degree of colour change of wood under the influence of ultraviolet radiation. This was due to chemical changes in wood during the treatment. Changes in lightness occurring within 20 h, irrespective of the temperature of treatment, accounted for about 30 - 60 % of the total change in pine sapwood and heartwood. Sapwood showed greater dynamics of colour change under the influence of light irradiation than heartwood. Thermo-mechanically modified pine sapwood is characterised by greater susceptibility to colour change under the influence of light irradiation than thermo-mechanically modified heartwood.

5 REFERENCES
5. LITERATURA

1. Bekhta, P.; Niemz, P., 2003: Effect of high temperature on the change in colour, dimensional stability and mechanical properties of spruce wood. Holzforschung, 57 (5): 539-546. https://doi.org/10.1515/HF.2003.080
2. Bekhta, P.; Proszyk, S.; Krystofiak, T., 2014: Colour in short term thermo-mechanically densified veneer of various wood species. European Journal of Wood and Wood Products, 72 (6): 785-797. https://doi.org/10.1007/s00107-014-0837-1
3. Diouf, P. N.; Stevanovic, T.; Cloutier, A.; Fang, Ch.-H.; Blanchet, P.; Koubaa, A.; Mariotti, N., 2011: Effects of thermo-hygro-mechanical densification on the surface characteristics of trembling aspen and hybrid poplar wood veneers. Applied Surface Sciences, 257 (8): 3558-3564. https://doi.org/10.1016/j.apsusc.2010.11.074
4. Gierlinger, N.; Jacques, D.; Grabner, M.; Wimmer, R.; Schwanninger, M.; Rozenberg, P.; Paques, L. E., 2004: Colour of larch heartwood and relationships to extractives and brown-rot decay resistance. Trees, 18 (1): 102-108. https://doi.org/10.1007/s00468-003-0290-y
5. González-Peña, M. M.; Hale, M. D. C., 2009: Colour in thermally modified wood of beech, Norway spruce and Scots pine. Part 2: property prediction from colour changes. Holzforschung, 63 (4): 394-401. https://doi.org/10.1515/hf.2009.077
6. Hon, D. N.-S.; Glasser, W., 1979: On possible chromophoric structures in wood and pulps. A survey of the present state of knowledge. Polymer-Plastics Technology and Engineering, 12 (2): 159-179. https://doi.org/10.1080/03602557908067670
7. Hon, D. N.-S.; Minemura, N., 1991: Color and Discoloration. U: D. N.-S. Hon; N. Shiraishi (ed.): Wood and Cellulose Chemistry. New York, Marcel Dekker Inc., pp. 395-454.
8. Huang, X.; Kocaefe, D.; Kocaefe, Y.; Boluk, Y.; Pichette, A., 2012: A spectrocolorimetric and chemical study on color modification of heat-treated wood during artificial weathering. Applied Surface Science, 258 (14): 5360-5369. https://doi.org/10.1016/j.apsusc.2012.02.005
9. Johansson, D.; Morén, T., 2006: The potential of colour measurement for strength prediction of thermally treated wood. Holz als Roh- und Werkstoff, 64 (2): 104-110. https://doi.org/10.1007/s00107-005-0082-8
10. Kollmann, F.; Fengel, D., 1965: Änderungen der chemischen Zusammensetzung von Holz durch thermische Behandlung. Holz als Roh- und Werkstoff 23: 461. https://doi.org/10.1007/BF02627217
11. Laine, K.; Belt, T.; Rautkari, L.; Ramsay, J.; Hill, C. A. S.; Hughes, M., 2013: Measuring the thickness swelling and set-recovery of densified and thermally modified Scots pine solid wood. Journal of Materials Science 48 (24): 8530-8538. https://doi.org/10.1007/s10853-013-7671-4
12. Laine, K.; Segerholm, K.; Wålinder, M.; Rautkari, L.; Hughes, M., 2016: Wood densification and thermal modification: Hardness, set-recovery and micromorphology. Wood Science and Technology, 50 (5): 883-894. https://doi.org/10.1007/s00226-016-0835-z
13. Laskowska, A., 2017: The influence of process parameters on the density profile and hardness of surface-densified birch wood (*Betula pendula* Roth). BioResources, 12 (3): 6011-6023. https://doi.org/10.15376/biores.12.3.6011-6023
14. Moya, R.; Fallas, R. S.; Bonilla, P. J.; Tenorio, C., 2012: Relationship Between Wood Color Parameters Measured by the CIELab System and Extractive and Phenol Content in Acacia mangium and Vochysia guatemalensis from Fast-Growth Plantations. Molecules, 17 (12): 3639-3652. https://doi.org/10.3390/molecules17043639
15. Nimz, H. H., 1973: Chemistry of potential chromophoric groups in beech lignin. Tappi Journal, 56 (5): 124-126.
16. Németh, K.; Vanó, V.; Faix, O., 1992: The effect of wood extractives on the photodegradation of wood. In: EWLP conf., Grenoble, France, 191-192.
17. Pandey, K. K., 2005: A note on the influence of extractives on the photo-discoloration and photo-degradation of wood. Polymer Degradation and Stability, 87 (2): 375-379. https://doi.org/10.1016/j.polymdegradstab.2004.09.007
18. Persze, L.; Tolvaj, L., 2012: Photodegradation of wood at elevated temperature: Colour change. Journal of Photochemistry and Photobiology B: Biology, 108: 44-47. https://doi.org/10.1016/j.jphotobiol.2011.12.008
19. Rautkari, L.; Laine, K.; Kutnar, A.; Medved, S.; Hughes, M., 2013: Hardness and density profile of surface densified and thermally modified Scots pine in relation to degree of densification. Journal of Materials Science, 48 (6): 2370-2375. https://doi.org/10.1007/s10853-012-7019-5
20. Sandermann, W.; Augustin, H., 1963: Chemische Untersuchungen über die thermische Zersetzung des Holzes. Erste Mitteilung: Stand der Forschung. Holz als Roh- und Werkstoff, 21: 256-265. https://doi.org/10.1007/BF02616316
21. Sharratt, V.; Hill, C. A. S.; Kint, D. P. R., 2009: A study of early colour change due to simulated accelerated sunlight exposure in Scots pine (*Pinus sylvestris*). Polymer Degradation and Stability, 94 (9): 1589-1594. https://doi.org/10.1016/j.polymdegradstab.2009.04.010
22. Tolvaj, L.; Mitsui, K., 2010: Correlation between hue angle and lightness of light irradiated wood. Polymer Degradation and Stability, 95 (4): 638-642. https://doi.org/10.1016/j.polymdegradstab.2009.12.004
23. Tu, D.; Su, X.; Zhang, T.; Fan, W.; Zhou, Q., 2014: Thermo-mechanical densification of Populus tomentosa var. tomentosa with low moisture content. BioResources, 9 (3): 3846-3856. https://doi.org/10.15376/biores.9.3.3846-3856
24. Ülker, O.; İmirzi, Ö.; Burdurlu, E., 2012: The effect of densification temperature on some physical and mechanical properties of Scots pine (*Pinus sylvestris* L.). BioResources, 7 (4): 5581-5592. https://doi.org/10.15376/biores.7.4.5581-5592
25. Wagenführ, R., 2007: Holzatlas. Fachbuchverlag Leipzig im Carl Hanser Verlag, München, Germany.
26. Waliszewska, B.; Prądzyński, W.; Zborowska, M.; Stachowiak-Wencek, A.; Waliszewska, H.; Spek-Dźwigała, A., 2015: The diversification of chemical composition of pine wood depending on the tree age. Annals of Warsaw University of Life Sciences – SGGW. Forestry and Wood Technology, 91: 182-187.
27. Yazaki, Y.; Collins, P. J., Mccombe, B., 1994: Variations in hot water extractives content and density of commer-

cial wood veneers from blackbutt (*Eucalyptus pilularis*). Holzforschung, 48 (s1): 107-111. https://doi.org/10.1515/hfsg.1994.48.s1.107
28. *** ISO 7724-3, 1984: Paints and varnishes – Colorimetry – Part 3: Calculation of colour differences. International Organization for Standardization, Geneva, Switzerland.
29. *** ISO 13061-1, 2014: Physical and mechanical properties of wood – Test methods for small clear wood specimens – Part 1: Determination of moisture content for physical and mechanical tests. International Organization for Standardization, Geneva, Switzerland.
30. *** ISO 13061-2 2014: Physical and mechanical properties of wood – Test methods for small clear wood specimens – Part 2: Determination of density for physical and mechanical tests. International Organization for Standardization, Geneva, Switzerland.

Corresponding address:

Assist. prof. AGNIESZKA LASKOWSKA Ph.D.

Department of Wood Sciences and Wood Preservation
Faculty of Wood Technology
Warsaw University of Life Sciences – SGGW
Nowoursynowska 159 St.
02 – 776 Warsaw, POLAND
e-mail: agnieszka_laskowska@sggw.pl

Marko Dušak[1], Denis Jelačić[2]

Production Management Model in Small and Medium Enterprises in Croatia

Model upravljanja proizvodnjom u malim i srednjim poduzećima u Hrvatskoj

Original scientific paper • Izvorni znanstveni rad
Received – prispjelo: 6. 6. 2017.
Accepted – prihvaćeno: 23. 5. 2018.
*UDK: 630*79*
doi:10.5552/drind.2018.1805

ABSTRACT • *Small and medium enterprises play a key role in the economy of the European Union as the main generators of employment and economic development. According to the official statistics of the EU, about 99.8 % of enterprises are small and medium. In order to be successful, the company needs to harmonize various parameters through strategic planning, preparation, organization and decision making. For the purpose of the research, two questionnaires were used, one for the purposes of descriptive statistics and χ^2 test, and the other for the purpose of AHP data analysis. The χ^{2-} test shows the opinion of surveyed experts and company managers, while the AHP method demonstrates the parameters considered most and least important for the company business. In contrast to the environmentally friendly production, which has shown to have the least significant impact on the management system, the market, promotion and marketing have the most significant impact. According to the results, production and business management model and block diagram were established.*

Key words: *small and medium enterprises, production and business management, block diagram, management model, parameters of effectiveness*

SAŽETAK • *Mala i srednja poduzeća kao osnovni generatori zapošljavanja i gospodarskog razvoja imaju ključnu ulogu u gospodarstvu EU-a. Prema službenoj statistici Unije, oko 99, 8 % poduzeća čine upravo mala i srednja poduzeća. Za uspješno poslovanje poduzeća potrebno je uskladiti brojne parametre koji se ostvaruju strateškim planiranjem, pripremom, organizacijom i donošenjem odluka. U radu su primijenjena dva anketna upitnika, jedan za potrebe deskriptivne statistike i χ^2-testa, a drugi za potrebe AHP analize podataka. Testom χ^2 prikazana su razmišljanja anketiranih eksperata i menadžera poduzeća, dok je AHP metodom ustanovljeno koji su parametri najvažniji za poslovanje poduzeća, a koji su manje važni. Najveći utjecaj na sustav upravljanja imaju tržište, promocija i marketing, a najmanji utjecaj ima ekološki čista proizvodnja. Na osnovi dobivenih rezultata uspostavljen je model upravljanja proizvodnjom i poslovanjem te izrađen blok-dijagram.*

Ključne riječi: *mala i srednja poduzeća, upravljanje proizvodnjom i poslovanjem, blok-dijagram, model upravljanja, parametri učinkovitosti*

[1] The author is a doctor of science in wood tecnology. [2]The author is a professor at the Faculty of Forestry,University of Zagreb, Croatia.
[1] Autor je doktor biotehničkih znanosti u polju drvne tehnologije. [2]Autor je profesor Šumarskog fakulteta Sveučilišta u Zagrebu, Hrvatska.

1 INTRODUCTION
1. UVOD

Today, micro, small and medium enterprises account for the majority of jobs. In addition, they provide a significant source of entrepreneurial spirit and innovation. Furthermore, there are approximately 23 million small and medium enterprises in the European Union. 75 million work posts account for 99.8 % of all enterprises (Jelačić *et al*., 2015).

According to the *Small Business Development Promotion Act*, entrepreneurs are classified by size into three categories, i.e. micro, small and medium enterprises. Micro enterprises are those that employ less than 10 workers and generate less than EUR 2.000,000 in operating revenues per year. On average, small entrepreneurs employ less than 50 workers p.a. and generate less than EUR 10.000,000 in operating revenues per year. In contrast, medium enterprises are those that employ more than 50 and less than 250 workers and generate a total annual turnover of more than EUR 10.000,000 (Ukić and Kuran, 2015).

Managing such companies is a continuous process that drives and directs business activity in order to achieve its goal. This type of business deals with issues such as financing, which is reflected in the inability to access the capital necessary for its establishment and development (OECD, 2016). The development of both the economy and enterprise is valued through management systems that, along with a certain number of people, business plans and financial flows, must be aligned with other factors in the production process in order to survive. Difficulty in managing small and medium enterprises stems from the inability to conduct a comprehensive market research. A small business owner must personally perform all essential managerial functions, and must deal with administrative issues (obtain work permits, deal with taxes and insurance, abide by the Act on Employment, Dismissal, Revision, etc.) (Bennett, 1994).

The management structure in the wood-processing sector (micro, small and medium enterprises) is reduced to a low level of knowledge and awareness of the benefits of the production management systems. The lack of standardized management systems that incorporate risk analysis tools, reduction of business risks and an array of other internationally-recognized management systems can have a significant negative impact on the business and life cycle of organizations, regardless of their size, structure or form of ownership (Britvić, 2011).

The support provided to businesses and SMEs development makes the structure of envisaged and coordinated activities and measures undertaken by different entities at different levels of decision making (Ren *et al*., 2015). Such a system requires efficient institutions or experts who are well familiar with entrepreneurship, business and development specific for this type of enterprise. Today, successful business operations and the development of small and medium enterprises require a quality solution to the problems related to their own technological and product development (Okolić, 2007).

The production itself needs to be well prepared and precisely planned, so that all jobs can be performed in a timely fashion, including the optimal consumption of all productive resources: materials, labor, money, information, instrumentation and energy (Grladinović *et al*., 2007).

Compared to large companies, small and medium enterprises have limited resources and little impact on the market (Kivijärvi and Tuominen, 1996). Their survival depends on the ability to get the most out of available resources and quickly find the market niche and adapt to it in an appropriate manner. Therefore, a rapid response to changes is considered the key to survival of SMEs (Zhang *et al*., 2009).

Innovation can be seen as a solution to the company's survival. For example, market share of more innovative companies tends to increase in volume, in contrast to the underperforming companies whose failure forces them to search for innovation opportunities. Consequently, the companies that base their progress on innovativeness stand a better chance of having higher export values (Pirc-Barčić and Motik, 2013).

The aim of this research was to present the current situation in small and medium enterprises and to propose a more efficient management system. The basic data was obtained by e-mail and phone calls. The collected data was analyzed by descriptive statistics, χ^2-test and AHP method. The establishment and proposal of the new model is based on the results obtained and previously published separately.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

For the purpose of this research, a survey questionnaire was distributed to 130 micro, small and medium wood processing and furniture manufacturing companies in 4 countries from the South East European region (Croatia, Macedonia, Serbia and Slovenia). Out of the total number of questionnaires, 117 were distributed to micro and small enterprises, and 13 questionnaires to medium enterprises. The questionnaire was sent to most companies via email, while some companies sent their responses by phone, through direct interview or by mail (Dillman, 2000). Out of 130 companies in total, only 30, and all of them from Croatia, responded to the distributed questionnaires and their responses were analyzed at a later stage. The research method consisted of collecting the data on the parameters of effectiveness of the production management system in small and medium businesses. Two questionnaires were produced. The first was used to describe descriptive statistics and perform the χ^2-test, while the other was used to implement the Analytical Hierarchy Process (AHP). The first questionnaire was divided into two parts. The first part contained general data about the company. The first group of questions (1-11) was posed directly to the owners or managers of the company. The second group consisted of 29 questions about the production management system parameters (12-40) measured by Liker four-level scale, and these were answered by the owners (managers) of the company as well as by external experts from the same 4 countries in South East European region (Croatia, Macedonia, Serbia and Slovenia), who were not employed in the companies, but whose responses were needed for the χ^2 test and the AHP method in order to compare the answers received by the company. These questions were posed in order to get the opinions of the company owners and external experts. The goal of such a survey response collection process was to determine the differences in responses between business managers and eternal experts. Additionally, a separate questionnaire that had been produced for the AHP method was filled out by experts to obtain the seven parameters and a certain set of relations between the parameters as a basis to compute the AHP. These seven parameters were obtained by assessing the importance of questions (alternatives) in the second part of the questionnaire (12-40). Excel and Word were used for the first survey questionnaire, and a free AHP online software (http://bpmsg.com/) for the second questionnaire.

