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HEATING VALUE OF THERMALLY TREATED WOOD

*Common ash (*Fraxinus excelsior* L.) wood was heat treated in an oven at the temperatures of 180°C, and 200°C under atmospheric pressure in the presence of air for 3, 6, 9, 12 hours, and the changes in higher heating value (HHV) of wood were studied. For untreated ash wood the value 19.51 MJ·kg⁻¹ was determined. Thermal treatment considerably increased the HHV of wood. The highest value was measured in sample that was thermally treated for 6 h at the temperature of 200°C. In this sample the value 20.78 MJ·kg⁻¹ was determined. Changes in HHV are a consequence of chemical changes in wood during treatment. Strong positive correlation between HHV and the ratio of the sum of lignin and extractives content to holocellulose content was observed.*

Keywords: thermal treatment, common ash, higher heating value, extractives, lignin, holocellulose

Introduction

The thermal modification of wood has long been recognized as a process enhancing wood properties by reducing moisture absorption, improving dimensional stability and increasing its decay resistance. First report about the effect of high-temperature treatment upon the physical properties of wood has been published in early 20th century. Ever since several commercial processes have been developed, such as ThermoWood®, PlatoWood®, OHT-Wood®, and RetificatedWood® [Hill 2006; Esteves and Pereira 2009].

Thermal modification is invariably performed between temperatures of 160°C and 260°C. The exposure of wood to heat results in many reactions, e. g. dehydration, hydrolysis, oxidation, depolymerization and degradation of wood components. In consequence of these processes the chemical composition of wood is altered. First volatile extractives and bound water are released from wood. The degradation of macromolecular components begins with an increasing temperature and prolonged exposure time. Hemicelluloses are the most thermally labile of the wood polymeric components. These amorphous polymers are depolymerized to oligosaccharides and monosaccharides that are subsequently decomposed to volatile compounds, such as methanol, acetic acid,

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furfural and others. Thermal lability increases with higher content of pentosans and acetyl groups in macromolecules. With comparison to hexosans, pentosans are the most susceptible to hydrolysis and dehydration reactions. Furthermore, the presence of acetyl groups leads to the formation of acetic acid, thereby, causing an acid-catalyzed degradation of polysaccharides. With respect to the above hardwood xylans are the least thermally stable from hemicelluloses [Fengel and Wegener 1984; Hill 2006; Esteves and Pereira 2009; Čabalová et al. 2018; Výbohová et al. 2018].

Cellulose is a long-chain polymer of β -D-glucose in the pyranose form. Hydroxyl groups present in cellulose macromolecules are involved in a number of intra- and intermolecular hydrogen bonds, which result in various ordered crystalline arrangements. The thermal resistance of amorphous and crystalline regions of cellulose is different. The amorphous regions of cellulose are more susceptible to thermal degradation and these regions probably exhibit similar thermal properties to the hexose components of hemicelluloses. On the other hand, the more ordered cellulose regions have higher thermal stability [Baeza and Freer 2001; Hill 2006; Park et al. 2010; Poletto et al. 2012].

The loss of polysaccharide material on heating leads to an increase in the content of the most thermally stable component of wood, which is lignin. Its content and composition depends on wood species. Softwood lignin is composed mainly of guaiacyl units, while hardwood lignin is composed of both guaiacyl and syringyl units. While softwood lignin appears to vary little between species, the structure of hardwood lignin varies greatly from one species to another. The major difference is the ratio of syringyl to guaiacyl units (S/G ratio). The syringyl content of the typical hardwood lignins varies between 20 and 60 %. In hardwood lignins is higher oxygen content than that of softwood lignins. It is caused by their higher methoxyl content (18-22%) as compared to softwood lignins (12-16%) [Fengel and Wegener 1984; Hon and Shiraishi 2001; Hill 2006; Santos et al. 2012].

