

CHANGES IN GROSS CALORIFIC VALUE OF THERMALLY TREATED SCOTS PINE (*PINUS SYLVESTRIS* L.) AND SESSILE OAK (*QUERCUS PETRAEA* L.) WOOD AND THEIR EXPLANATION USING FTIR SPECTROSCOPY

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ABSTRACT

Scots pine (*Pinus sylvestris* L.) and Sessile oak (*Quercus petraea* L.) wood were thermally treated in an oven at the temperatures of 160°C, and 200°C under atmospheric pressure in the presence of air for 3 and 9 hrs. The mass loss and gross calorific value were determined. Non-treated wood samples achieved a gross calorific value of 22 193 J·g⁻¹ for pine wood and 19 277 J·g⁻¹ for oak wood. Whereas the calorific value of pine wood with increasing severity of treatment decreased, in the case of oak it increased. The mass loss increased with increasing treatment severity by both wood species. Mentioned differences in pine and oak wood behaviour using ATR-FTIR spectroscopy were explained. In the case of pine wood with increasing temperature and time of exposure a decrease of resin acids was observed. This may be contributed to decrease in GCV. In the case of oak wood, mainly at temperature of 200°C the degradation of hemicelluloses was observed that results in relative increasing in the lignin content with followed increase in the GCV.

KEYWORDS: Gross calorific value, mass loss, pine, oak, thermal treatment, FTIR.

INTRODUCTION

Thermal treatment is a very effective way of improving the most important properties of wood. As a result of thermally induced chemical changes in the macromolecular constituents, the physical and biological properties of the wood are altered. Its ability to absorb water will be greatly reduced therefore it is particularly suitable for the production of wooden items that are used in humid environments. Moreover, its dimensional stability and the resistance to microbiological attack will be enhanced. Thermally treated wood does not need any coating or chemical preservatives. During treatment it becomes discolored to darker shades similar

Gross calorific value

The GCV values of the test samples of thermally treated Scots pine wood and Sessile oak wood compared to the non-treated samples are shown in Fig. 3. The results of the determination of the GCV show different values between the non-treated samples of both wood species as well as the effect of duration and temperature of the thermal treatment. Higher GCV value was obtained for non-treated sample of Scots pine wood compared to Sessile oak wood. The difference between these values was of $2916 \text{ J}\cdot\text{g}^{-1}$ and it was caused by a different chemical composition of investigated wood species. It was found that energy content of different wood components varied depending on its elemental composition (Dietenberger and Hasburgh 2016, Geffertová 2009, Tillman 1978, White 1986). Lignin that is rich in carbon and hydrogen has a gross calorific value about $23.2 - 27.4 \text{ MJ}\cdot\text{kg}^{-1}$. For holocellulose that has higher oxygen content the GCV in the range $17.5 - 18.8 \text{ MJ}\cdot\text{kg}^{-1}$ was found. The highest GCV values (about $32 - 37 \text{ MJ}\cdot\text{kg}^{-1}$) were found in extractives. In general, hardwoods contain more hemicelluloses than softwoods but less lignin (Baeza and Freer 2001). Therefore the GCV of Sessile oak wood might be lower than Scots pine wood. In addition, Scots pine wood is characterized by a high resin content, which also increases its GCV. Other authors reported GCV values for Sessile oak of $19685 \text{ J}\cdot\text{g}^{-1}$ and Scots pine of $22360 \text{ J}\cdot\text{g}^{-1}$ (Nosek and Holubčík 2016, Alakangas 2005).

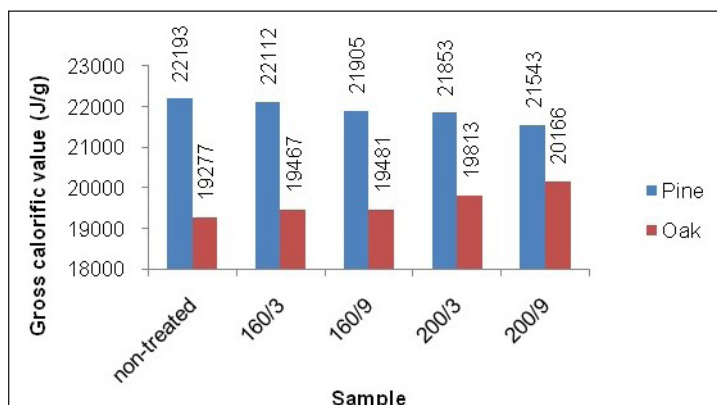


Fig. 3: Gross calorific value of Scots pine and Sessile oak wood.