The χ^2-test determines whether there is a relationship between the two variables and thus shows the probability of the relationship between them. The χ^2-test was run on the group of questions 12-40. The aim of the above test was to show which questions were *statistically very significant*, *significant*, or *not statistically significant* at all (Grubišić, 2004).

Analytical Hierarchy process or shorter AHP is one of multi-criteria decision making tools that have been used in decision making to help decision makers choose the best decision among several alternatives (Motik *at al.*, 2010). In this paper, the AHP method was used to rank the performance parameters that affect the production management system in small and medium businesses. If Consistency Ratio (CR) ≤ 0.10 for a matrix A, then the estimates of relative importance of criteria are considered acceptable. In the opposite case, it has to be investigated why inconsistency of estimates is unacceptably high. Therefore, the assessed relative importance of the estimates of the matrix A in our example is not sufficiently consistent. It is necessary to improve the consistency of the assessment so that the CR ≤ 0.10 requirement is met (Lisjak, 2011).

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

The first group of questions (1-11) provides general company-related information provided directly by managers or business owners. Figures (1-6) demonstrate the basic results pertaining to the surveyed companies such as the type of company, their legal form, markets, manufacturing processes, equipment in terms of machinery and the production program.

The second part of the questionnaire consisted of questions related to production management system parameters (12-40). These 29 questions were divided into 7 major groups, which consequently were the parameters for AHP analysis of the production and business management system. The results of the χ^2 –test

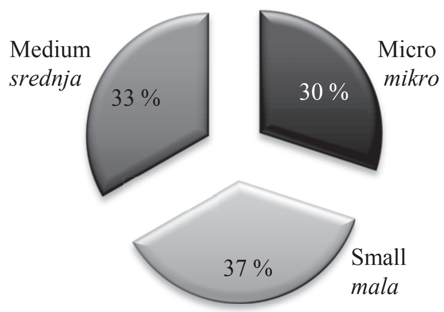


Figure 1 Type of business
Slika 1. Vrsta poduzeća

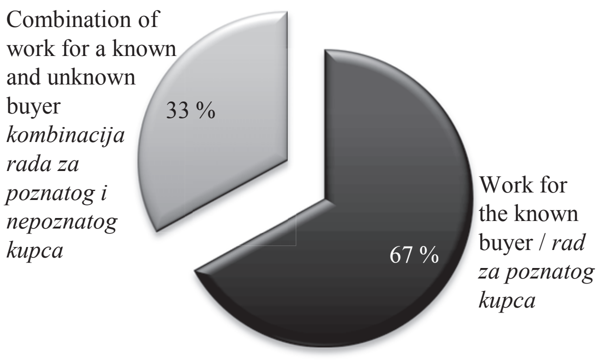


Figure 3 Production management organization
Slika 3. Organizacija upravljanja proizvodnjom

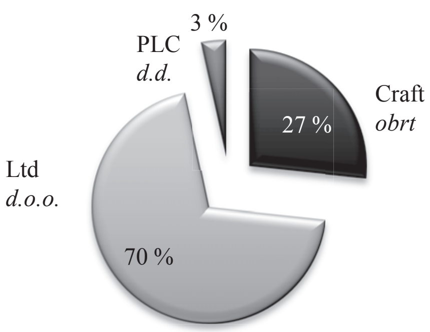


Figure 2 Legal forms of companies
Slika 2. Pravni oblici poduzeća

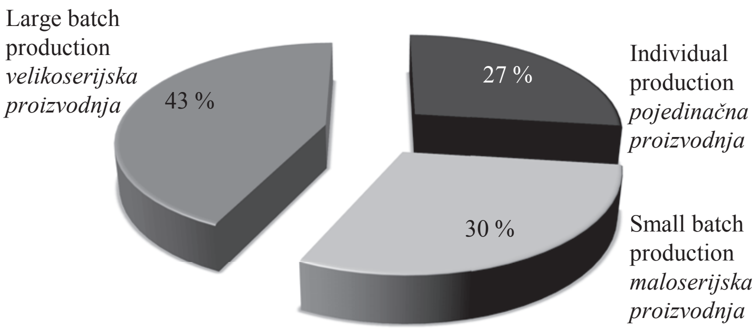


Figure 4 Production processes
Slika 4. Proizvodni procesi

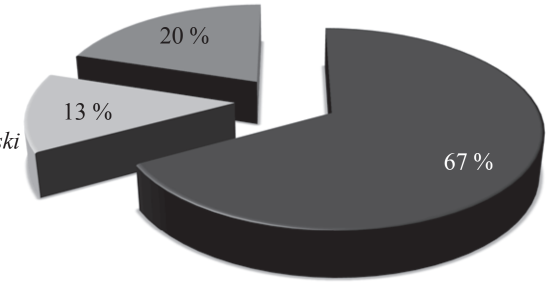


Figure 5 Equipment in terms of machinery
Slika 5. Opremljenost poduzeća strojevima

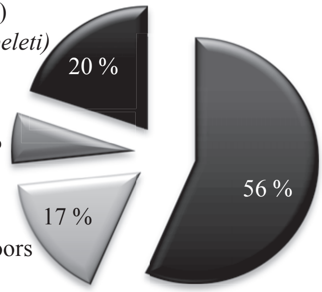


Figure 6 Production program of the company
Slika 6. Proizvodni program poduzeća

were previously published separately (Dušak *et al.,* 2017), but as they were the basis for this research they will be explained here.

The questions from the questionnaire, 29 of them, with 135 statements all together, were divided into 7 groups: VPOSP - Leadership, Policy, and Organizational Structure of the Company; PKUPRP - Process Culture, Management Processes, and Production Deadlines; PPKP - Range of Products and Quality of Products; TPM - Marketing and Market Activities of the Company; LJP - Human Resources; ITSPT - Information Technology and Modern Production Technology; EČP - Environmentally friendly production. Those groups were used for AHP analysis afterwards.

Answers from managers and external experts on each question and each statement were placed into relationship according to χ^2–test requirements to establish the differences in opinions between managers who deal with these problems within the companies and external experts who deal with these issues as external consultants for the companies.

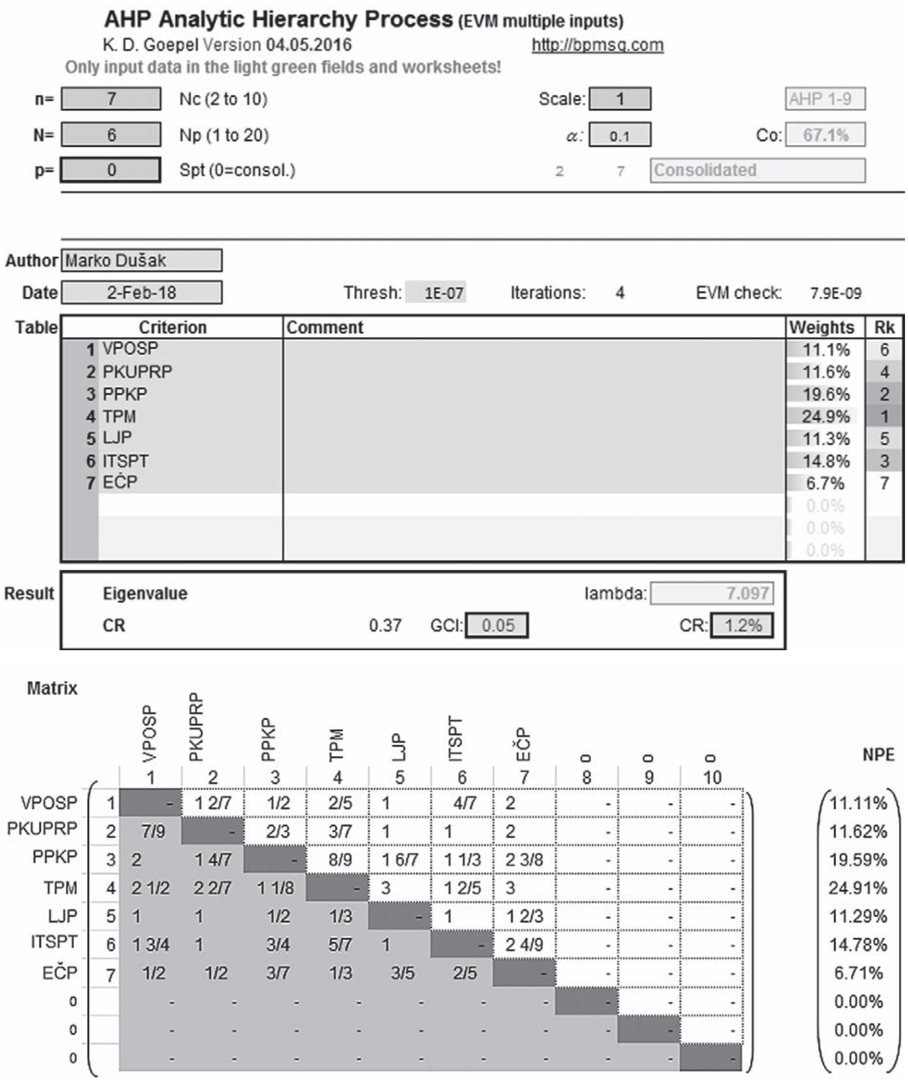
The χ^2-test was conducted as the Pearson's Chi Square with obtained P values: $p <= 0.001$ – the differences are *statistically very highly significant* (99.9 %), $0.001 < p <= 0.01$ – the differences are *highly significant* (99.0 %), $0.01 < p <= 0.05$ – the differences are *significant* (95.0 %), $p > 0.05$ – the difference is *not statistically significant* (90.0 %).

According to the results obtained in the research, all of the P values showed that there was a *highly* or *very highly significant* difference between answers given by managers and by external experts to each individual statement in each individual question in the questionnaire. A *very highly significant* difference was found in several statements of the questions, such as organized work posts, work conditions, personal sales, higher product quality, quality management system and lean production system.

To be able to help managers to make a quality decision about problems that occur in their production and business management systems, it was necessary to establish which process of the production and business management system should be taken care of the most, and which management parameter to pay the most attention to. Therefore, the AHP analysis was performed.

As mentioned earlier, for the purposes of AHP method, the second questionnaire was developed. It consisted of 7 groups of parameters, mentioned above, placed in pairs of direct relationship to each other. The same external experts, as in χ^2–test analysis, were asked to answer the AHP questionnaire. The AHP analysis was conducted on each of the answered questionnaire, the Consistency Ratio (CR) was checked, and those questionnaires where CR was higher than 10 % were considered non-consistent and they were excluded from the research. Therefore, 6 out of 10 questionnaires were taken into consideration and put into overall AHP analysis presented in Figure 7 (Dušak *et al.,* 2017).

Figure 7 shows that the parameters, ranked according to the AHP method starting from the most important parameters or factors to those that are considered least important, indicate that the market, promotion and marketing have the most significant impact on the production management system in small and medium businesses (24.9 %), followed by the production program and product quality (19.6 %), information tech-



		VPOSP 1	PKUPRP 2	PPKP 3	TPM 4	LJP 5	ITSPT 6	EČP 7	0 8	0 9	0 10	NPE
VPOSP	1	-	1 2/7	1/2	2/5	1	4/7	2	-	-	-	11.11%
PKUPRP	2	7/9	-	2/3	3/7	1	1	2	-	-	-	11.62%
PPKP	3	2	1 4/7	-	8/9	1 6/7	1 1/3	2 3/8	-	-	-	19.59%
TPM	4	2 1/2	2 2/7	1 1/8	-	3	1 2/5	3	-	-	-	24.91%
LJP	5	1	1	1/2	1/3	-	1	1 2/3	-	-	-	11.29%
ITSPT	6	1 3/4	1	3/4	5/7	1	-	2 4/9	-	-	-	14.78%
EČP	7	1/2	1/2	3/7	1/3	3/5	2/5	-	-	-	-	6.71%
0		-	-	-	-	-	-	-	-	-	-	0.00%
0		-	-	-	-	-	-	-	-	-	-	0.00%
0		-	-	-	-	-	-	-	-	-	-	0.00%

Figure 7 Results of AHP analysis - consolidated data
Slika 7. Rezultati AHP analize – konsolidirani podaci
VPOSP - Leadership, Policy, and Organizational Structure of the Company / *vodstvo, politika i organizacijska struktura poduzeća;* PKUPRP – Process Culture, Management Processes, and Production Deadlines / *procesna kultura, upravljački procesi i rokovi proizvodnje;* PPKP – Range of Products and Quality of Products / *proizvodni program i kvaliteta proizvoda;* TPM – Marketing and Market Activities of the Company / *tržište, promocija i marketing;* LJP – Human Resources / *ljudski potencijali; ITSPT* – Information Technology and Modern Production Technology / *informacijska tehnologija, suvremena proizvodna tehnologija;* EČP – Environmentally friendly production / *ekološki prihvatljiva proizvodnja; Nc* – Number of criteria (2 – 10) / *broj kriterija (2 – 10); Np* – Number of participants (1 – 20) / *broj ispitanika (1 – 20);* Selected participant (0 = consolidated) / *izabrani ispitanik (0 = ukupan); Co* – Consensus / *ugovorena vrijednost (67,1 %); CR* – Consistency ratio / *omjer konzistencije; GCI* – Geometric consistency index / *indeks geometrijske konzistencije; NPE* – Normalized principal Eigenvector / *normalizirani glavni svojstveni vektor*

nology and modern production technology (14.8 %), the process culture, management processes and production deadlines (11.6 %), human resources (11.3 %), leadership, policy and organizational structure of the company (11.1 %), and environmentally friendly production as the least important (6.7 %).

The block diagram shows the order of decision making activities when entering the market (Figure 8). The model uses the stated goal (the new product) with the seven parameters of effectiveness to demonstrate the profitability of innovation in the new product development. If all the answers were *positive*, then the innovation, production program, production technology, management system, human resources, organizational structure and production ecology would give the innovative product the boost to enter the market. Quite the opposite, if all the answers were *negative*, the product would remain as it is. Some innovations do not require a positive answer to all statements. Innovation in a product that does not require the change in production technology or in human resources, is still an innovation on a smaller scale, not a radical one, and it can still bring some good results and benefits to the market. The same statement stands for each innovation on a smaller scale that can result in a better position on the market and bring benefits to the company.

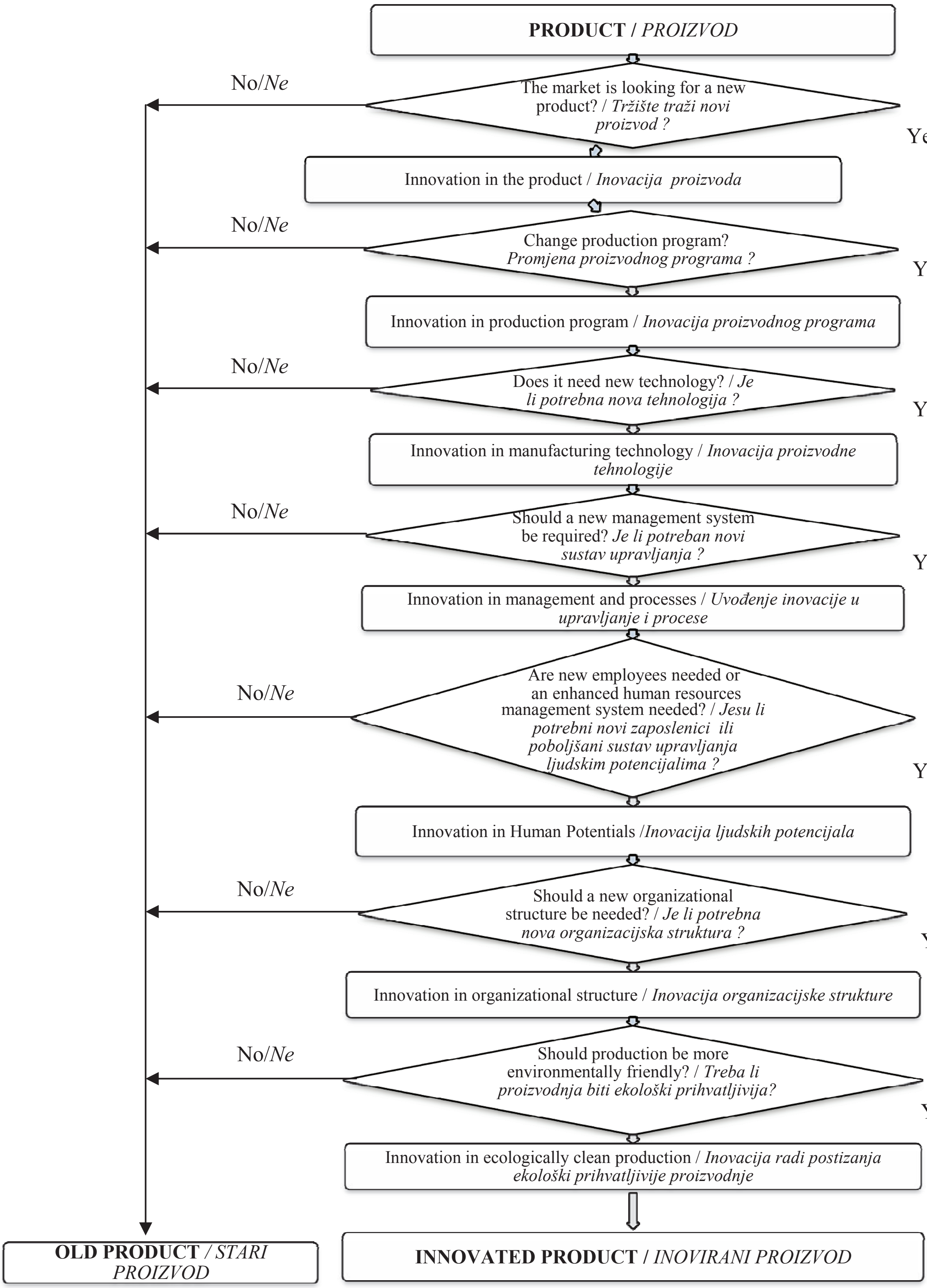


Figure 8 Block diagram of the order of activities in decision making in small and medium businesses
Slika 8. Blok-dijagram redoslijeda aktivnosti pri donošenju odluka u malim i srednjim poduzećima

According to the developed block diagram, it was necessary to establish the organization model for small and medium enterprises (Figure 9) that could help make the decision process in a company easier and faster and meet the requirements of the turbulent and ever-changing market for wood products and furniture.