Heating value of wood components depends on their elemental composition. Lignin is rich in carbon and hydrogen, which are the main heat producing elements. Hereby its heating value is higher than that of carbohydrates. Although the extractives are a minor component of wood, they raised the higher heating values of the wood. Inorganic elements present in wood play also certain role. These elements will remain after burning as ash, which content in wood biomasses ranges between 0.08 to 2.3%. High content of inorganic elements in the fuel generally reduces its heating value [Telmo and Lousada 2011; Dzurenda et al. 2013; Dzurenda and Pňakovič 2016].

In the literature, there are a lot of research results about color, biological resistance, chemical and mechanical properties of thermally modified wood [Esteves et al. 2013; Kačík et al. 2015; Wang et al. 2015; Kučerová et al. 2016; Kačíková et al. 2017; Andor and Lagaňa 2018; Bubeníková et al. 2018; Čabalová et al. 2018; Kúdela and Andor 2018; Výbohová et al. 2018]. However,

chemical changes during thermal treatment of wood modified also its energetic value and fire-technical characteristics. Nevertheless, these features of thermally treated wood have seldom been studied.

In this study, the changes in higher heating value of wood due to thermal treatment are studied for two reasons. The first reason is to examine changes in one of the main fire-technical characteristics of wood due to its thermal modification. The second reason is to determine the heating value of thermally modified wood in context of its energetic valuation when it reaches the end of lifecycle.

Materials and methods

Heat treatment

Eight groups, each having 15 samples, were heat treated in a laboratory oven under atmospheric pressure in the presence of air. The treatment was performed for 3, 6, 9, and 12 h at two different temperatures of 180, and 200°C. The time for reheating the oven to the required temperature after inserting the samples was 10 min. After the treatment, the samples were placed in a desiccator over silica gel, where they were cooled.

Chemical analyses

The wood samples were mechanically disintegrated to sawdust. Fractions of 0.5 to 1.0 mm were extracted in a Soxhlet apparatus with a mixture of ethanol and toluene, according to ASTM D1107-96 [2013]. The lignin content was determined according to ASTM D1106-96 [2013] and the holocellulose content was determined according to Wise et al. [1946].

Determining the higher heating value

The higher heating value of a solid material indicates the amount of energy created when one kg of absolutely dry wood is burned and all water created in burning process is condensed. A Calorimeter system C 200 (IKA®-WERKE GmbH & Co. KG, Staufen, Germany) was used to measure the higher heating value. Evaluation was performed by Cal Win software. The samples were analyzed according to the standards STN ISO 1928:2003-07. From wood samples disintegrated to sawdust, tablets were prepared using the PIKE Crush IR (PIKE Technologies, Madison WI, USA) digital press. Samples were dried to absolute dry matter in a laboratory oven. The weight of the sample before combustion was approximately 0.5 g, and it was weighed on the analytical balance with an accuracy of 0.0001 g. In the calorimeter, samples were completely incinerated in a pure oxygen environment at 30 Bar. Benzoic acid was used as a thermochemical standard during the experiment.

The higher heating value of the sample was calculated as follows:

$$H_0 = (C \cdot \Delta T - Q_{\text{External 1}} - Q_{\text{External 2}}) / m \quad (1)$$

- m weight of fuel sample,
 ΔT increase in water temperature in the inner container,
 C heat capacity of calorimeter system,
 $Q_{\text{External 1}}$ correction value for the heat energy generated by the cotton thread as ignition aid,
 $Q_{\text{External 2}}$ correction value for the heat energy from other burning aids.

Results and discussion

Higher heating value (HHV) for untreated ash wood was $19.51 \text{ MJ} \cdot \text{kg}^{-1}$. This result is in accordance with previously published data by Krzysik [1975] and slightly lower than reported Porankiewicz et al. [2016]. As shown in Figure 1, heat treatment considerably increased the heating values of wood samples. The maximum value was measured in sample that was heat treated for 6 h at the temperature of 200°C . In this sample HHV increased approximately about 6.5% compared to untreated wood. Further increasing in treatment time slightly decreased its value.