Changes in GCV of Scots pine and Sessile oak wood caused by thermal treatment have an opposite trend. During the thermal treatment of the Scots pine wood a downward trend in GCV values with increasing temperature and treatment duration was observed. For sample P160/3, the GCV decreased by 0.35%, for sample P160/9 by 1.30%, for sample P200/3 by 1.53%, and for sample P200/9 by 2.93%, compared to non-treated Scots pine sample. On other hand, the GCV values increase with increasing temperature and thermal treatment duration in the case of Sessile oak wood. The GCV increase by 0.95% for sample O160/3, by 1.06% for sample O160/9, by 2.78% for sample O200/3 and by 4.61% for sample O200/9, compared to non-treated Sessile oak wood.

The GCV values shown in Fig. 3 were determined at 0% moisture content. We chose these conditions to make the results comparable to each other and not to be affected by the moisture content factor. This is the worst scenario in terms of fire protection. In general, the GCV values decrease with increasing moisture content. In practice, each wood product has a certain moisture

content, which also applies to thermo-wood, but in the case of thermally treated wood, there can be found the decrease in its equilibrium moisture content and consequently also decrease in its swelling and drying. Compared to non-treated wood, thermally treated wood absorbs significantly less moisture in the form of water vapor. The hygroscopic equilibrium moisture of thermally treated wood is about 30-50% lower than any of other wood, including impregnated wood. At a temperature of about 20°C, when the relative humidity of the air is about 60-70%, the equilibrium moisture content of the thermally treated wood is about 6-7%. If the air relative humidity rises to 80%, the equilibrium wood moisture content is about 8%. Thus, the moisture content of thermally treated wood is about 6-8% (Reinprecht and Vidholdová 2011). Tab. 2 shows the values of gross calorific value calculated to 8% moisture content.

Tab. 2 Resulting GCV at 8 % moisture content.

Sample	Gross calorific value (J·g ⁻¹)
P	20 418 ± 80.21
P160/3	20 344 ± 93.83
P160/9	20 153 ± 46.20
P200/3	20 105 ± 85.54
P200/9	19 820 ± 73.65
O	17 735 ± 42.57
O160/3	17 910 ± 52.72
O160/9	17 928 ± 18.66
O200/3	18 228 ± 91.10
O200/9	18 553 ± 28.38

It is known that chemical composition of wood varied due to its thermal treatment. In our experiments chemical changes using ATR-FTIR spectroscopy were studied (see Fig. 4 and Fig. 5).

In the Scots pine wood spectra, a decrease in the intensity of the typical absorption band for resin acids at 1693 cm⁻¹ can be observed with increasing temperature and treatment duration. Also, a decrease in peak intensity in the range of 3000-2800 cm⁻¹, which is attributed to the stretch vibrations of -CH in the -CH₂ and -CH₃ groups, may also be caused by the release of resin acids from wood. Many authors (Ekeberg 2006, Traoré 2018) found that resin acids are notable components in pine wood extractives. Furthermore, at the temperature of 200°C and treatment time 9 h the decrease in intensity of characteristic peaks for aromatic skeletal vibrations at wavenumber 1510 cm⁻¹ can be observed. This might be caused by degradation of lignin and aromatic extractives. Although lignin is considered to be the most thermally stable component of wood, some thermal degradation of lignin can occur at relatively low temperatures (Hill 2006, Brebu and Vasile 2010). From aromatic extractives pine wood contains mainly phenolic compounds, which cause darkening of wood in the light and have been implicated in the decay resistance of pine wood and also stilbenes, especially pinosylvin (Fengel and Wegener 1984, Ekeberg et al. 2006). The decomposition of extractives due to thermal treatment contributes to the mass loss. Because extractives have a highest GCV values from all wood components, their decomposition and release from wood decreases the calorific value of thermally treated wood