The newly established model was developed based on AHP analysis and block diagram and it meets the requirements of the market classified in 7 groups of production and business management parameters. Each group consists of parameters the company should think of when entering the market and it was a part of the first questionnaire, which was the basis for this research (Dušak *et al.*, 2017). Usually, the organization models place different functions or group of parameters of the same of similar importance on the same

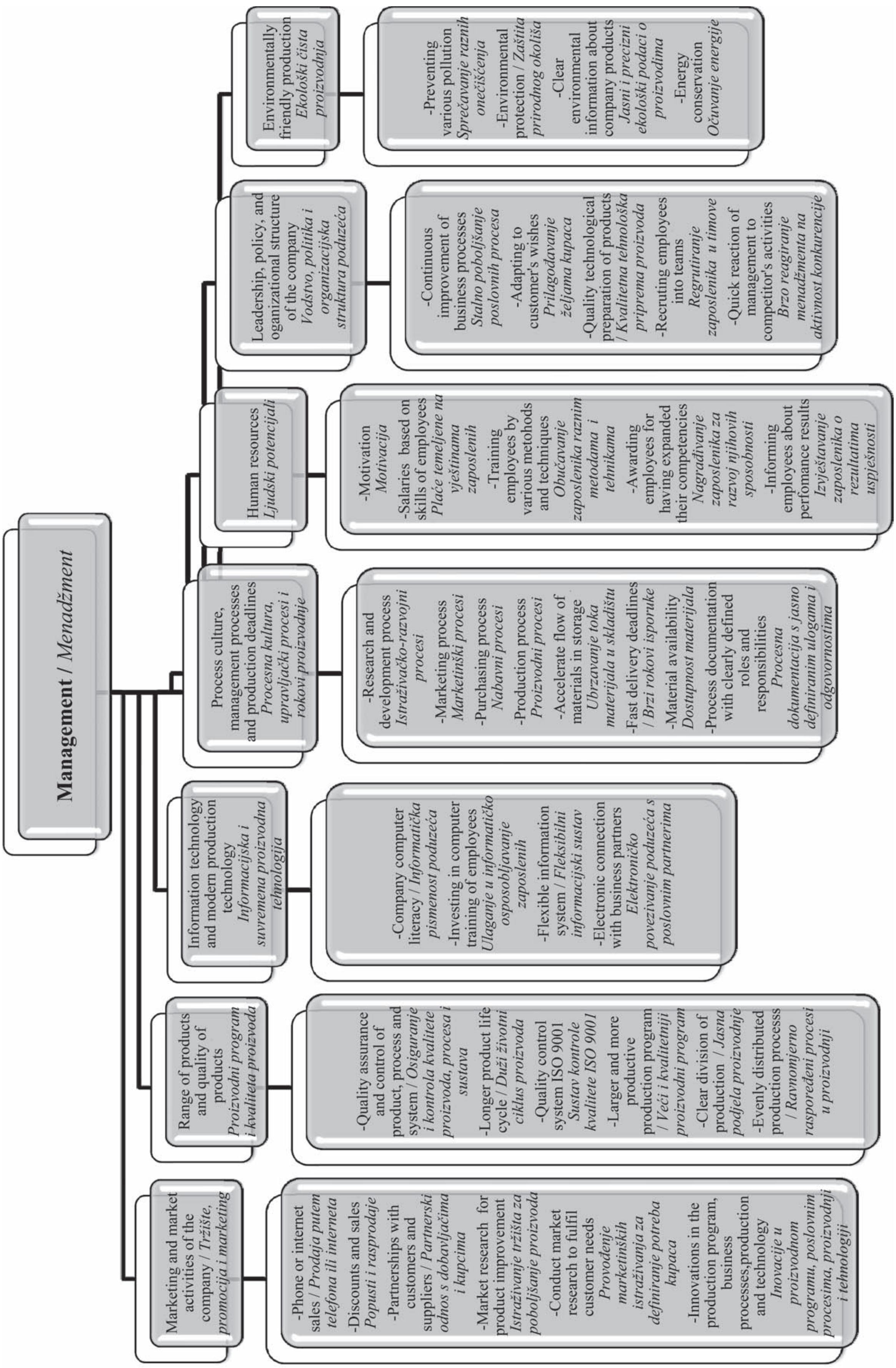


Figure 9 Organization model in small and medium businesses
Slika 9. Organizacijski model u malim i srednjim poduzećima

level. The groups of parameters in this model are almost at the same level and they are almost equally important in decision making process, but some of the parameters or groups of parameters, according to AHP analysis, have slightly higher priority. Therefore, they are not at exactly the same level, but slightly moved up or down according to priority they achieved in the analysis.

The model is flexible and if the company management decides to go into the innovations in information technology or in human resources, it could bring a specific group of parameters up front in the model and make the decision making process easier, faster and more effective.

Also, small and medium companies usually do not have enough staff to deal with all these issues at the same time and discuss them during weekly meetings or otherwise. That is especially relevant to small and micro companies, where one or two persons have to make decisions on all issues. Therefore, they need some kind of model that will give priorities to some issues and make the whole decision making process easier and faster.

4 CONCLUSION
4. ZAKLJUČAK

The presented data indicate that the small and medium enterprises provide an above-average contribution to the business economy in Croatia.

The aim of this research was to present the current situation of small and medium companies in the wood industry in Croatia, and show possible solutions to various problems in the production management systems.

The AHP method demonstrated the order of effectiveness parameters of the production management system, and revealed, based on expert opinion, which factor in the production process should be dealt with more attention and which with less. The model itself showed the cost-effectiveness of innovation related to certain factors with the purpose of obtaining a new product. The company cannot be characterized as creative and innovative by itself. This requires internal organization and external environment as the foundation for innovative action, and the above-mentioned responses within the model show exactly that.

Further to the above, this research is important because it represents the structure of an improved production management in small and medium businesses. The results of the surveyed companies and experts indicate the current situation in the surveyed companies in Croatia. Apart from the lack of staff, information and modern production technology, the companies have also not been receiving enough incentives from the state, government or various agencies. Therefore, based on the presented models, the decision making process in small and medium enterprises can be easier, faster and more efficient. These models are the tools for small and medium enterprises to be more innovative and to respond more promptly to market requirements.

5 REFERENCES
5. LITERATURA

1. Bennett, R., 1994: Management. Potecon, pp. 54-70.
2. Britvić J., 2011: Moderni sustavi upravljanja u organizacijama. Praktični menadžment, Stručni časopis za teoriju i praksu menadžmenta, 2 (1): 72-80.
3. Dillman, D. A., 2000: Mail and Internet Surveys – the Tailored Design Method. John Wiley & Sons, Inc., New York, NY.
4. Dušak, M.; Jelačić, D.; Pirc-Barčić, A.; Novakova, R., 2017: Improvements to the Production Management System of Wood-processing in Small and Medium Enterprises in Southeast Europe. Bioresources, 12 (2): 3303-3315. https://doi.org/10.15376/biores.12.2.3303-3315
5. Grladinović, T.; Kropivšek, J.; Oblak, L., 2007: Modern production and business management in wood processing and furniture manufacture. Drvna industrija, 58 (2): 77-87.
6. Grubišić, A., 2004: Hi-kvadrat i njegove primjene. Seminarski rad. Sveučilište u Zagrebu, Fakultet elektrotehnike i računarstva, Zagreb.
7. Jelačić, D.; Šatanova, A.; Sedliačikova, M.; Zavadsky, J.; Zavadska, Z., 2015: Process Model of Quality Cost Monitoring for Small and Medium Wood-Processing Enterprises. Drvna industrija, 66 (4): 329-338. https://doi.org/10.5552/drind.2015.1437
8. Kivijärvi, H.; Tuominen, M., 1996: A decision aid in strategic planning and analysis of a wood-processing company. Computers and Industrial Engineering, 31(1-2): 467-470. https://doi.org/10.1016/0360-8352(96)00176-3
9. Lisjak, D., 2011: Primjena AHP metode kao alata za optimalni izbor opreme. Predavanje. Hrvatsko društvo održavatelja (HDO), Zagreb.
10. Motik, D.; *Šegotić*, K.; Jazbec, A., 2010: Application of AHP model and survey results in deciding on a product line in furniture industry. Drvna industrija, 61(2): 83-87.
11. OECD, 2016: Financing SMEs and Entrepreneurs 2016: An OECD Scoreboard. OECD Publishing, Paris. https://doi.org/10.1787/fin_sme_ent-2016-en
12. Okolić, M., 2007: Sistem za podršku razvoja malih i srednjih poduzeća. Diplomski rad, Fakultet poslovne ekonomije, Banja Luka.
13. Pirc-Barčić, A.; Motik, D., 2013: Innovation and Innovativeness in Medium-Low Tech/Low-Tech Industries – Wood Industry. Drvna industrija, 64 (3): 247-255. https://doi.org/10.5552/drind.2013.1301
14. Ren, S.; Eisingerich, A. B.; Tsai, H. T., 2015: How do marketing, research, and development capabilities, and degree of internationalization synergistically affect the innovation performance of small and medium-sized enterprises (SMEs)? A panel data study of Chinese SMEs. International Business Review, 24 (4): 642-651. https://doi.org/10.1016/j.ibusrev.2014.11.006
15. Ukić, Lj.; Martić Kuran, L., 2015: Uloga i značaj malih i srednjih poduzetnika na ruralnim područjima Dalmatinske zagore. Zbornik radova Veleučilišta u Šibeniku, 1-2.
16. Zhang, J.; Li, H.; Ziegelmayer, J. L., 2009: Resource or capability? A dissection of SMEs it infrastructure flexibility and its relationship with it responsiveness. The Journal of Computer Information Systems, 50 (1): 46-53.

Corresponding address:

MARKO DUŠAK, Ph. D.

Promid, Ltd., Nikole Tesle 32
Križevci, 48260, CROATIA
e-mail: marko-dusak1@hotmail.com

Alper Aytekin[1]

Using Hybrid Method in Selecting Timber Factory Location

Primjena hibridnog postupka pri odabiru lokacije za drvoprerađivački pogon

Preliminary paper • Prethodno priopćenje
Received – prispjelo: 9. 6. 2017.
Accepted – prihvaćeno: 13. 6. 2018.
*UDK: 630*832.11*
doi:10.5552/drind.2018.1736

ABSTRACT • *The selection of location is vital for a timber factory to keep on functioning. It is a significant decision during the setup of a business and the preparation of projects. Therefore, dual scaling method often used for selecting the timber factory location and Analytic Hierarchy Process (AHP) have been used in this study. While the AHP method and the double weighing method were previously used separately, the aim of this study was to use these two studies together in order to obtain more reliable results. For this purpose, in the Western Black Sea region of Turkey, five different candidate cities were selected for the establishment of a factory site for timber production: Bartin, Bolu, Kastamonu, Karabük and Zonguldak. At the same time, a total of ten factors including raw materials, labor, market, construction costs, energy and fuel, water, transportation, tax, security and social environment were determined. As a result of the study, the hybrid method, which is based on the average of both methods, yielded more reliable results.*

Keywords: *timber factory location, Dual Scaling, Analytic Hierarchy Process*

SAŽETAK • *Odabir lokacije za drvoprerađivački pogon vrlo je važan činitelj održivosti njegova poslovanja i jedna od najvažnijih odluka pri pokretanju poslovanja i pripremi projekta. U radu je predstavljena hibridna metoda odlučivanja koja je kombinacija metode dvostrukog skaliranja, često korištene za odabir lokacije pogona za preradu drva, i metode analitičkoga hijerarhijskog procesa (AHP metoda). Dosada su AHP metoda i metoda dvostrukog skaliranja primjenjivane zasebno, a cilj je ovog rada povećati pouzdanost rezultata odlučivanja primjenom obje metode zajedno. S tim je ciljem u regiji Zapadno Crno more u Turskoj identificirano pet lokacija za pokretanje drvoprerađivačke proizvodnje: gradovi Bartin, Bolu, Kastamonu, Karabük i Zonguldak. Istodobno je postavljeno deset kriterija koji su obuhvatili sirovinu, radnu snagu, tržište, troškove izgradnje, energiju i gorivo, vodu, transport, porez, sigurnost i društveno okružje. Rezultat studije pokazao je da hibridna metoda, koja se temelji na srednjoj vrijednosti obiju metoda, daje pouzdanije rezultate nego svaka od tih metoda zasebno.*

Ključne riječi: *lokacija drvoprerađivačkog pogona, metoda dvostrukog skaliranja, metoda analitičkoga hijerarhijskog procesa*

1 INTRODUCTION
1. UVOD

Business location is generally the geographical place where the organization provides the main services. The location for a manufacturing business can be defined as the most suitable place for carrying out the main functions such as provision, production, storage and distribution, and the related economic purposes. Location is a compulsory life space for an organization to go on running and develop. The most suitable

[1] Author is associated professor at Bartın University, Department of Management Information Systems, Bartin, Turkey.
[1] Autor je izvanredni profesor Odjela za upravljanje informacijskim sustavima, Sveučilište u Bartinu, Bartin, Turska.

location for an economic business is the place where it can provide productive services at minimum cost and maximum profit after being established. The most suitable locations for the businesses, whose main aim is to prosper and bring benefit, are the places where they can fulfill these aims (Barutçugil, 1988).

The selected location is, in strict sense, "the place where business production activities are carried out". In broad sense, it is defined as "the most suitable place where the fundamental functions of a business, such as provision, production, storage and distribution and business income, will be at the maximum level and business cost at the minimum level, meaning that the business will be able to meet the necessary conditions for reaching its goals"; "the place meeting most appropriately the necessary technical and economic conditions for production compared to other locations"; "the place where the sum of expenses is at the lowest level"; "the place where there is no saving from the expenses and transportation costs from the selected location to a newly established location by means of replacement analysis" (İlter, 2001).

The selection of business location is a constant problem. New businesses are being established all the time. A specific industry can be completely replaced in 30-40 years as a result of the fact that one of the factors affecting the selection of location loses its importance while another gains importance. A factory location satisfying the ideal conditions may lose this characteristic due to several reasons such as the changing environmental factors over time, and the changes in the place and scale of demand sources. Consequently, the convenience of the place, the change of location and other alternatives are the challenges that are frequently considered in every factory (Kobu, 1989).

The location selection is an important decision when establishing a business and developing projects. Thorough analysis is required before making a decision. Likewise, this decision is a factor that shapes the cost, profitability and running of a business organization in the future. Changing the location later is very hard and expensive. Therefore, the most affordable and profitable place should be selected among the alternatives while determining the location.

The location of an organization and its selection is one of the most important strategic issues in terms of investment decisions. The selection of location is not only important commercially but it also includes the aspects such as income distribution, local development differences, benefits from environmental factors and incentive schemes, exogeneity based on the gathering of business organizations in the same region that could be connected to each other.