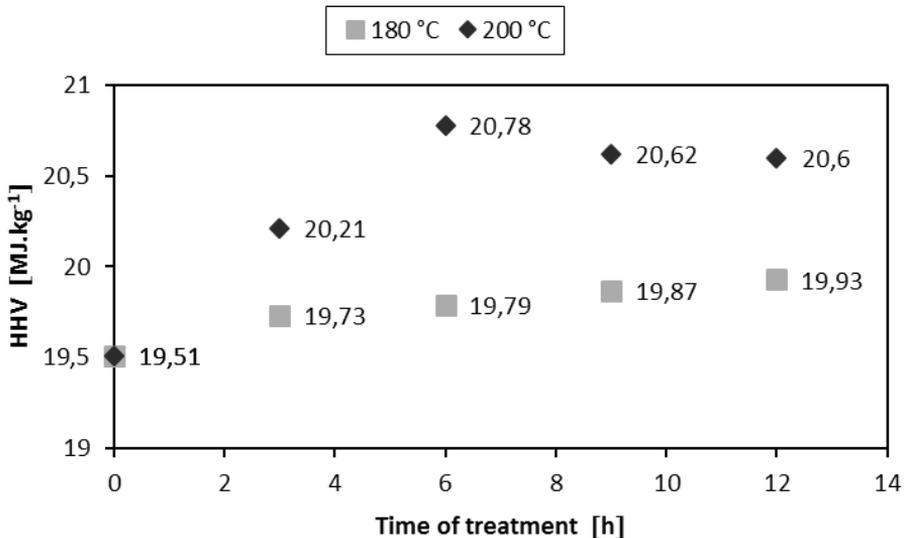


Fig. 1. Higher heating value (HHV) of thermally treated wood

Because energy content in different wood components is varied, chemical composition of wood is a main factor that affects the HHV. Lignin and

extractives that are rich in carbon and hydrogen have higher heating values. The higher content of oxygen in polysaccharides decreases its energy. In the literature, values of HHV for isolated wood components can be found. Published results confirm that polysaccharide components of wood have lower energy content than aromatic lignin. Geffertová [2009], Geffertová and Geffert [2011, 2013], Kára et al. [1997], White [1987] and Tillman [1978] determined the HHV of lignin in the range from 25.50 to 27.4 MJ·kg⁻¹, while for holocellulose it is ranging from 17.5 to 18.8 MJ·kg⁻¹.

The changes in chemical composition of thermally treated ash wood are shown in Table 1.

Table 1. Chemical composition of thermally treated ash wood [according to Výbohová et al. 2018].

Sample	Extractives	Lignin	Holocellulose
	(%)	(%)	(%)
Control	3.80 ±0.17	22.16 ±0.32	79.53 ±0.28
180°C, 3h	4.33 ±0.53	22.19 ±0.22	72.25 ±0.27
180°C, 6h	4.56 ±0.34	22.60 ±0.29	70.84 ±0.07
180°C, 9h	5.33 ±0.42	23.05 ±0.37	65.81 ±0.09
180°C, 12h	5.42 ±0.36	23.36 ±0.14	62.12 ±0.14
200°C, 3h	6.86 ±0.59	24.03 ±0.11	60.89 ±0.09
200°C, 6h	6.63 ±0.47	28.27 ±0.44	53.87 ±0.14
200°C, 9h	6.26 ±0.55	30.28 ±0.26	56.70 ±0.10
200°C, 12h	6.06 ±0.61	30.84 ±0.82	57.42 ±0.31

Data represent mean values ± standard deviations.

The content of extractives due to thermal treatment increased, the maximum in the sample after 3 h of heat treatment at a temperature of 200°C was determined. This was attributed to the release of degradation products of carbohydrates and lignin in the extraction mixture, or by their condensation reactions with the extractives originally present in untreated wood. This result was comparable to other studies [Wang et al. 2015; Severo et al. 2016]. According to Pelaez-Samaniego et al. [2014], the decrease in extractives in more severe conditions could be due to the cracking and devolatilization of lignin intermediates or due to the formation of extra char by further polycondensation.

In our study, positive correlation between HHV and the content of extractives was observed (Fig. 2). The correlation coefficient 0.8639 was determined. This result is in agreement with previously published data. Telmo and Lousada [2011] also found, that extractives positively contributed to the

heating value of wood. Fuwape [1990] reported that removal of the extractives caused reduction in the HHV.

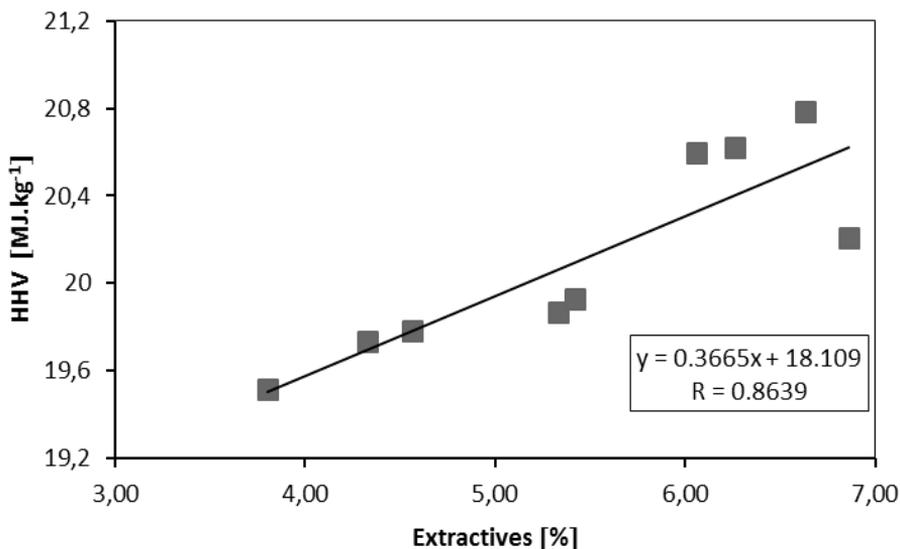


Fig. 2. Correlation between higher heating value and the content of extractives

An important role for heating value of wood plays the ratio of main wood components - lignin and holocellulose. Lignin is rich in carbon and hydrogen, which are the main heat producing elements. Hereby its heating value is higher than that of holocellulose. During the thermal treatment the increase in the content of lignin with an increase in severity of the treatment were observed. This increase is partially relative because the content of hemicelluloses decreases. The content of D-xylose, which in untreated wood was 18.05%, decreased after 12 h of thermal treatment at 200°C to 7.08% [Výbohová et al. 2018]. to literature [Nuopponen et al. 2004; Wikberg and Maunu 2004; Tumen et al. 2010; Da Silva et al. 2013] the increase in lignin content may have been also the consequence of the condensation reactions of lignin with hemicelluloses cleavage products or of lignin macromolecule cross-linking. The formation of more condensed structure of lignin was affirmed also in our thermally treated ash wood samples [Výbohová et al. 2018]. Degradation of hemicelluloses was also reflected in decrease in holocellulose content. The decrease was more noticeable at the temperature of 200°C. According to previously published data [González-Pena et al. 2009; De Moura et al. 2012; Wang et al. 2015; Kučerová et al. 2016; Výbohová et al. 2018] the degradation of polysaccharidic components of wood begins with degradation of hemicelluloses. In comparison to hemicelluloses, cellulose is more thermally stable, especially due to its crystalline structure. As shown in Figure 3, the ratio lignin/holocellulose increased with an increase in treatment time. This increase is most considerable by higher temperature.