There are several factors that influence the decision about the business location and that should be evaluated during this process. The factors to be taken into consideration for the selection of business location are the following:
- economic and quantitative factors,
- quality factors,
- non-economic factors.

Economic and quantitative factors could be listed as raw material and transportation, demand centers and product distribution, labor market, wage level and all other relevant costs. Quality factors include geodetic parameters such as educational opportunities, environmental awareness of the organization, labor force quality and substructure state. Non-economic factors are the parameters related to military, political and the firm's own strategy (Anonymous, 1985).

There are several basic principles for selecting the business location. These principles are as follows (Üçüncü, 2003):
- Requirements about factory location should be determined objectively and scientifically;
- Characteristics of the selected location that influence the factory services should be identified;
- Selected location studies should be conducted at specific stages and in proper order without mixing them;
- Experts and organizations should be determined, whose experience and knowledge could be beneficial in every phase;
- The decision on selecting the location should be made after a comprehensive consideration and proper evaluation of the state of location factors;
- Comprehensive, suitable, complete and certain information should be obtained from various sources.

2 MATERIALS AND METHOD
2. MATERIJALI I METODE

Five different candidate cities, namely Bartın, Bolu, Kastamonu, Karabük and Zonguldak, have been determined in the Black Sea Region for selecting the location of a timber factory, which will produce annually 13.000 m^3 of lumber (Figure 1).

Besides, ten factors in total have been determined such as Raw Material, Labor Force, Market, Construction Cost, Energy and Fuel, Water, Transportation, Tax, Security, Social Environment, all of which would affect the investment.

2.1. Dual Scaling Method
2.1. Metoda dvostrukog skaliranja

Importance scores are given to the factors affecting the selection of the location between 0 and 10 (it could be between 0 and 100 or 0 and 1) according to production efficiency and importance level. Similarly, the scores that candidate locations will be able to get from each factor range from 0 to 10. The weighted scores that candidate locations will get from each factor are obtained by multiplying the importance scores and the scores of the candidate cities. The scores of candidate locations are added separately to each candidate location, and thus total scores are found. Total scores determine the evaluation order of the candidate locations. The candidate location having the highest total weight is selected as the right location (Üçüncü 2003).

2.2 Analytic Hierarchy Process (AHP)
2.2. Analitički hijerarhijski proces (AHP)

The Analytic Hierarchy Process (AHP) is a multi-criteria decision making method that helps the decision-

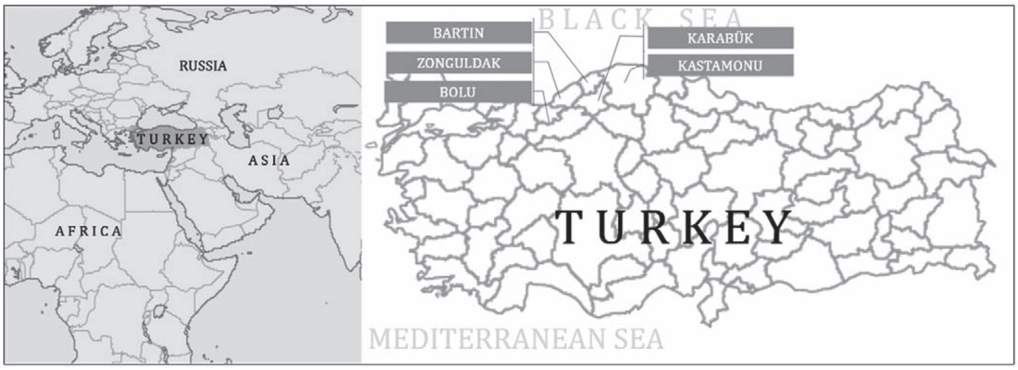


Figure 1 Candidate cities on the map
Slika 1. Prikaz potencijalnih lokacija (gradova) na karti

maker face a complex problem with multiple conflicting and subjective criteria (for example selecting a location or investment, project ranking, etc.). AHP is a mathematical method considering group and individual priorities, and evaluating the quantitative and qualitative variables together in the course of decision making. Several papers have addressed the AHP success stories in very different fields (Zahedi, 1986; Golden *et al*, 1989; Shim, 1989; Vargas, 1990; Saaty and Forman, 1992; Forman and Gass, 2001; Kumar and Vaidya, 2006; Ho, 2008; Liberatore and Nydick, 2008).

The use of personal judgment for decision making problems has increased on a remarkable scale recently. Efforts have been made to recognize specific decision making mechanisms considering the observations of the decision makers in different psychological and sociological situations through AHP. The aim of this method was to enable decision makers to make decisions more effectively (Saaty, 1980). This method has attracted considerable attention and has been applied for the solution of most decision making problems in real life.

The first step in AHP is to determine the factors and sub-factors in line with the purpose of the decision maker. Initially, the purpose is set in AHP, and the factors influencing the purpose in line with this purpose are tried to be determined. In this stage, a survey study and opinion of the experts in this area could be obtained and applied to specify all the factors influencing the purpose in line with this purpose.

Psychologists argue that it is easier and more accurate to express one's opinion on only two alternatives than simultaneously on all the alternatives. It also allows consistency and cross checking between different pairwise comparisons. AHP uses a ratio scale, which, contrary to methods using interval scales (Kainulainen *et al.*, 2009), requires no units in the comparison. The judgement is a relative value or a quotient a/b of two quantities a and b having the same units (intensity, meters, utility and so on). The decision-maker does not need to provide a numerical judgement; instead a relative verbal appreciation, more common in our daily lives, is sufficient.

Dual comparison decision matrixes are formed in order to determine the significance level between each other after specifying the purpose, factor and sub-factors. While forming these matrixes, 1-9 significance scale by Saaty (1990) is used. Provided that the decision made at the end of the study is influential for most people, dual comparison decision matrixes are formed by integrating the judgment of different people. A plenty of researchers recommend the use of geometric average method in this integration process so as to obtain consistent dual comparison matrixes (Tam and Tummala, 2001). 1-9 significance scale suggested by Saaty provides the best results. The other significance scales such as 1-5, 1-7, 1-15 and 1-20 fail to find the appropriate solution. The significance scale values and meanings are explained in Table 1 (Saaty, 1980). The formation of dual comparison decision matrixes is the most important stage of AHP. According to the data by dual comparison decision matrixes, the judgments are converted into a matrix in AHP. If a_{ij} is indicated as dual comparison score of *i.* and *j.*, a_{ij} value is obtained from $1/a_{ij}$ equivalence. This characteristic is called correspondence (Saaty, 1999). After creating dual comparison decision matrixes, the following step is to calculate the priorities or weight vectors. The method requires the normalization of the comparison matrix, adding the values in each column. The next step is to divide each cell by the total of the column. Based on this normalized matrix, the overall or final priorities are obtained by calculating the average value of each row. In the AHP, the pairwise comparisons in a judgment matrix are considered to be adequately consistent if the corresponding consistency ratio (CR) is less than 10 % (Saaty, 1980). In the AHP, the consistency ratio is defined as CR, where CR = CI/RI. To calculate the consistency index (CI), the corresponding column value in the decision matrix is multiplied by the values of the priority vectors that have emerged. After this phase, CI value $(\lambda enb-n)/n-1$ is found via the solution of the equations system. Consistency rate (CR) is obtained by dividing the obtained CI values by the Random Integrity Index. RI value takes different values according to the number "*n*". However, calculating the eigen values and eigen vectors of this equation system is very complicated and time-consuming especially for large-scale matrixes ($n>5$).

Table 1 Superiority values used in AHP Methodology
Tablica 1. Vrijednosti relativnih važnosti u AHP metodi

Value *Intenzitet važnosti*	**Definition** / *Definicija*	**Explanation** / *Objašnjenje*
1	Equal importance *jednako važno*	Two factors are equally important. *Dva kriterija ili alternative imaju jednaku važnost.*
3	Moderate importance *umjereno važnije*	Experience and judgment slightly favor one over the other. *Na temelju iskustva i procjene daje se umjerena prednost jednom kriteriju ili alternativi u odnosu prema drugome.*
5	Strong importance *znatno važnije*	Experience and judgment strongly favor one over the other. *Na temelju iskustva i procjene daje se velika prednost jednom kriteriju ili alternativi u odnosu prema drugome.*
7	Very strong importance *izrazito važnije, dokazano važnije*	One factor favors over another. *Jedan kriterij ili alternativa izrazito se favorizira u odnosu prema drugome.*
9	Extreme importance *ekstremno važnije*	The evidence showing one factor favoring over the other has a high reliability. *Dokazi na osnovi kojih se favorizira jedan kriterij ili alternativa u odnosu prema drugome potvrđeni su s najvećom uvjerljivošću.*
2,4,6,8	Intermediate values *međuvrijednosti*	The values between two successive judgments to be used when compromise is necessary. *Vrijednosti između dviju uzastopnih prosudbi koje* će *se primijeniti kada je potrebno napraviti kompromis*.

The methods, which are easier to calculate and will give approximate results instead of the above system of equations, are preferred in the implementation (Saaty, 2000). A common method used for calculating the priority vectors is this: Normalized matrix is found by dividing every column value into the related column sum separately, and every sequence value is averaged with reference to the normalized matrix, and these values are the importance weights found for each factor. The priority vector is formed via these weights.

Finally, the result matrix is found by multiplying weights vector and binary matrixes. Thus, the objective is accomplished by selecting the most suitable alternative for the criteria identified among the alternatives.

Data were obtained by conducting a questionnaire with 14 experts in the field. Those who deviated from these data have been eliminated. The average of the answers given by the remaining 11 experts was used in the study. The data of the work is also the actual data used in an investment project.

2.3 Conversion of data appropriate for AHP method
2.3. Pretvorba podataka prikladnih za AHP metodu

The data, which were obtained as a result of dual scaling and an algorithm developed in the study, are turned into data sets to be used by the AHP method. The formulas are the following:

$$t_{ij} = \frac{a_{ij}}{Mak(a_{ij})} \cdot 8 + 1 \quad (1)$$

$$z_{ij} = \frac{t_{ij}}{Min(t_{ij})} \quad (2)$$

Where:
a_{ij} – data set obtained via dual scaling
$Mak(a_{ij})$ – the highest number in the data set
t_{ij} – normalized data for AHP
$Min(t_{ij})$ – the lowest number in the data set
z_{ij} – data used for AHP.

3 RESULTS
3. REZULTATI

The factors, determined beforehand for Timber Factory, should be weighted before dual scaling method. The loads of the necessary factors have been identified so as to determine the factory location during the installation of the timber factory (Table 2). The data were obtained by averaging the data recommended by 11 experts.

The data in the study are primarily evaluated in regard to Dual Scaling method. The results obtained via Dual Scaling method are presented below (Table 3). The data were obtained by averaging the data recommended by 11 experts.

The data sets are made usable for AHP by using normalization formulas developed in the following step (Table 4).

Table 2 Values of factors to be used in dual scaling method
Tablica 2. Vrijednosti kriterija koji će se primijeniti u metodi dvostrukog skaliranja

No	**Factors** / *Kriteriji*	**Value** *Vrijednost*
1	Raw material / *sirovina*	10.0
2	Labor force / *radna snaga*	8.0
3	Market / *tržište*	9.5
4	Energy and fuel / *energija i gorivo*	5.1
5	Social environment / *društveno okružje*	3.3
6	Water / *voda*	2.0
7	Tax / *porez*	7.5
8	Construction cost / *troškovi izgradnje*	7.3
9	Transportation / *transport*	7.9
10	Security / *sigurnost*	2.5

Table 3 Coefficients and rough values of candidate cities by factors
Tablica 3. Koeficijenti i okvirne vrijednosti gradova kandidata s obzirom na zadane kriterije

No	Factors / *Kriteriji*	Value *Vrijed-nost*	BARTIN		BOLU		ZONGUL-DAK		KARABÜK		KASTA-MONU	
1	Raw material / *sirovina*	10.0	8.3	83.00	9.3	93.00	8.1	81.00	7.5	75.00	8.8	88.00
2	Labor force / *radna snaga*	8.0	5.0	40.00	8.7	69.6	8.5	68.00	6.8	54.40	7.4	59.2
3	Market / *tržište*	9.5	7.0	66.50	8.9	84.55	7.1	67.45	6.4	60.80	7.1	67.45
4	Energy and fuel / *energija i gorivo*	5.1	8.5	43.35	7.3	37.23	7.5	38.25	8.1	41.31	8.2	41.82
5	Social environment *društveno okružje*	3.3	5.0	16.50	8.8	29.04	6.5	21.45	6.0	19.80	6.3	20.79
6	Water / *voda*	2.0	7.2	14.40	9.1	18.20	7.3	14.60	7.6	15.20	9.0	18.00
7	Tax / *porez*	7.5	8.9	66.75	7.2	54.00	7.3	54.75	7.9	59.25	8.1	60.75
8	Construction cost *troškovi izgradnje*	7.3	5.1	37.23	8.6	62.78	4.5	32.85	8.1	59.13	8.0	58.40
9	Transportation / *transport*	7.9	5.5	43.45	9.6	75.84	5.5	43.45	5.2	41.08	5.4	42.66
10	Security / *sigurnost*	2.5	9.5	23.75	9.1	22.75	9.0	22.50	8.7	21.75	8.8	22.00

Table 4 Conversion of data sets to data to be used by AHP
Tablica 4. Skupovi podataka pretvoreni u podatke kojima će se koristiti AHP metoda

No	Factors / *Kriteriji*	BARTIN	BOLU	ZONGULDAK	KARABÜK	KASTAMONU
1	Raw material / *sirovina*	3.07287	3.36538	3.15385	3.03714	3.39316
2	Labor force / *radna snaga*	2.00405	3.17308	3.29060	2.78957	2.91453
3	Market / *tržište*	2.65182	3.23718	2.81197	2.64810	2.81197
4	Energy and fuel / *energija i gorivo*	3.13765	2.72436	2.94872	3.24934	3.18803
5	Social environment / *društveno okružje*	2.00405	3.20513	2.60684	2.50663	2.53846
6	Water / *voda*	2.71660	3.30128	2.88034	3.07250	3.46154
7	Tax / *porez*	3.26721	2.69231	2.88034	3.17860	3.15385
8	Construction cost / *troškovi izgradnje*	2.03644	3.14103	1.92308	3.24934	3.11966
9	Transportation / *transport*	2.16599	3.46154	2.26496	2.22370	2.23077
10	Security / *sigurnost*	3.46154	3.30128	3.46154	3.46154	3.39316

Step 1:

The matrixes in Table 5 have been found as a result of forming the priority matrixes of the candidate cities for each factor.

Step 2:

The column values of every matrix are added up and they are divided into the data in that column (Table 6, 7).