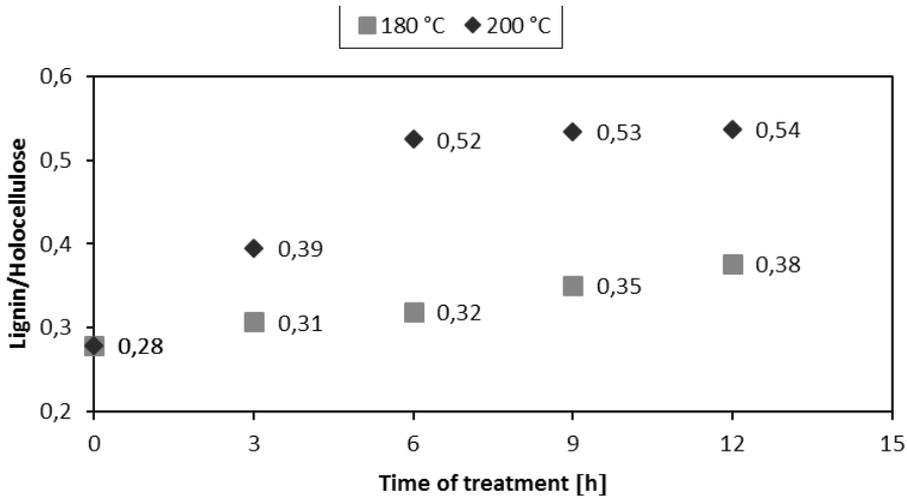


Fig. 3. The ratio of lignin/holocellulose content in thermally treated ash wood [according to Výbohá et al. 2018]

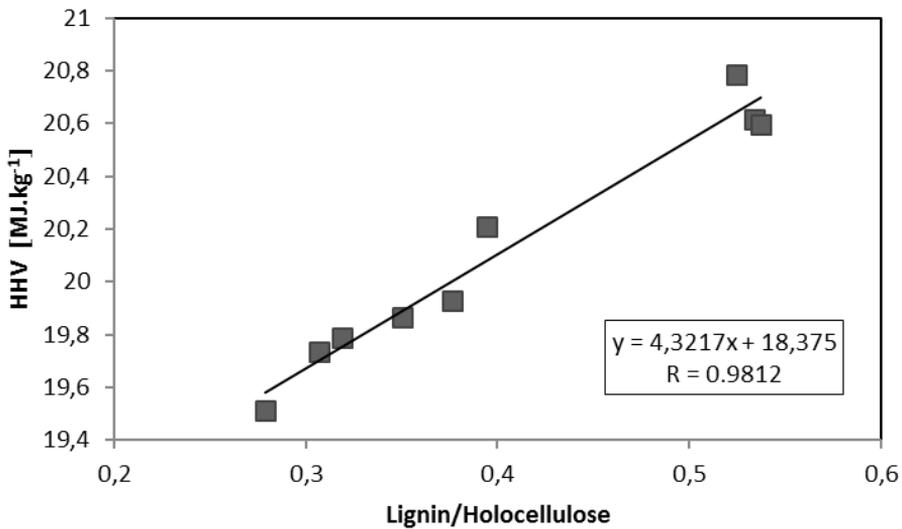


Fig. 4. Correlation between higher heating value (HHV) and the ratio lignin/holocellulose

Changes in the ratio of main wood components caused by heating affected the heating value of thermally treated wood (Fig. 4). The positive correlation between HHV and the ratio lignin/holocellulose was observed. The correlation coefficient 0.9812 was determined. Demirbas [2003] also found a highly significant correlation between the HHV of the various biomass materials and the lignin.

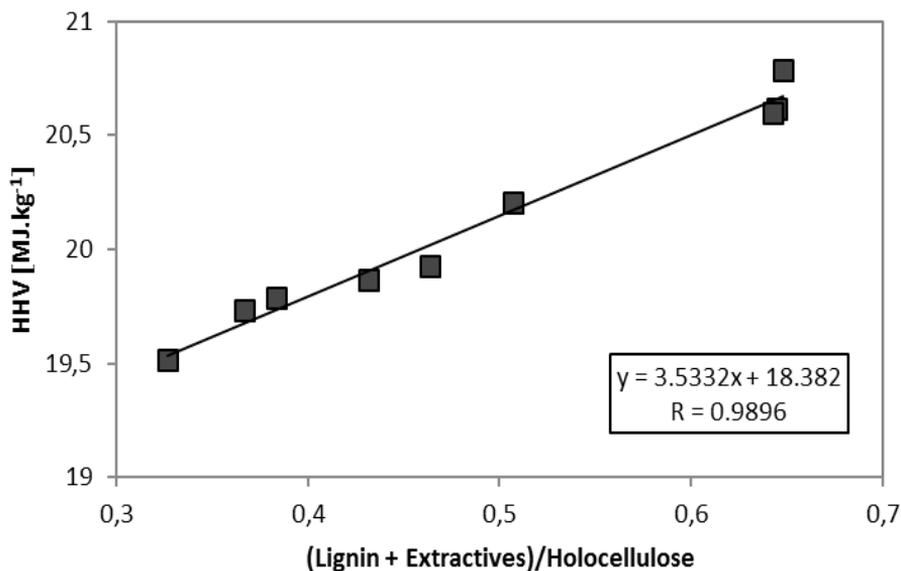


Fig. 5. Correlation between higher heating value (HHV) and the ratio (lignin + extractives)/holocellulose

As mentioned above the energetic value of lignin and extractives is higher than that of polysaccharides. Therefore it is obvious that higher content of lignin and extractives increased the HHV of wood whereas holocellulose has the opposite effect. For that reason we examined the correlation between HHV and the ratio of the sum of lignin and extractives content to holocellulose content (Fig. 5). We found the positive correlation with correlation coefficient 0.9896. Similar results have been reported for various softwood and hardwood species by Telmo and Lousada [2011].

Conclusions

Thermal treatment is an environmentally friendly process to improvements in dimensional stability, resistance to microbiological attack or color of wood. In this study, common ash (*Fraxinus excelsior* L.) wood was heat treated in an oven at the temperatures of 180°C, and 200°C under atmospheric pressure in the presence of air for 3, 6, 9, 12 hours, and the changes in higher heating value of wood due to thermal treatment were studied.

Higher heating value of wood samples increased with extension of time of treatment at the temperature of 180°C. At the temperature of 200°C the HHV considerably increased to 6 h of treatment, with increased time its value slightly decreased. It is a result of chemical changes in wood during treatment. Due to treatment the content of holocellulose decreased and the content of lignin and

extractives increased. Strong positive correlation between HHV and the ratio of the sum of lignin and extractives content to holocellulose content was observed.

Based on obtained results it can be concluded that the intensity of changes in HHV, which is an important fire-technical property of wood, depends on thermal treatment conditions. Besides that, thermal treatment positively affects the energetic valuation of wood when it reaches the end of lifecycle.

References

- Andor T., Lagaňa R.** [2018]: Selected properties of thermally treated ash wood. *Acta Facultatis Xylogologiae Zvolen* 60 [1]: 51-60. DOI: 10.17423/afx.2018.60.1.06
- Baeza J., Freer J.** [2001]. Chemical characterization of wood and its components. In: Hon, D.N.-S., Shiraishi, N. (Eds.). *Wood and cellulosic chemistry*, second ed. Marcel Dekker, Inc., New York, NY, 275-384
- Bubeníková T., Luptáková J., Kačíková D., Kačík F.** [2018]: Characterization of macromolecular traits of lignin from heat treated spruce wood by size exclusion chromatography. *Acta Facultatis Xylogologiae Zvolen* 60 [2]: 33-42. DOI: 10.17423/afx.2018.60.2.03
- Čabalová I., Kačík F., Lagaňa R., Výboňová E., Bubeníková T., Čaňová I., Ďurkovič J.** [2018]: Effect of thermal treatment on the chemical, physical, and mechanical properties of pedunculate oak (*Quercus robur* L.) wood. *BioResources* 13 [1]: 157-170
- Da Silva M.R., Machado G.D.O., Brito J.O., Calil Junior C.** [2013]: Strength and stiffness of thermally rectified eucalyptus wood under compression. *Materials Research – Ibero-American Journal of Materials* 16 [5]: 1077-1083. DOI: 10.1590/S1516-14392013005000086
- De Moura L.F., Brito J.O., Da Silva F.G.** [2012]: Effect of thermal treatment on the chemical characteristics of wood from *Eucalyptus grandis* W. Hill ex Maiden under different atmospheric conditions. *Cerne* 18 [3]: 449-455. DOI: 10.1590/S0104-77602012000300012
- Demirbas A.** [2003]: Relationships between heating value and lignin, fixed carbon, and volatile material contents of shells from biomass products. *Energy Sources* 25 [7]: 629-635. DOI: 10.1080/00908310390212336
- Dzurenda L., Pňakovič L.** [2016]: Influence of the burning temperature of the non-volatile combustible content of wood and bark of plantation-grown, fast-growing tree species upon ash production, and its properties in terms of fusibility. *BioResources* 11 [3]: 6464-6476. DOI: 10.15376/biores.11.3.6464-6476
- Dzurenda L., Ridzik L., Dzurenda M.** [2013]: Ash of biofuels – Green wood chips made of dendromass from willows and poplars grown on plantations. *Acta Facultatis Xylogologiae* 55 [1]: 111-118
- Esteves B.M., Pereira H.M.** [2009]: Wood modification by heat treatment: A review. *BioResources* 4 [1]: 370-404. DOI: 10.15376/biores.4.1.0370-0404
- Esteves B., Velez Marques A., Domingos I., Pereira, H.** [2013]: Chemical changes of heat treated pine and eucalypt wood monitored by FTIR. *Maderas. Ciencia y Tecnologia* 15 [2]: 245-258. DOI: 10.4067/S0718-221X2013005000020
- Fengel D., Wegener G.** [1984]: *Wood: chemistry, ultrastructure, reaktions*. Walter de Gruyter, Berlin