Table 5 Priority matrixes of candidate cities
Tablica 5. Prioritetne matrice gradova kandidata

Raw material *Sirovina*	BARTIN	BOLU	ZONGULDAK	KARABÜK	KASTAMONU
BARTIN	1.00000	0.91308	0.97433	1.01177	0.90561
BOLU	1.09519	1.00000	1.06707	1.10808	0.99181
ZONGULDAK	1.02635	0.93714	1.00000	1.03843	0.92947
KARABÜK	0.98837	0.90246	0.96299	1.00000	0.89508
KASTAMONU	1.10423	1.00825	1.07588	1.11722	1.00000

Labor force *Radna snaga*	273-281	BOLU	ZONGULDAK	KARABÜK	KASTAMONU
BARTIN	1.00000	0.63158	0.60902	0.71841	0.68761
BOLU	1.58333	1.00000	0.96429	1.13748	1.08871
ZONGULDAK	1.64198	1.03704	1.00000	1.17961	1.12903
KARABÜK	1.39197	0.87914	0.84774	1.00000	0.95712
KASTAMONU	1.45432	0.91852	0.88571	1.04480	1.00000

Market *Tržište*	BARTIN	BOLU	ZONGULDAK	KARABÜK	KASTAMONU
BARTIN	1.00000	0.81918	0.94305	1.00141	0.94305
BOLU	1.22074	1.00000	1.15122	1.22245	1.15122
ZONGULDAK	1.06039	0.86865	1.00000	1.06188	1.00000
KARABÜK	0.99860	0.81803	0.94173	1.00000	0.94173
KASTAMONU	1.06039	0.86865	1.00000	1.06188	1.00000

Table 5 Priority matrixes of candidate cities
Tablica 5. Prioritetne matrice gradova kandidata

Energy and oil *Energija i gorivo*	**BARTIN**	**BOLU**	**ZONGULDAK**	**KARABÜK**	**KASTAMONU**
BARTIN	1.00000	1.15170	1.06407	0.96563	0.98420
BOLU	0.86828	1.00000	0.92391	0.83844	0.85456
ZONGULDAK	0.93978	1.08235	1.00000	0.90748	0.92493
KARABÜK	1.03560	1.19270	1.10195	1.00000	1.01923
KASTAMONU	1.01606	1.17020	1.08116	0.98113	1.00000

Social environment *Društveno okružje*	**BARTIN**	**BOLU**	**ZONGULDAK**	**KARABÜK**	**KASTAMONU**
BARTIN	1.00000	0.62526	0.76877	0.79950	0.78947
BOLU	1.59933	1.00000	1.22951	1.27866	1.26263
ZONGULDAK	1.30079	0.81333	1.00000	1.03998	1.02694
KARABÜK	1.25078	0.78207	0.96156	1.00000	0.98746
KASTAMONU	1.26667	0.79200	0.97377	1.01270	1.00000

Water *Voda*	**BARTIN**	**BOLU**	**ZONGULDAK**	**KARABÜK**	**KASTAMONU**
BARTIN	1.00000	0.82289	0.94315	0.88417	0.78480
BOLU	1.21523	1.00000	1.14614	1.07446	0.95370
ZONGULDAK	1.06027	0.87249	1.00000	0.93746	0.83210
KARABÜK	1.13101	0.93070	1.06671	1.00000	0.88761
KASTAMONU	1.27422	1.04854	1.20178	1.12662	1.00000

Tax *Porez*	**BARTIN**	**BOLU**	**ZONGULDAK**	**KARABÜK**	**KASTAMONU**
BARTIN	1.00000	1.21353	1.13431	1.02787	1.03594
BOLU	0.82404	1.00000	0.93472	0.84701	0.85366
ZONGULDAK	0.88159	1.06984	1.00000	0.90617	0.91328
KARABÜK	0.97288	1.18062	1.10355	1.00000	1.00785
KASTAMONU	0.96530	1.17143	1.09496	0.99221	1.00000

Construction cost *Troškovi izgradnje*	**BARTIN**	**BOLU**	**ZONGULDAK**	**KARABÜK**	**KASTAMONU**
BARTIN	1.00000	0.64834	1.05895	0.62672	0.65278
BOLU	1.54241	1.00000	1.63333	0.96667	1.00685
ZONGULDAK	0.94433	0.61224	1.00000	0.59184	0.61644
KARABÜK	1.59560	1.03448	1.68966	1.00000	1.04157
KASTAMONU	1.53192	0.99320	1.62222	0.96009	1.00000

Transportation *Transport*	**BARTIN**	**BOLU**	**ZONGULDAK**	**KARABÜK**	**KASTAMONU**
BARTIN	1.00000	0.62573	0.95631	0.97405	0.97096
BOLU	1.59813	1.00000	1.52830	1.55666	1.55172
ZONGULDAK	1.04569	0.65432	1.00000	1.01856	1.01533
KARABÜK	1.02664	0.64240	0.98178	1.00000	0.99683
KASTAMONU	1.02991	0.64444	0.98491	1.00318	1.00000

Security *Sigurnost*	**BARTIN**	**BOLU**	**ZONGULDAK**	**KARABÜK**	**KASTAMONU**
BARTIN	1.00000	1.04854	1.00000	1.00000	1.02015
BOLU	0.95370	1.00000	0.95370	0.95370	0.97292
ZONGULDAK	1.00000	1.04854	1.00000	1.00000	1.02015
KARABÜK	1.00000	1.04854	1.00000	1.00000	1.02015
KASTAMONU	0.98025	1.02783	0.98025	0.98025	1.00000

Step 3:

Necessary coefficients for raw material factor to be used in the main matrix are obtained by finding the line averages of these new values (Table 7).

The exact matrix is found as follows by repeating the same process for the other factors (Table 8).

After the matrix is found as a result of comparison between the factors among the candidate cities, a new matrix is similarly formed in the consequence of priority comparisons applied among the factors themselves (Table 9).

Table 6 Summation of matrix columns of raw material factor
Tablica 6. Sažetak matričnih stupaca kriterija sirovine

Raw material / *Sirovina*	**BARTIN**	**BOLU**	**ZONGULDAK**	**KARABÜK**	**KASTAMONU**
BARTIN	1.00000	0.91308	0.97433	1.01177	0.90561
BOLU	1.09519	1.00000	1.06707	1.10808	0.99181
ZONGULDAK	1.02635	0.93714	1.00000	1.03843	0.92947
KARABÜK	0.98837	0.90246	0.96299	1.00000	0.89508
KASTAMONU	1.10423	1.00825	1.07588	1.11722	1.00000
Total / *Ukupno*	5.21414	4.76094	5.08027	5.27550	4.72197

Table 7 The average of matrix lines of raw material factor
Tablica 7. Proračun srednjih vrijednosti matričnih linija za kriterij sirovine

Raw material *Sirovina*	**BARTIN**	**BOLU**	**ZONGULDAK**	**KARABÜK**	**KASTAMONU**	**Raw material** *Sirovina*
BARTIN	0.191786	0.191786	0.191786	0.191786	0.191786	0.191786
BOLU	0.210042	0.210042	0.210042	0.210042	0.210042	0.210042
ZONGULDAK	0.196840	0.196840	0.196840	0.196840	0.196840	0.196840
KARABÜK	0.189556	0.189556	0.189556	0.189556	0.189556	0.189556
KASTAMONU	0.211776	0.211776	0.211776	0.211776	0.211776	0.211776
Total / *Ukupno*	1.000000	1.000000	1.000000	1.000000	1.000000	1.000000

Table 8 Values of factors for each candidate city
Tablica 8. Vrijednosti kriterija za svaki grad kandidat

Factors / *Kriteriji*	**BARTIN**	**BOLU**	**ZONGULDAK**	**KARABÜK**	**KASTAMONU**
Raw material / *sirovina*	0.191786	0.210042	0.196840	0.189556	0.211776
Labor force / *radna snaga*	0.141411	0.223900	0.232193	0.196839	0.205657
Market / *tržište*	0.187262	0.228598	0.198571	0.186999	0.198571
Energy and fuel / *energija i gorivo*	0.205773	0.178669	0.193383	0.213098	0.209077
Social environment / *društveno okružje*	0.155822	0.249211	0.202692	0.194900	0.197375
Water / *voda*	0.176034	0.213921	0.186644	0.199096	0.224305
Tax / *porez*	0.215340	0.177449	0.189842	0.209500	0.207869
Construction cost / *troškovi izgradnje*	0.151188	0.233195	0.142772	0.241236	0.231608
Transportation / *transport*	0.175427	0.280356	0.183443	0.180101	0.180674
Security / *sigurnost*	0.202677	0.193294	0.202677	0.202677	0.198674

Table 9 Superiority matrix among factors
Tablica 9. Matrica superiornosti kriterija

	Raw material *Sirovina*	**Labor force** *Radna snaga*	**Market** *Tržište*	**Energy and fuel** *Energija i gorivo*	**Social environment** *Društveno okružje*	**Water** *Voda*	**Tax** *Porez*	**Construction cost** *Troškovi izgradnje*	**Transportation** *Transport*	**Security** *Sigurnost*
Raw material *Sirovina*	1.00000	1.21622	1.04651	1.77165	2.47253	3.46154	1.28571	1.31579	1.22951	3.00000
Labor force *Radna snaga*	0.82222	1.00000	0.86047	1.45669	2.03297	2.84615	1.05714	1.08187	1.01093	2.46667
Market / *Tržište*	0.95556	1.16216	1.00000	1.69291	2.36264	3.30769	1.22857	1.25731	1.17486	2.86667
Energy and fuel *Energija i gorivo*	0.56444	0.68649	0.59070	1.00000	1.39560	1.95385	0.72571	0.74269	0.69399	1.69333
Social environment / *Društveno okružje*	0.40444	0.49189	0.42326	0.71654	1.00000	1.40000	0.52000	0.53216	0.49727	1.21333
Water / *Voda*	0.28889	0.35135	0.30233	0.51181	0.71429	1.00000	0.37143	0.38012	0.35519	0.86667
Tax / *Porez*	0.77778	0.94595	0.81395	1.37795	1.92308	2.69231	1.00000	1.02339	0.95628	2.33333
Construction cost / *Troškovi izgradnje*	0.76000	0.92432	0.79535	1.34646	1.87912	2.63077	0.97714	1.00000	0.93443	2.28000
Transportation *Transport*	0.81333	0.98919	0.85116	1.44094	2.01099	2.81538	1.04571	1.07018	1.00000	2.44000
Security *Sigurnost*	0.33333	0.40541	0.34884	0.59055	0.82418	1.15385	0.42857	0.43860	0.40984	1.00000
Total / *Ukupno*	6.72000	8.17297	7.03256	11.90551	16.61538	23.26154	8.64000	8.84211	8.26230	20.16000

Table 10 Determination of factor loads
Tablica 10. Određivanje opterećenosti kriterija

No	Factors / *Kriteriji*	Value *Vrijednost*
1	Raw material / *sirovina*	0.148809524
2	Labor force / *radna snaga*	0.122354497
3	Market / *tržište*	0.142195767
4	Energy and fuel / *energija i gorivo*	0.083994709
5	Social environment *društveno okružje*	0.060185185
6	Water / *voda*	0.042989418
7	Tax / *porez*	0.115740741
8	Construction cost *troškovi izgradnje*	0.113095238
9	Transportation / *transport*	0.121031746
10	Security / *sigurnost*	0.049603175
	Total / *Ukupno*	1.000000000

Table 11 Results matrix
Tablica 11. Matrica rezultata

Candidate cities *Gradovi kandidati*	Results *Rezultati*	%
BOLU	0.220791	22.08
KASTAMONU	0.205971	20.60
KARABÜK	0.200452	20.05
ZONGULDAK	0.192778	19.28
BARTIN	0.180007	18.00

The loads of the factors have been identified as shown in Table 10 by conducting similar processes as in step 2 and 3.

Step 4:

After multiplying the last two matrixes, the values indicate which city stands out in the selection of the factory location (Table 11).

It has been determined, with 22.08 %, that it would be most appropriate to establish the planned timber factory in Bolu.

4 DISCUSSION AND CONCLUSION
4. RASPRAVA I ZAKLJUČAK

It is clearly stated in the literature that multi-criteria decision making techniques and the results obtained using AHP are more effective when used together (Kurttilaa *et al.*, 2000; Gürbüz *et al.*, 2013; Okello *et al.*, 2014). The aim of this study was to show that the result is more effective when combining the dual scaling method, which is a more subjective method, with AHP.

Considering the results of dual scaling, Bolu is a good option for the timber factory planned to be established with the value of 546.99 (23.25 %). Bolu has ranked first with 0.2208 (22.08 %) as a result of the evaluation via AHP.

It can be seen that Bolu achieved this result based on some important factors such as raw material, labor force and market. It is striking that both methods used in the study gave similar results. It is understood in the evaluation method that Bolu is proceeding with 22.66 % compared to other cities, where both methods were averaged (Table 12).

Although the ranking seems the same resulting from both methods, the increase in Zonguldak, Karabük and Kastamonu stands out, while there is a decrease in Bolu and Bartın according to the AHP method. The increase is especially dramatic and remarkable in Zonguldak and Karabük.

A similar result arising from the evaluation of the candidate cities appears in the comparison of the loads. The anticipated loads for the factors that will determine the location are such as to affect the results directly. The most important factor in dual scaling method, raw material, is the factor having the highest weight (0.1488) in accordance with AHP. The factor having the lowest weight, Water, has the lowest weight in AHP method with 0.0429.

It is very important to go through the details again before selecting the timber factory location. All the alternatives must be assessed before determining the location where large-scale factories, requiring large investments, will be established. As a result of this study, applying the AHP method after the implementation of dual scaling method will cause the planners check their point of view. Such evaluation will provide reconsideration of the factors regarded as less important.

This study will provide a different viewpoint for the selection of timber factory location. This approach has been applied for the first time in this area. By taking the average of the results obtained by these two methods at the end of the study, the evaluation according to these data will lead the decision makers to make decisions in a more reliable way.

The results of this study show that not only can the timber factory location be selected, but in other areas it can be used to determine the factory location. The location of the paper mill, fiberboard mill and chipboard mill can also be selected.

Table 12 Comparison of the results obtained by two methods and hybrid method
Tablica 12. Usporedba rezultata dobivenih zasebnom primjenom metode odlučivanja i hibridne metode

Candidate cities *Gradovi kandidati*	Dual Scaling *Dvostruko skaliranje*		AHP		Hybrid method *Hibridna metoda*
	Value / *Vrijednost*	%	Value / *Vrijednost*	%	%
BARTIN	434.93	18.48	0.180007	18.00	18.24
BOLU	546.99	23.25	0.220791	22.08	22.66
ZONGULDAK	444.30	18.88	0.192778	19.28	19.08
KARABÜK	447.72	19.03	0.200452	20.05	19.54
KASTAMONU	479.07	20.36	0.205971	20.60	20.48

Table 13 Comparison of factor loads by both methods
Tablica 13. Usporedba opterećenosti kriterija pri svakoj metodi odlučivanja

No	**Factors /** *Kriteriji*	**Value (Dual Scaling)** *Vrijednost (dvostruko skaliranje)*	**Value (AHP)** *Vrijednost (AHP)*
1	Raw material / *sirovina*	10.0	0.148809524
2	Labor force / *radna snaga*	8.0	0.122354497
3	Market / *tržište*	9.5	0.142195767
4	Energy and fuel / *energija i gorivo*	5.1	0.083994709
5	Social environment / *društveno okružje*	3.3	0.060185185
6	Water / *voda*	2.0	0.042989418
7	Tax / *porez*	7.5	0.115740741
8	Construction cost / *troškovi izgradnje*	7.3	0.113095238
9	Transportation / *transport*	7.9	0.121031746
10	Security / *sigurnost*	2.5	0.049603175
	Total / *Ukupno*		

5 REFERENCES
5. LITERATURA

1. Barutçugil, İ., 1988: Production System and Management Techniques. Uludağ University Publication Number: 163, Bursa, Turkey.
2. Forman, E.; Gass, S., 2001: The analytic hierarchy process – An exposition. Operations Research, 49 (4): 469-486. https://doi.org/10.1287/opre.49.4.469.11231
3. Golden, B.; Wasil, E.; Harker, P., 1989: The Analytic Hierarchy Process: Applications and Studies. Heidelberg, Germany: Springer-Verlag. https://doi.org/10.1007/978-3-642-50244-6
4. Gürbüz, T.; Albayrak, Y. E.; Alaybeyoğlu, E., 2013: Criteria Weighting and 4P's Planning in Marketing Using a Fuzzy Metric Distance and AHP Hybrid Method, 7 (1): 94-104. https://doi.org/10.1080/18756891.2014.853936
5. Ho, W., 2008: Integrated analytic hierarchy process and its applications – A literature review. European Journal of Operational Research, 186 (1): 211-228. https://doi.org/10.1016/j.ejor.2007.01.004
6. İlter, E., 2001: Preparation of Investment Projects, Evaluation and Monitoring, Bolu, Turkey.
7. Kainulainen, T.; Leskinen, P.; Korhonen, P.; Haara, A.; Hujala, T., 2009: A statistical approach to assessing interval scale preferences in discrete choice problems. Journal of the Operational Research Society, 60 (2): 252-258. https://doi.org/10.1057/palgrave.jors.2602554
8. Kobu, B., 1989: Production Management, Istanbul University, Faculty of Business Publication Number: 211, İstanbul, Turkey.
9. Kumar, S.; Vaidya, O., 2006: Analytic hierarchy process: An overview of applications. European Journal of Operational Research, 169 (1): 1-29. https://doi.org/10.1016/j.ejor.2004.04.028
10. Kurttilaa, M.; Pesonena, M.; Kangasb, J.; Kajanusa, M., 2000: Utilizing the analytic hierarchy process (AHP) in SWOT analysis – a hybrid method and its application to a forest-certification case. Forest Policy and Economics, 1 (1): 41-52. https://doi.org/10.1016/S1389-9341(99)00004-0
11. Liberatore, M.; Nydick, R., 2008: The analytic hierarchy process in medical and health care decision making: A literature review. European Journal of Operational Research, 189 (1): 194-207. https://doi.org/10.1016/j.ejor.2007.05.001
12. Okello, C.; Pindozzi, S.; Faugno, S.; Boccia, L., 2014: Appraising Bioenergy Alternatives in Uganda Using Strengths, Weaknesses, Opportunities and Threats (SWOT) – Analytical Hierarchy Process (AHP) and a Desirability Functions Approach, Energies 2014, 7 (3): 1171-1192. https://doi.org/10.3390/en7031171
13. Saaty, T.; Forman, E., 1992: The Hierarchy Of: A Dictionary of Hierarchies. Pittsburgh, PA: RWS Publications.
14. Saaty, T., 1980: The Analytic Hierarchy Process, McGraw-Hill, New York.
15. Saaty, T., 1990: The Analytic Hierarchy Process in Conflict Management. International Journal of Conflict Management, 1 (1): 47-68. https://doi.org/10.1108/eb022672
16. Saaty, T., 1999: The Analytic Hierarchy Process for Decision Making, Kobe, Japan.
17. Saaty, T., 2000: Fundamentals of Decision Making and Priority Theory. RWS Publications, Pittsburgh, USA.
18. Shim, J., 1989: Bibliography research on the analytic hierarchy process (AHP). Socio-Economic Planning Sciences, 23 (3): 161-167. https://doi.org/10.1016/0038-0121(89)90013-X
19. Tam, M. C. Y.; Tummala, V. M. R., 2001: An Application of the AHP in Vendor Selection of a Telecommunications System. The International Journal of Management Science, 29 (2): 171-182. https://doi.org/10.1016/S0305-0483(00)00039-6
20. Üçüncü, K., 2003: Facilities Planning, Karadeniz Technical University, Faculty of Forestry Publication Number: 68, Trabzon, Turkey.
21. Vargas, L., 1990: An overview of the analytic hierarchy process and its applications. European Journal of Operational Research, 48 (1): 2-8. https://doi.org/10.1016/0377-2217(90)90056-H
22. Zahedi, F., 1986: The analytic hierarchy process: A survey of the method and its applications. Interface, 16 (4): 96-108. https://doi.org/10.1287/inte.16.4.96
23. *** Anonymous, 1985: Preparation and Evaluation of Investment Projects. Research and External Relations Department, Ankara, Turkey.

Corresponding address:

Assoc. Prof. ALPER AYTEKIN, Ph.D.

Bartin University
Faculty of Economics and Administrative Sciences
Department of Management Information Systems
74100, Bartin, TURKEY
e-mail:aytekin@bartin.edu.tr

Majid Kiaei, Masoud Behzadi Rad[1], Naghmeh Amani[2]

Influence of Densification Temperature on Some Physical and Mechanical Properties of *Pterocarya Fraxinifolia* Wood

Utjecaj temperature pri ugušćivanju drva *Pterocarya fraxinifolia* na njegova fizikalna i mehanička svojstva

Preliminary paper • Prethodno priopćenje
Received – prispjelo: 30. 8. 2017.
Accepted – prihvaćeno: 13. 6. 2018.
*UDK: 630*812.463; 630*812.7*
doi:10.5552/drind.2018.1750

ABSTRACT • *This study has been conducted to investigate the influence of temperature levels in the densification process by hot-press methods on the physical and mechanical properties of false walnut wood (Pterocarya fraxinifolia). For this purpose, wood specimens from five standing trees were compressed at different densification temperatures (110, 140 and 170 °C). Then, the data of oven dry density, modulus of rupture, modulus of elasticity in bending and withdrawal strength of nail of compressed wood were analyzed by SPSS software. Analysis of variance (ANOVA) indicated that the densification temperature had significant effects on the physical and mechanical properties. The most suitable temperature level was 140 °C for a higher density, modulus of rupture, modulus of elasticity in bending, and withdrawal strength of nail in the densification of false walnut wood. Increase of 27 % in the density, 80 % in the modulus of elasticity (MOE), 252 % in the modulus of rupture (MOR) and 215 % in the withdrawal strength of nail were obtained after densification.*

Keywords: *false walnut wood, densification temperature, physical properties, mechanical properties*

SAŽETAK • *Studija je provedena kako bi se istražio utjecaj temperature na fizikalna i mehanička svojstva drva „lažnog“ oraha (Pterocarya fraxinifolia) u procesu njegova ugušćivanja metodom toplog prešanja. Za tu namjenu izrađeni su drvni uzorci od pet stabala te su podvrgnuti procesu ugušćivanja pri različitim temperaturama (110, 140 i 170 °C). Nakon toga određena je i analizirana gustoća drva u apsolutno suhom stanju, modul loma, modul elastičnosti pri savijanju i čvrstoća držanja čavala ugušćenog drva. Analiza varijance (ANOVA) pokazala je da temperatura procesa ugušćivanja ima znatan utjecaj na fizikalna i mehanička svojstva drva. Najboljom temperaturom procesa povećanja gustoće drva, modula loma, modula elastičnosti pri savijanju i čvrstoće držanja čavala ugušćenog drva „lažnog“ oraha pokazala se ona od 140 °C. Nakon ugušćivanja zabilježeno je povećanje gustoće drva od 27 %, modula elastičnosti od 80 %, modula loma od 252 % i čvrstoće držanja čavala od 215 %.*

Ključne riječi: *„lažno“ drvo oraha, temperatura ugušćivanja, fizikalna svojstva drva, mehanička svojstva drva*

[1] Authors are associate professor and associate professorat Department of Wood and Paper Science and Technology, Chaloos Branch, Islamic Azad University, Chaloos, Iran. [2] Author is young Ph.D. student at Young Researcher and Elites Club, Chaloos Branch, Islamic Azad University, Chaloos, Iran.

[1] Autori su izvanredni profesori Odjela za znanost i tehnologiju drva i papira, *Chaloos Branch*, Islamsko sveučilište *Azad*, Chaloos, Iran. [2] Autor je Ph.D. student Young Researcher and Elites Club, *Chaloos Branch*, Islamsko sveučilište *Azad*, Chaloos, Iran.

1 INTRODUCTION
1. UVOD

False walnut wood *(Pterocarya fraxinifolia)* is a species of Jouglandaceae family. The height of these trees reaches 35 m and diameter at breast height 130 cm. This species grows in northern Iran from Astara (Guilan province) to Minoodashat (Golestan province). It grows in mixed stands with alder, maple, hornbeam, ash, etc. Approximately 0.33 % of northern forests in Iran are covered with false walnut wood. It is a species of wood with low density (Ebrahimi *et al*., 2004). Thermo-mechanical modification is a technique of wood densification that combines heat treatment with mechanical compression. In the mentioned modification, densification occurs with buckling of cell walls, which reduces pore-volume (Kutnar *et al.*, 2009; Candan *et al.,* 2013). In order to ensure suitable properties of the modified wood, modification should occur at an ideal temperature, in which the amorphous polymers of wood (lignin and hemicelluloses) pass from the glassy state to the rubbery state (Akerholm and Salmén, 2004). It is defined as the glass transition temperature (*T*g) and it varies with species and moisture content used. To this point, wood can be compressed without collapse in the cell wall structure (**Sözbir** and Bektas, 2017; Esteves *et al*., 2017; Tu *et al*., 2014).

There are widespread reports on wood densification. Madhoushi *et al*. (2012) indicated that the percentage of densification significantly influence the density of poplar wood, especially at higher compression percentages (50 %). Also, the amount of densification has significant influence on the withdrawal strength of nails (up to 220 %) and screws (up to 120 %). Compared with control specimens, *MOR* and *MOE* were increased by 70 % and 40 %, respectively.

Edalat *et al.* (2008) investigated the densification of paulownia wood by hot-press method. They indicated significant influence of densification temperature and compression percentage on the mechanical properties. The highest mechanical properties of wood specimens were found in 50 % compression.

Ulcer *et al.* (2012) reported that the increase in densification temperature decreased strength properties of Scots pine wood. The most suitable densification temperature for increasing bending, shear and compression strength was 120 °C, and 140 °C for increasing radial and tangential hardness. Alen *et al.* (2009) stated that, at temperatures above 100 °C, the intermolecular and intramolecular chemical bonds begin to break with a rate that would intensify as the heating time increases. This phenomenon could be due to thermal softening and loss of amorphous polysaccharides, which are responsible for a tight combination of cellulosic fibers and amorphous matrix including lignin. Bond breakage can also be attributed to the possibility of lignin relocation. Jiang *et al.* (2009) reported that treatment at 160 °C is probably enough to cause lignin molecules, which are located between the fibril aggregates, to change their position and damage the adhesive linkage of lignin with cellulose fibrils.

According to relative investigations, the densification temperature level is one of the most important factors in wood densification. This study aims to enhance thermo-mechanically the density of false walnut wood by pressing it in a stable pressure and heat at different temperatures. The main objective of this research was to determine the impact of densification temperature on the physical and mechanical properties of false walnut wood.

2. MATERIALS AND METHODS
2. MATERIJALI I METODE

For the present study, 5 logs of *Pterocarya fraxinifolia* tree were cut from Sari forests. Then specimens were made to determine their density and moisture content. Densification temperature was the variable factor of the present study and it was tested at three different levels of 110, 140 and 170 ºC with 6 repetitions. To have similar sample dimensions for mechanical properties, length and width (400 × 80 mm) of all samples were considered equal. However, the thickness of specimens corresponded to compression percentage in order to reach 20 mm thickness for all samples after compression. Therefore, according to 30 % compression, the primary thickness of samples was considered as 28.5 mm. The thickness of control samples was considered as 20 mm. The prepared samples were from sapwood and tangential section. The thickness of all samples was measured after cutting and it was recorded as T_0. After that, the samples with primary moisture of 15 % were put into a laboratory oven at the temperature of 50 ºC for 72 h to decrease their moisture to 5 % and prepare them for pressing.

Heating was done so that the hot surface of the press made contact with sample surfaces without compressing the wood. All samples were heated for 5 minutes. After final heating, all samples were exposed to the final pressure of 40 kg/cm^2, which was applied on wood surfaces to complete the compression process. The final thicknesses were controlled by 20 mm steel plates. The keeping time for final thickness was 4 minutes in all treatments. After sample compression and after opening the press surfaces, the samples were transferred to the oven and kept at 50 ºC to prevent the creation of disadvantages resulting from rapid reduction of densification temperature. After one hour the thickness of samples was measured and it was recorded as T_1. All samples were kept at 21 ºC and relative moisture of 65 % for 3 weeks and their thickness was measured again and it was recorded as T_2.

2.1 Oven dry density
2.1. Gustoća u apsolutno suhom stanju

The density was determined in accordance with ISO 3131 (25×20×20 mm). This property is defined as the ratio of weight and volume of the specimen in the oven dry state. The number of specimens for oven dry density was 24 (18 specimens for densified wood and 6 specimens for control).

2.2 *MOR* and *MOE*
2.2. Modul loma (*MOR*) i modul elastičnosti (*MOE*)

Modulus of rupture (*MOR*) and modulus of elasticity (*MOE*) were determined according to ISO 3133 standard (370 ×20×20 mm). Specimens were conditioned at temperature of 20 °C and 65±5 % relative humidity until they reached equilibrium moisture content of about 12 %. The load was applied in the tangential direction. Bending of specimens was applied on Instron (model 4486). 24 specimens were examined for each mechanical property (18 specimens for densified wood and 6 specimens for control).

2.3 Withdrawal strength of nail
2.3. Čvrstoća držanja čavala

Examination of withdrawal strength of nail was carried out with a mechanical test system connected to a computer equipped with strength data analysis software. Length and Penetration depth of nails were 30 and 1.6 mm, respectively, according to the BS EN 1383-1999 (50×50×20 mm) standards. This property was calculated by dividing the maximum force (N) and the nail penetration length (mm).

2.4 Statistical analysis
2.4. Statistička analiza

In this study, the influence of densification temperature on oven dry density, modulus of rupture (*MOR*), modulus of elasticity (*MOE*) and withdrawal strength of nail on densification of false walnut wood were analyzed by analysis of variance (ANOVA) and SPSS statistical software (IBM SOFTWARE, Armonk, New York, version 21), and a Duncan multi domain test was conducted to compare the means at a 95 % confidence level.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

Descriptive statistical analysis of oven dry density and mechanical properties of densified false walnut wood are given in Table 1. The analysis of variance (ANOVA) related to whether or not the temperature level applied in densification was effective relative to the oven dry density, modulus of elasticity, modulus of rupture and withdrawal strength of nail is given in Table 2. Table 2 shows that temperature level affected all the investigated properties (p<0.05). Table 3 shows the homogeneity test results related to the temperature levels that created a difference according to the values of oven dry density, *MOE*, *MOR* and withdrawal strength of nail.

After the process of densification, oven dry density of false walnut increased from 445 kg/m^3 to 564 kg/m^3 at all temperature levels, and a 27 % increase in density was achieved. Since the control specimens and

Table 1 Descriptive statistical analysis of density and mechanical properties of densified false walnut wood
Tablica 1. Deskriptivna statistička analiza gustoće i mehaničkih svojstava ugušćenog drva „lažnog“ oraha

Wood properties / *Svojstva drva*		**Mean** *Srednja vrijednost*	**Standard deviation** *Standardna devijacija*	**Variation coefficient** *Koeficijent varijacije* %
Oven dry density, g/m^3 *gustoća u apsolutno suhom stanju,* g/m^3	Control	445	39	8.76
	110	532	11	2.06
	140	564	28	4.96
	170	519	36	6.93
Modulus of elasticity, N/mm^2 *modul elastičnosti,* N/mm^2	Control	3195.49	131.21	4.11
	110	5359.30	140.15	2.62
	140	5740.74	548.82	9.56
	170	5245.62	208.77	3.98
Modulus of rupture, N/mm^2 *modul loma,* N/mm^2	Control	21.17	3.21	15.16
	110	59.47	8.07	13.57
	140	74.55	9.45	12.67
	170	54.42	1.88	3.45
Withdrawal strength of nail, N/mm *čvrstoća držanja čavala,* N/mm	Control	7.80	1.66	21.28
	110	15.86	2.39	15.06
	140	24.52	4.72	19.24
	170	13.80	2.49	18.04

Table 2 Analysis of variance (ANOVA) related to the effect of temperature level on some physical and mechanical properties of densified wood
Tablica 2. Analiza varijance (ANOVA) vezana za utjecaj temperature na određena fizikalna i mehanička svojstva ugušćenog drva

Variables *Svojstva*	***F***	***p*-value** *p-vrijednost*	**Significant** *Značajno* (p<0.05)
Oven dry density, g/m^3 / *gustoća u apsolutno suhom stanju,* g/m^3	10.689	0.001	×
Modulus of elasticity, N/mm^2 / *modul elastičnosti,* N/mm^2	55.084	0.001	×
Modulus of rupture, N/mm^2 / *modul loma,* N/mm^2	41.184	0.001	×
Withdrawal strength of nail, N/mm / *čvrstoća držanja čavala,* N/mm	9.798	0.002	×

Table 3 Homogeneity tests related to the determination of temperature levels that create a difference based on the values of oven dry density, MOE, MOR and withdrawal strength of nail
Tablica 3. Testovi homogenosti vezani za određivanje temperature procesa ugušćivanja drva koja utječe na razliku gustoće u apsolutno suhom stanju, na modul elastičnosti, modul loma i čvrstoću držanja čavala

Variables *Svojstva*	**Densification temperature** *Temperatura ugušćivanja* °C	**Number of specimens** *Broj uzoraka*	**Homogeneity group** *Grupa homogenosti*		
			A	B	C
Oven dry density, g/m³ *gustoća u apsolutno suhom stanju,* g/m³	Control	6	445		
	170	6		519	
	110	6		532	
	140	6		564	
Modulus of elasticity, N/mm² *modul elastičnosti,* N/mm²	Control	6	3195.49		
	170	6		5245.62	
	110	6		5359.30	
	140	6			5740.74
Modulus of rupture, N/mm² *modul loma,* N/mm²	Control	6	21.17		
	170	6		54.42	
	110	6		59.47	
	140	6			74.55
Withdrawal strength of nail, N/mm *čvrstoća držanja čavala,* N/mm	Control	6	7.80		
	170	6	13.80	13.80	
	110	6		15.86	
	140	6			24.52

densified specimens appeared in separate homogeneity groups, the densification process was judged to be significantly affected by oven dry density. There are no significant differences among density values of the densified specimens heated to 110, 140 and 170 °C.

After the process of densification, *MOE* of false walnut increased from 3195 to 5740 N/mm² at all temperature levels, and 80 % increase in *MOE* was achieved. Control specimens and densified specimens appeared in separate homogeneity groups according to Duncan's tables. There are no significant differences among the *MOE* values of the densified specimens heated to 110, 140 and 170 °C. The differences in the *MOE* between densified specimens at the temperature of 110 and 170 °C was not significant. The differences in the *MOE* between densified specimens at the temperature of 110 and 140 °C, and the modulus of elasticity (*MOE*) of the densified specimens at 140 and 170 °C were significant.