- Fuwape J.A.** [1990]: Effect of extractives on heating value of *Gmelina arborea*. Journal of Tropical Forest Science 4 [4]: 281-285
- Geffertová J.** [2009]: Spařovací teplo hydrolyzovaného brezového dřeva. Acta Facultatis Xylogiae 51 [2]: 63-69
- Geffertová J., Geffert A.** [2011]: Vřba *Salix viminalis* – klon ULV. Čast' 3: energetický obsah hlavných složek dřeva (Willow *Salix viminalis* - ULV clone. Part 3: Energy content of the major constituents of wood). Proceedings of: Selected processes at the wood processing: IX. international symposium, 7-9 September 2011. Štúrovo: 172-177
- Geffertová J., Geffert A.** [2013]: Zmeny smrekového dřeva vplyvom termického pôsobenia. (Changes in spruce wood due to thermal treatment). Proceedings of: Selected processes at the wood processing: X. international symposium, 11-13 September 2013. Ružomberok: 220-229
- González-Pena M.M., Curling S.F., Hale, M.D.C.** [2009]: On the effect of heat on the chemical composition and dimensions of thermally-modified wood. Polymer Degradation and Stability 94 [12]: 2184-2193. DOI: 10.1016/j.polymdegradstab.2009.09.003
- Hill C.** [2006]. Wood modification. Chemical, thermal and other processes. John Wiley and Sons, Chichester
- Hon D.N.S., Shiraiishi N.** [2001]: Wood and cellulosic chemistry. Marcel Dekker, New York
- Kačík F., Šmíra P., Kačíková D., Veřková V., Nasswetrová A., Vacek, V.** [2015]: Chemical alterations of pine wood saccharides during heat sterilisation. Carbohydrate polymers 117: 681-686
- Kačíková D., Bubeníková T., Kačík F., Veřková V., Eřtoková A., Ragan B.** [2017]: Comparison of thermal degradation course of selected wood species. JTACC+V4: 1st Journal of thermal analysis and calorimetry conference and 6th V4 (Joint Czech-Hungarian-Polish-Slovakian) thermoanalytical conference: 241-242
- Kára J., Srámek V., Hutla P., Stejskal F., Kopická A.** [1997]. Využití biomasy pro energetické účely (Biomass use for energy purposes). CEA, Praha
- Krzysik F.** [1975]: Nauka o Drewnie (Wood science), Państwowe Wydawnictwo Naukowe, Warszawa
- Kučerová V., Lagaňa R., Výbohová E., Hýřošová T.** [2016]: The effect of chemical changes during heat treatment on the color and mechanical properties of fir wood. BioResources 11 [4]: 9079-9094. DOI: 10.15376/biores.11.4.9079-9094
- Kúdela J., Andor T.** [2018]: Beech wood discoloration induced with specific modes of thermal treatment. Annals of Warsaw University of Life Sciences – SGGW. Forestry and Wood Technology 103: 64-69
- Nuopponen M., Vuorinen T., Jamsa S., Viitaniemi P.** [2004]: Thermal modifications in softwood studied by FTIR and UV resonance Raman spectroscopies. Journal of Wood Chemistry and Technology 24 [1]: 13-26. DOI: 10.1081/WCT-120035941
- Park S., Baker J.O., Himmel M.E., Parilla P.A., Johnson D.K.** [2010]: Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance. Biotechnology for Biofuels 3 [10]: 1-10
- Pelaez-Samaniego M.R., Yadama V., Garcia-Perez M., Lowell E., McDonald A.G.** [2014]: Effect of temperature during wood torrefaction on the formation of lignin liquid intermediates. Journal of Analytical and Applied Pyrolysis 109: 222-233. DOI: 10.1016/j.jaap.2014.06.008