Since the lowest *MOR* (21.17 N/mm²) was obtained in the control specimens of false walnut wood, the densification process increased *MOR*. The highest mean value of *MOR* was found in densified specimens at the temperature of 140 °C (74.55 N/mm²). The differences in the *MOR* between densified specimens at the temperature of 110 and 170 °C was not significant. The differences in the *MOR* between densified specimens at the temperature of 110 and 140 °C, and the modulus of rupture (*MOR*) of the densified specimens at 140 and 170 °C were significant.

After the densification process, the withdrawal strength of nail of false walnut wood increased from 7.80 to 24.52 N/mm at all temperature levels, and a 215 % increase in withdrawal strength of nail was achieved. Since the lowest withdrawal strength of nail (7.80 N/mm) was obtained in the control specimens, densification process increased the withdrawal strength of nail. The highest mean value of withdrawal strength of nail was found in densified specimens at the temperature of 140 °C (24.52 N/mm). Control specimens and densified specimens at the temperature of 110 °C and 140 °C appeared in separate homogeneity groups according to Duncan's tables.

The increase of temperature in the densification process affected all the strength properties of false walnut wood. The increase of the densification temperature level from 110 °C to 140°C in the false walnut wood affected the *MOE* (5359.30 and 5740.74 N/mm²), *MOR* (59.47 and 74.55 N/mm²) and withdrawal strength of nail (15.86 and 24.52 N/mm²). The raising of the densification temperature to 170 °C decreased the MOE value to 5245.62 N/mm², the *MOR* value to 54.42 N/mm² and withdrawal strength of nail value to 13.80 N/mm. The reason for the reduction of mechanical strength at 170 °C can be the change in chemical properties, change of wood cell wall, and the increase of intercellular space (Ülker *et al*., 2012; Jiang *et al*., 2009; Alen *et al.,* 2002).

4 CONCLUSIONS
4. ZAKLJUČAK

The main conclusions of this study are summarized below:

1. Densification process at temperatures of 110 °C, 140 °C and 170 °C affected the investigated physical and mechanical properties of false walnut wood.
2. By increasing the densification temperature to 140 °C, oven dry density and mechanical properties increased, but there was a reduction when the densification temperature increased to 170 °C.
3. The most suitable temperature level for densification of false walnut wood is 140 °C considering higher oven dry density, *MOR*, *MOE*, and withdrawal

strength of nail. The oven dry density and mechanical properties of densified samples were improved compared to control specimens in false walnut wood

5 REFERENCES
5. LITERATURA

1. Akerholm, M.; Salmen L., 2004: Softening of wood polymers induced by moisture studied by dynamic FTIR spectroscopy. Journal of Applied Polymer Science, 94: 2032-2040. https://doi.org/10.1002/app.21133
2. Alen, R.; Kotilainen, R.; Zaman, A., 2002: Thermochemical behavior of Norway spruce (Picea abies) at 180 – 225 °C. Wood Science and Technology, 3 (2): 163-171. https://doi.org/10.1007/s00226-001-0133-1
3. Candan, Z.; Korkut, S.; Unsal, O., 2013: Thermally compressed poplar wood (TCW): Physical and Mechanical Properties. Drvna industrija, 64 (2): 107-211. https://doi.org/10.5552/drind.2013.1216
4. Ebrahimi, E. A.; Sagheb Talebi, K. H.; Gorji Bahri, Y., 2004: Site demands of false walnut (*Pterocarya fraxinifolia*) in Vaz experimental forest of Mazandran province. Iranian Journal of Forest and Poplar, 12 (4): 481-507.
5. Edalat, H. R.; Tabarsa, T.; Reisi, M., 2008: Densification of Paullownia wood by using of hot-press. Iranian Journal of Wood and Paper Science Research, 23 (2): 136-148.
6. Esteves, B.; Ribeiro, F.; Cruz-Lopes, L.; Domingos, J. F. I., 2017: Densification and heat treatment of maritime pine wood. Wood Research, 62 (3): 373-388.
7. Jiang, J.; Lu, J.; Huang, R.; Li, X., 2009: Effect of time and temperature on the viscoelastic properties off Chinese fir wood. Drying Technology, 27: 1229-1234. https://doi.org/10.1080/07373930903266726
8. Kutnar, A.; Kamke, F. A.; Sernek, M., 2009: Density Profile and Morphology of viscoelastic Thermal Compressed Wood. Wood Science and Technology, 43 (1-2): 57-68. https://doi.org/10.1007/s00226-008-0198-1
9. Madhoushi, M.; Grey, M.; Tabarsa, T; Rafighi, A., 2012: Nail and Screw Withdrawal Strength, MOE and MOR in Densified Poplar Wood. Journal of Wood and Forest Science and Technology, 18 (4): 45-58.
10. Tu, D.; Su, X.; Zhang, T.; Fan, W.; Zhou, Q., 2014: Thermo-mechanical densification of *Populus tomentosa* var. tomentosa with low moisture content. Bioresources, 9 (3): 3846-3856. https://doi.org/10.15376/biores.9.3.3846-3856
11. Sözbir, G. D.; Bektas I., 2017: The effect of heat Modification and densification on physical properties of poplar wood. Drvna industrija, 68 (4): 315-321. https://doi.org/10.5552/drind.2017.1719
12. Ülker, O.; Imirzi, O.; Burdurlu, E., 2012: The effect of densification temperature on some physical and mechanical properties of scots pine (*Pinus sylvestris* L.). BioResources, 7 (4): 5581-5592. https://doi.org/10.15376/biores.7.4.5581-5592
13. *** ISO 3131. 1975: Standard Test Method for Density of Regular Solids. International Organization for Standardization, Geneva, Switzerland.
14. *** ISO 3133. 1975: Wood- Determination of ultimate strength in static bending, International Organization for Standardization, Geneva, Switzerland.
15. *** British Standards Institution BS EN 1383:1999: Timber structures. Test methods. Pull-through resistance of timber fasteners.

Corresponding address:

Assoc. Prof. MAJID KIAEI, Ph.D.

Department of Wood and Paper Science
and Technology
Chaloos Branch, Islamic Azad University
Chaloos, IRAN
e-mail: Mjd_kia59@yahoo.com, Mjd-kia59@iauc.ac.ir

Gostujuće predavanje o sigurnosti, životnom vijeku i trendovima razvoja modernih alata za obradu drva održano na Drvnotehnološkom odsjeku Šumarskog fakulteta

Kao dio dugogodišnje suradnje tvrtke Leitz GmbH & Co.KG i Drvnotehnološkog odsjeka Šumarskog fakulteta prvi je put održano gostujuće predavanje gospodina Željka Pekeča, dipl. ing., voditelja Odjela za primjenu i optimizaciju alata u tvrtki Leitz GmbH & Co.KG. Generacije studenata koji su u sklopu kolegija Strojevi za obradu drva išli na terensku nastavu u pogone tvrtke Leitz u Riedau u Austriji sigurno se sjećaju uvijek zanimljivih i aktualnih predavanja što ih je gospodin Pekeč održavao prije samih posjeta pogonima za proizvodnju alata. Ovaj put imali smo tu čast i zadovoljstvo da je jedno takvo predavanje naslova *Sigurnost, životni vijek i trendovi razvoja modernih alata za obradu drva* održao i na našem Fakultetu, pred brojnim zainteresiranim studentima i djelatnicima Drvnotehnološkog odsjeka.

Slika 1. Gospodina Željka Pekeča uvodno je predstavila profesorica Beljo Lučić

Slika 2. Djelatnici i studenti Šumarskog fakulteta sa zanimanjem su pratili predavanje inženjera Pekeča

Sigurnost rada iznimno je bitna u radu sa strojevima za mehaničku obradu drva zbog još uvijek velike zastupljenosti strojeva s ručnim posmakom u drvnoj industriji. Ako se usto uzme u obzir i izneseni podatak da ozljede pri radu sa strojevima za obradu drva u Austriji svake godine rezultiraju troškovima u visini 8,8 mil. EUR, jasno je koliko je taj problem važan za studente koji će nakon završetka studija raditi u industriji te moraju biti dobro upoznati s trenutačnim stanjem i regulativom na tom području. Tako smo imali priliku čuti koje su sve novosti i na što treba paziti pri radu i izboru alata koji su najčešći „krivci" za ozljede na radu, a to su kružne pile i glodalice. Studenti su upoznati sa zahtjevima norme EN 847-1 – *Tools for Woodworking. Safety requirements. Milling tools, circular saw blades*, koju će, naravno, morati poštovati u svom budućem radu te pri primjeni alata tvrtke Leitz, sukladno zahtjevima norme.

Osim navedene norme, bilo je riječi i o zahtjevima koji se odnose na glodala s drškom (EN 847-2 – *Tools for Woodworking. Safety requirements. Requirements for the shank of shank-mounted milling tools*), kao i o tome kako je ta norma primijenjena na alate tvrtke Leitz.

U predavanju je svoje mjesto našao još jedan veliki ergonomski problem. Riječ je o buci koja nastaje pri radu s alatima za obradu drva. Jedan od glavnih „dežurnih krivaca" u tom segmentu obrade drva jesu kružne pile. Kako je poznato, Leitz već godinama ulaže znatne napore u smanjenje buke koju stvaraju listovi kružnih pila tijekom rada, a posredno nastoji i povećati kvalitetu obrađene plohe jer se na taj način smanjuje lateralno gibanje listova pila. U tom smislu možemo izdvojiti njihove AS – Anti Schall kružne pile s viskoelastičnom folijom kao prigušnim materijalom, koje redovito stvaraju manju buku nego listovi drugih kružnih pila. Na predavanju je detaljno prikazan novi tip listova kružnih pila pod nazivom WhisperCut, koje svojom konstrukcijom, oštricama od umjetnih dijamanata, malom visinom zuba, promjenjivim korakom ozubljenja i drugim rješenjima za smanjenje buke svode razinu buke na samo 78 dB(A) te omogućuju fini rez s minimalnim silama rezanja i, posljedično, malom mogućnošću povratnog udara, te su iznimno postojane.

Svatko tko radi s alatima za mehaničku obradu odvajanjem čestica svjestan je da, ovisno o tome od kojeg je materijala oštrica za obradu određene vrste drva, prije ili kasnije mora ponovo naoštriti alat kako bi

Slika 3. Jedna od tema predavanja bili su i materijali od kojih se izrađuju oštrice alata

mu vratio njegova početna rezna svojstva. Osim te „dosadne“ potrebe, manja postojanost alata utječe i na varijabilne troškove proizvodnje, koje svakako želimo smanjiti kako bismo bili konkurentniji na tržištu. Da bi se povećala postojanost oštrice reznog dijela alata, poduzima se niz zahvata.

Gospodin Pekeč je u predavanju detaljno prikazao napredak koji je ostvaren u području razvoja materijala za oštrice alata, pogotovo za oštrice od tvrdih sinteriranih metala i umjetnih dijamanata, te upoznao studente s postupcima njihove proizvodnje. Neke od zanimljivosti koje su se čule na predavanju svakako je i činjenica da se kobalt kao vezivi materijal u oštricama od tvrdih metala sve češće zamjenjuje željezo-kobaltom, niklom i kadmijem te da se time postiže i bolja kemijska otpornost tih materijala, što bitno povećava postojanost alata pri obradi kemijski reaktivnih vrsta drva u određenim uvjetima obrade, kao i povoljniji utjecaj brušenja (npr. *microfinish*, *micrograin*, *standard*) na postojanost alata s oštricama od tvrdih metala.

U dijelu predavanja o oštricama alata napravljenima od sinteriranih dijamanata zanimljivo je bilo čuti kakav je postupak proizvodnje oštrica od polikristalnih i monokristalnih dijamanata te kako različite prevlake oštrica, najčešće na bazi titan-nitrida, utječu na povećanje postojanosti alata. Tako se čuo zanimljiv podatak da alati s oštricama na koje se nanose prevlake trgovačkog naziva *Marathon*, a osobito ako se nanose na oštrice od brzoreznih čelika (npr. pri blanjanju), imaju od tri do pet puta dulji životni vijek od noževa bez prevlake, a za prevlake TDC (Tungsten Diamond Coating) na oštricama od tvrdih metala povećavaju postojanost alata i do tri puta, što bitno smanjuje varijabilne troškove.

Kako će naši studenti nakon završetka studija raditi u drvnoj industriji te bi je trebali i u budućnosti unapređivati, bitno ih je upoznati s trendovima u razvoju alata kako bi te novitete mogli pravilno iskoristiti u svojim budućim tvrtkama te tako pridonijeti povećanju njihove konkurentnosti na svjetskom tržištu. Neki od osnovnih trendova koji su izdvojeni u predavanju jesu smanjenje buke pri radu strojeva i alata, ušteda materijala (povećanje iskorištenja), veća produktivnost i ono o čemu svako malo čujemo i čitamo – *Industry 4.0.*

Kao što otprije znamo, Leitz ulaže znatne napore u smanjenje buke koju alati stvaraju tijekom rada, ali dodatno je prikazan i napredak u sinergiji alata i stroja u tom smislu, koja se očituje u namjenskoj konstrukciji samog alata, ali i odsisnih ušća te sustava odsisa.

Na području poboljšanja iskorištenosti materijala znatan je napredak postignut u razvoju uskolisnih kružnih pila te sada možemo računati na širine propiljka od 1,2 mm i posmične brzine od 55 m/min, uz zadovoljavajuću kvalitetu obrađene plohe, što je rezultiralo povećanjem iskorištenja materijala za 25 % i porastom produktivnosti za 50 %.

Radi povećanja produktivnosti, posebna je pozornost pridana i smanjenju prašine koja nastaje za vrijeme obrade i nakuplja se u radnom prostoru stroja te time posredno utječe na smanjenje produktivnoga radnog vremena, na potrebu češćeg servisiranja stroja i povećava troškove proizvodnje. Bitan napredak u tom dijelu ostvaren je uz pomoć sustava usmjeravanja strugotine, tzv. DFC (Dust Flow Control), a za potrebe glodanja i nestinga na CNC strojevima nude se i Leitz turbine, čime se postiže bitno smanjenje zaprašenosti radnog prostora oko stroja. Nadalje, postignut je znatan napredak u poboljšanju kvalitete obrađene plohe pri nizu obrada, a zbog povećanja posmičnih brzina povećan je i kapacitet. Na CNC strojevima bitan je napredak ostvaren i u povećanju obodne brzine alata (HSC – High Speed Cutting), što je osobito važno za glodala manjih promjera, kojima su obodne brzine povećane do 120 m/s, a omogućena je i brža zamjena alata. Napredak u brzini rezanja izravno je povezan s krutošću sustava alat – stroj, što se očituje pri većim frekvencijama vrtnje radnog vretena. Kako bi se postigla zadovoljavajuća krutost i balansiranost, razvijen je sustav toplinskog upinjanja alata pod nazivom ThermoGrip®, koji je cjenovno iznimno konkurentan u usporedbi s ostalim hidrauličkim sustavima upinjanja. Sve te tehnologije primijenjene su i u seriji profilnih glodala ProfilCut Q.

Na kraju je prezentirana primjena sustava za praćenje stanja alata koji omogućuje kontinuirano mjerenje parametara obrade u ovisnosti o duljini puta zahvata alata, te povezivanje s ERP (Enterprise Resource Planning) sustavom radi kontinuirane kontrole alata i stvaranja baze podataka za bolje i informiranije donošenje odluka u proizvodnji te za međusobno umrežavanje strojeva. U tom segmentu Leitz sigurno ima štošta ponuditi jer se ta tvrtka još 1990-ih godina u svojoj proizvodnji počela koristiti „inteligentnim alatima“ s identifikacijskim čipovima.

Ovo zanimljivo i korisno predavanje gospodina Željka Pekeča, dipl. ing., nagrađeno je velikim pljeskom prisutnih te mu i ovim putem zahvaljujemo nadajući se da će uskoro održati još neko slično predavanje, ako ne na našem Fakultetu, onda u sklopu terenske nastave studenata Drvnotehnološkog odsjeka.

izv. prof. dr. sc. Igor Đukić

Anisoptera spp.

NAZIVI

Anisoptera Korth. botanički je rod iz porodice *Dipterocarpaceae.* Obuhvaća deset vrsta drva međusobno sličnih svojstava, a trgovačkog naziva: krabak (Njemačka, Tajland); mersawa (Njemačka, Francuska, Velika Britanija, Malezija, Nizozemska, Indonezija); ven ven (Vijetnam); phdiec (Kambodža), bac (Laos); kaunghmu (Burma); sanai, malai (Indonezija); palosapis (Filipini); bella rosa (Sjedinjene Američke Države).