- Poletto M., Zattera A.J., Forte M.M.C., Santana R.M.C.** [2012]: Thermal decomposition of wood: Influence of wood components and cellulose crystallite size. *Bioresource Technology* 109: 148-153
- Porankiewicz B., Tylman M., Wieczorek D., Bocho-Janiszewska A., Klimaszewska E., Wieloch G.** [2016]: The combustive heat of thirteen deciduous wood species. *BioResources* 11 [2]: 4402-4414.
- Santos R. B., Capanema E. A., Balakshin M. Y., Chang H., Jameel H.** [2012]: Lignin structural variation in hardwood species. *Journal of Agricultural and Food Chemistry* 60: 4923-4930. DOI: 10.1021/jf301276a
- Severo E.T.D., Calonego F.W., Sansígolo C.A., Bond B.** [2016]: Changes in the chemical composition and decay resistance of thermally-modified *Hevea brasiliensis* wood. *PLOS One* 11 [3]: e0151353. DOI: 10.1371/journal.pone.0151353
- Telmo C., Lousada J.** [2011]: The explained variation by lignin and extractive contents on higher heating value of wood. *Biomass and bioenergy* 35: 1663-1667
- Tillman D.A.** [1978]. *Wood as an energy resource*. Academic Press, New York
- 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. DOI: 10.15376/biores.5.3.1936-1944
- Výbohová E., Kučerová, V., Andor, T., Balážová, Ž., Veřková, V.** [2018]: The effect of heat treatment on the chemical composition of ash wood. *BioResources* 13 [4]: 8394-8408. DOI: 10.15376/biores.13.4.8394-8408
- Wang X., Wu Z., Fang L., Wei P., Fei B., Liu J.** [2015]: Changes of chemical composition, crystallinity, and Fourier transform infrared spectra of Eucalypt pellita wood under different vacuum heat treatment temperatures. *Forest Products Journal* 65 [7-8]: 346-351. DOI: 10.13073/FPJ-D-13-00099
- White R.** [1987]. Effect of lignin content and extractives on the higher heating value of wood. *Wood and Fiber Science* [19] 4: 446-452
- Wikberg H., Maunu S. L.** [2004]: Characterization of thermally modified hard- and softwoods by C-13 CPMAS NMR. *Carbohydrate Polymers* 58 [4]: 461-466. DOI: 10.1016/j.carbpol.2004.08.008
- Wise L.E., Murphy M., Addieco A.A.** [1946]: Chlorite holocellulose, its fractionation and bearing on summative wood analysis and on studies on the hemicelluloses. *Paper Trade Journal* 122 [3]: 35-43

List of standards

- ASTM D1106-96:2013** Standard test method for acid-insoluble lignin in wood
- ASTM D1107-96:2013** Standard test method for ethanol-toluene solubility of wood
- STN ISO 1928:2003-07** Tuhé palivá. Stanovenie spalného tepla a výpočet výhrevnosti (Solid fuels. Determination of combustion heat and calculation of calorific value)

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