NALAZIŠTE

Drveće roda *Anisoptera* prirodno je rasprostranjeno u tropskim kišnim šumama jugoistočne Azije, od Bangladeša do Nove Gvineje. Prema kriterijima Međunarodne unije za očuvanje prirode i prirodnih resursa (IUCN), čak je devet vrsta tog roda na popisu vrsta čiji se broj primjeraka zbog gubitka staništa smanjuje. Konvencija o međunarodnoj trgovini ugroženim vrstama (CITES) nema ih na svojemu popisu te se drvom roda *Anisoptera* trguje na međunarodnom tržištu.

STABLO

Stabla *Anisoptera* visoka su od 30 do 45 (60) metara. Duljine debla kreću im se od 20 do 25 (30) metara, a prsni im je promjer od 0,8 do 1,0 (2,5) metara. Deblo je pravilnoga, cilindričnog oblika. Kora mladih stabala je glatka, a u zrelog je drveća ispucana, žućkasta do smećkasta. Debljina kore je od 1,0 do 2,5 centimetara.

DRVO

Makroskopska obilježja

Drvo je rastresito porozno. Bjeljika i srževina međusobno se razlikuju bojom. Srževina je žućkasta do žutosmeđa, a s vremenom potamni. Bjeljika je blijedo žuta, uska, širine od 2 do 5 centimetara.

Granica goda slabo je uočljiva. Pore i drvni traci uočljivi su povećalom.

Mikroskopska obilježja

Traheje su pretežito pojedinačne, rjeđe su u paru i radijalno su raspoređene. Njihov promjer iznosi 155...215...260 mikrometara, a gustoća im je 4...6...7 po kvadratnome milimetru poprečnog presjeka. Volumni udio traheja je od 24 do 30 %. Često su ispunjene tilama i smeđim sržnim tvarima.

Aksijalni je parenhim drva apotrahealno raspoređen, u kratkim tangentnim nizovima, te je paratrahealno vazicentričan, uzak, često unilateralan i paratrahealno oskudan. Volumni je udio aksijalnog parenhima od 2 do 8 %. Staničje drvnih trakova je heterogeno, visine 800...1300...1650 mikrometara, a širine 64...128...157 mikrometara, odnosno od 4 do 7 stanica. Gustoća drvnih trakova je 3...5...7 po milimetru poprečnog presjeka. Volumni udio drvnih trakova iznosi 16 do 38 %. U stanicama drvnih trakova ima silikata. Drvna su vlakanca libriformska i vlaknaste traheide, a dugačka su 1270...1525...1780 mikrometara. Debljina staničnih stijenki vlakanaca je 5,8...8,2...11,6 mikrometra, a promjer njihova lumena 3,8...6,8...15,5 mikrometara. Volumni je udio vlakanaca od 30 do 53 %.

Fizička svojstva

Gustoća apsolutno suhog drva, ρ_o	560...660...740 kg/m^3
Gustoća prosušenog drva, ρ_{12-15}	595...700...780 kg/m^3
Gustoća sirovog drva, ρ_s	od 900 do 1100 kg/m^3
Poroznost	od 57 do 61 %
Radijalno utezanje, β_r	4,3...6,3...9,8 %
Tangentno utezanje, β_t	7,1...8,6...12,2 %
Volumno utezanje, β_v	11,5...15,0...22,2 %

Mehanička svojstva

Čvrstoća na tlak	40...51...69 MPa
Čvrstoća na vlak, paralelno s vlakancima	72...76...83 MPa
Čvrstoća na vlak, okomito na vlakanca	3,8...4,8...5,6 MPa
Čvrstoća na savijanje	72...90...132 MPa
Tvrdoća prema Brinellu, paralelno s vlakancima	24...36...48 MPa
Tvrdoća prema Brinellu, okomito na vlakanca	15...23...30 MPa
Modul elastičnosti	8,6...11...13,8 GPa

TEHNOLOŠKA SVOJSTVA

Obradivost

Drvo se dobro ručno i strojno obrađuje. Lako se ljušti, pili, blanja, brusi, buši i polira.

Sušenje

Drvo se sporo i dobro suši. Rizik od vitoperenja i stvaranja pukotina vrlo je malen. Parenjem drva iz njega se izlučuju smolne tvari.

Trajnost i zaštita

Prema normi HRN-EN 350, 2016, srž drva slabo je otporna na gljive truležnice (razred otpornosti 4) te slabo otporna na napad termita (razred otpornosti M). Srž je slabo permeabilna (razred 3 – 4). Prema normama, drvo se može upotrebljavati u uvjetima razreda opasnosti 1 (u unutarnjim prostorima).

Uporaba

Drvo se upotrebljava u industriji furnira te za izradu furnira za šperploče, za proizvodnju manje vrijednog namještaja i dijelova namještaja, unutarnje stolarije, podova i parketa koji nisu previše opterećeni, kao i za izradu drvenih kutija i sanduka.

Sirovina

Na tržištu se pojavljuje u obliku trupaca dužine 4 – 6 metara, najčešće srednjeg promjera 60 – 100 centimetara.

Literatura

1. Richter, H. G.; Dallwitz, M. J., 2000: Commercial timbers: descriptions, illustrations, identification, and information retrieval. In English, French, German, and Spanish. Version: 4th May 2000. http://biodiversity.uno.edu/delta/.
2. Wagenführ, R.; Scheiber, C., 1974: HOLZATLAS, VEB Fachbuchverlag, Leipzig, 419-421.
3. *** HRN EN 350, 2016: Trajnost drva i proizvoda na osnovi drva – Ispitivanje i razredba otpornosti drva i materijala na osnovi drva na biološke štetnike.
4. *** 1972: Handbook of Hardwoods, 2nd Edition. London: Her Majestys Stationery Office, The Trinity Press, Worchester and London, 109-110.
5. *** 1964: Wood dictionary, Commercial and Botanical Nomenclature of World-Timbers, Volume I, Elsevier publishing company, Amsterdam.
6. https://tropix.cirad.fr/FichiersComplementaires/EN/Asia/MERSAWA.pdf, preuzeto 25. kolovoza 2018.

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

Errata corrige:
Editorial office apologies for unintentional error in title of article at 201 page of last issue of Journal. It is written *Nesogordonia papaverifera* (A. Chev.) R. Capuron instead *Nothofagus procera* Oerst.

Upute autorima

Opće odredbe

Časopis *Drvna industrija* objavljuje znanstvene radove (izvorne znanstvene radove, pregledne radove, prethodna priopćenja), stručne radove, izlaganja sa savjetovanja, stručne obavijesti, bibliografske radove, preglede te ostale priloge s područja biologije, kemije, fizike i tehnologije drva, pulpe i papira te drvnih proizvoda, uključujući i proizvodnu, upravljačku i tržišnu problematiku u drvnoj industriji.

Predaja rukopisa podrazumijeva uvjet da rad nije već predan negdje drugdje radi objavljivanja ili da nije već objavljen (osim sažetka, dijelova objavljenih predavanja ili magistarskih radova odnosno disertacija, što mora biti navedeno u napomeni) te da su objavljivanje odobrili svi suautori (ako rad ima više autora) i ovlaštene osobe ustanove u kojoj je istraživanje provedeno. Cjelokupni sadržaj Drvne industrije dostupan je za skidanje s interneta, tiskanje, daljnju distribuciju, čitanje i ponovno korištenje bez ograničenja sve dok se naznače autor(i) i originalni izvor prema Creative Commons Attribution 4.0 International License (CC BY). Autor(i) zadržavaju izdavačka prava bez ograničenja.

Znanstveni i stručni radovi objavljuju se na hrvatskome, uz sažetak na engleskome, ili se pak rad objavljuje na engleskome, sa sažetkom na hrvatskom jeziku. Naslov, podnaslovi i svi važni rezultati trebaju biti napisani dvojezično. Ostali se članci uglavnom objavljuju na hrvatskome. Uredništvo osigurava inozemnim autorima prijevod na hrvatski. Znanstveni i stručni radovi podliježu temeljitoj recenziji najmanje dvaju recenzenata. Izbor recenzenata i odluku o klasifikaciji i prihvaćanju članka (prema preporukama recenzenata) donosi Urednički odbor.

Svi prilozi podvrgavaju se jezičnoj obradi. Urednici će od autora zahtijevati da tekst prilagode preporukama recenzenata i lektora, te zadržavaju i pravo da predlože skraćivanje ili poboljšanje teksta. Autori su potpuno odgovorni za svoje priloge. Podrazumijeva se da je autor pribavio dozvolu za objavljivanje dijelova teksta što su već negdje objavljeni te da objavljivanje članka ne ugrožava prava pojedinca ili pravne osobe. Radovi moraju izvještavati o istinitim znanstvenim ili tehničkim postignućima. Autori su odgovorni za terminološku i metrološku usklađenost svojih priloga. Radovi se šalju elektroničkom poštom na adresu:

drind@sumfak.hr ili techdi@sumfak.hr

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.

Prva stranica poslanog rada treba sadržavati puni naslov, ime(na) i prezime(na) autora, podatke o zaposlenju autora (ustanova, grad i država) te sažetak s ključnim riječima (duljina sažetka približno 1/2 stranice A4).

Posljednja stranica treba sadržavati titule, zanimanje, zvanje i adresu (svakog) autora, s naznakom osobe s kojom će Uredništvo biti u vezi.

Znanstveni i stručni radovi moraju biti sažeti i precizni. Osnovna poglavlja trebaju biti označena odgovarajućim podnaslovima. Napomene se ispisuju na dnu pripadajuće stranice, a obrojčavaju se susljedno. One koje se odnose na naslov označuju se zvjezdicom, a ostale uzdignutim arapskim brojkama. Napomene koje se odnose na tablice pišu se ispod tablica, a označavaju se uzdignutim malim pisanim slovima, abecednim redom.

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 : 1".

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.

Web stranice

***1997: "Guide to Punctuation" (online), University of Sussex, www.informatics.sussex.ac.uk/department/docs/punctuation/node00.html. First published 1997 (pristupljeno 27. siječnja 2010).

Autoru se prije konačnog tiska šalje pdf rada. Rad je potrebno pažljivo pročitati, ispraviti te vratiti Uredništvu s listom ispravaka te s formularom za prijenos autorskih prava na izdavača. Ispravci su ograničeni samo na tiskarske pogreške: dodaci ili znatnije promjene u radu naplaćuju se. Autori znanstvenih i stručnih radova besplatno dobivaju po jedan primjerak časopisa. Autoru svakog priloga također se dostavlja besplatan primjerak časopisa.

Dodatne informacije o načinu pisanja znanstvenih radova mogu se naći na web adresi:

www.ease.org.uk/publications/author-guidelines

Instructions for authors

General terms

The "Drvna industrija" ("Wood Industry") journal publishes scientific papers (original scientific papers, review papers, previous notes), professional papers, conference papers, professional information, bibliographical and survey articles and other contributions related to biology, chemistry, physics and technology of wood, pulp and paper and wood products, including production, management and marketing issues in the wood industry.
Submission of a paper implies that the work has not been submitted for publication elsewhere or published before (except in the form of an abstract or as part of a published lecture, review or thesis, in which case it must be stated in a footnote); that the publication is approved by all co-authors (if any) and by the authorities of the institution where the research has been carried out. The complete content of the journal *Drvna industrija* (Wood Industry) is available on the Internet permitting any users to download, print, further distribute, read and reuse it with no limits provided that the author(s) and the original source are identified in accordance with the Creative Commons Attribution 4.0 International License (CC BY). The authors retain their copyrights.
The scientific and professional papers shall be published either in Croatian, with an extended summary in English, or in English with an extended summary in Croatian. The titles, headings and all the relevant results shall be presented bilingually. Other articles are generally published in Croatian. The Editor's Office shall provide the translation into Croatian for foreign authors. The scientific and professional papers will be subject to a thorough review by at least two selected referees. The Editorial Board shall make the choice of reviewers, as well as the decision about the classification of the paper and its acceptance (based on reviewers' recommendations).
All contributions are subject to proofreading. The editors will require authors to modify the text in the light of the recommendations made by reviewers and language advisers, and they reserve the right to suggest abbreviations and text improvements. Authors are fully responsible for the contents of their contributions. It shall be assumed that the author has obtained the permission for the reproduction of portions of text published elsewhere, and that the publication of the paper in question does not infringe upon any individual or corporate rights. Papers shall report on true scientific or technical achievement. Authors are responsible for the terminological and metrological consistency of their contributions. The contributions are to be submitted by e-mail to the following address: E-mail: drind@sumfak.hr

Details

Papers submitted shall consist of no more than 15 single-sided DIN A-4 sheets of 30 double-spaced lines, including tables, figures and references, appendices and other supplements. Longer papers should be divided into two or more continuing series. The text should be written in doc format, fully written using Times New Roman font (text, graphs and figures), in normal style without additional text editing.
The first page of the paper submitted should contain full title, name(s) of author(s) with professional affiliation (institution, city and state), abstract with keywords (approx. 1/2 sheet DIN A4).
The last page should provide the full titles, posts and address(es) of each author with indication of the contact person for the Editor's Office.
Scientific and professional papers shall be precise and concise. The main chapters should be characterized by appropriate headings. Footnotes shall be placed at the bottom of the same page and consecutively numbered. Those relating to the title should be marked by an asterix, others by superscript Arabic numerals. Footnotes relating to the tables shall be printed under the table and marked by small letters in alphabetical order.
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.
Materials and methods should be as precise as possible to enable other scientists to repeat the experiment. The main experimental data should be presented bilingually.
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.
The number of figures shall be limited to those absolutely necessary for clarification of the text. The same information must not be presented in both a table and a figure. Figures and tables should be numbered separately with Arabic numerals, and should be referred to in the text with clear remarks ("Table 1" or "Figure 1"). Titles, headings, legends and all the other text in figures and tables should be written in both Croatian and English.
Figures should be inserted into the text. They should be of 600 dpi resolution, black and white (color photographs only on request and extra charged), in jpg or tiff format, completely clear and understandable without reference to the text of the contribution.
All graphs and tables shall be black and white (unless requested otherwise with additional payment). Tables and graphs should be inserted into the text in their original format in order to insert them subsequently into the Croatian version. If this is not possible, original document should be sent in the format in which it was made (excel or statistica format).
The captions to figures and drawings shall not be written in block letters. Line drawings and graphs should conform to the style of the journal (font size and appearance). Letters and numbers shall be sufficiently large to be readily legible after reduction of the width of a figure or table. Photomicrographs should have a mark indicating magnification, preferably in micrometers. Magnification can be additionally indicated at the end of the figure title, e.g. "Mag. 7500:1".
Discussion and conclusion may, if desired by authors, be combined into one chapter. This text should interpret the results relating to the problem outlined in the introduction and to related observations by the author(s) or other researchers. Repeating the data already presented in the "Results" chapter should be avoided. Implications for further studies or application may be discussed. A conclusion shall be expressed separately if results and discussion are combined in the same chapter. Acknowledgements are presented at the end of the paper. Relevant literature shall be cited in the text according to the Harvard system ("name – year"), e.g. (Bađun, 1965). In addition, the bibliography shall be listed at the end of the text in alphabetical order of the author's names, together with the title and full quotation of the bibliographical reference. The list of references shall be selective, and each reference shall have its DOI number (http://www.doi.org) (check at http://www.crossref.org).:

Example of references

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.):
Müller, D. 1977: Beitrag zur Klassifizierung asiatischer Baumarten. Mitteilung der Bundesforschungsanslalt für Forst- und Holzwirtschaft Hamburg, Nr. 98. Hamburg: M. Wiederbusch.

Websites:
***1997: "Guide to Punctuation" (online), University of Sussex, www.informatics.sussex.ac.uk/department/docs/punctuation/node00.html. First published 1997 (Accessed Jan. 27, 2010).

The paper will be sent to the author in pdf format before printing. The paper should be carefully corrected and sent back to the Editor's Office with the list of corrections made and the form for the transfer of copyrights from the author to the publisher. Corrections should be limited to printing errors; amendments to or changes in the text will be charged. Each contributor will receive 1 copy of the journal.

Further information on the way of writing scientific papers can be found on the following website:

www.ease.org.uk/publications/author-guidelines


Hrvatska kvaliteta
spinvalis
tvornica namještaja d.d.
Udobnost življenja
Spin Valis d.d.
Industrijska 24
Požega
034/311-175
prodaja@spinvalis.hr
Prodavaonica Zagreb
Avenija Dubovnik 14
01/6520-898
salonzg@spinvalis.hr
dizajn: Aurea Grupa d.o.o.
www.spinvalis.hr