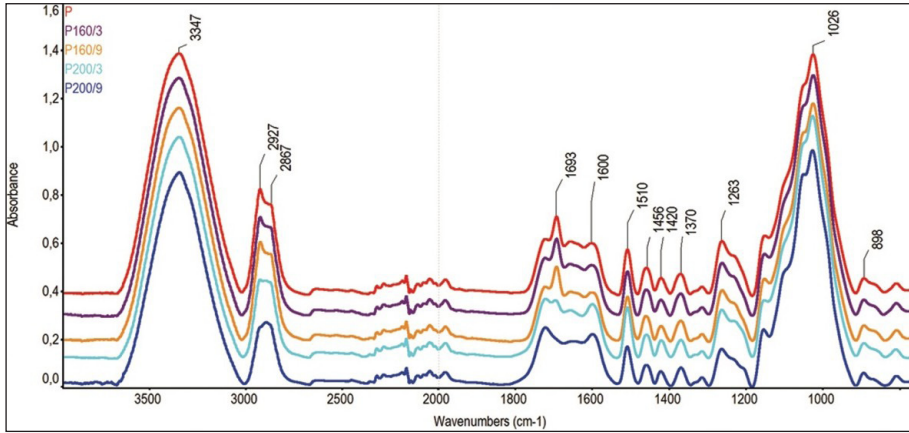


Fig. 4: FTIR spectra of non-treated and thermally treated Scots pine (*Pinus sylvestris* L.) wood.

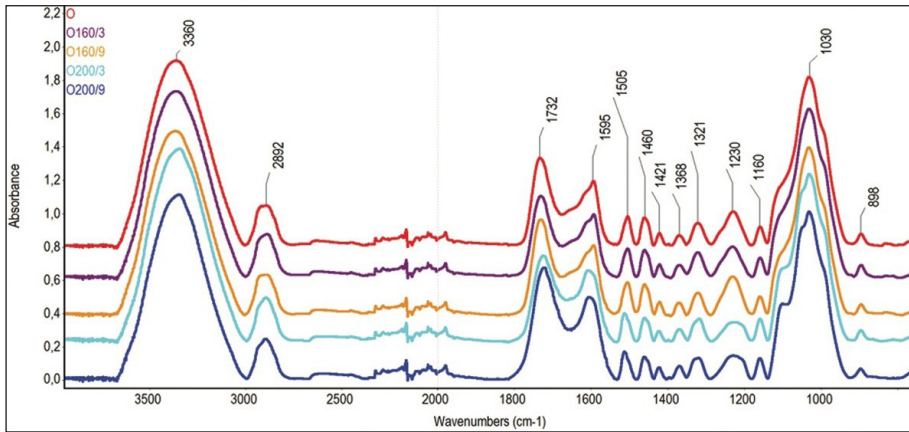


Fig. 5: FTIR spectra of non-treated and thermally treated Sessile oak (*Quercus petraea* L.) wood.

In the FTIR spectra of oak wood, the carbonyl peak at 1732 cm^{-1} initially at the temperature of 160°C and the time 3 hrs mildly decreased. The decrease at the beginning of the heat treatment might be due to the breaking of acetyl or acetoxy groups in xylan. However, at longer treatment time and at the temperature of 200°C it markedly increased. Heating in air causes oxidation of the hydroxyl groups resulting in an increase of carbonyl and subsequently of carboxyl groups (Fengel and Wegener 1984). Furthermore, with increasing treatment severity, the shift in a maximum from 1732 cm^{-1} to 1720 cm^{-1} was observed. This appearance also suggested that in the wood components new carbonyl or carboxyl groups are formed (Esteves et al. 2013).

In the non-treated Sessile oak wood spectra the characteristic peak for aromatic ring at 1505 cm^{-1} can be observed. The maximum of mentioned peak shifts to 1514 cm^{-1} with increasing temperature and treatment duration. A similar trend was observed also by Geffert et al. (2019) in the case of oak wood steaming. According to Faix (1991), this band

has maximum at about 1505 cm^{-1} for hardwood lignin and at about 1510 cm^{-1} for softwood lignin. Shifting the maximum of this peak to higher wavenumber can be due to the decrease of the methoxyl groups in lignin which would lead to a lignin more similar to softwood or to the loss of syringyl units. Syringyl monomers are generally less condensed by C-C bonds than guaiacyl monomers and are more liable to be released by a thermal degradation (Faix et al. 1990).

The decrease in the intensity of absorption band at 1243 cm^{-1} in spectra of oak wood suggests that mainly at the temperature of 200°C the degradation of more labile hemicelluloses occurred. The process begins with the partial degradation of long hemicellulose chains into shorter ones and then follows with their decomposition through monosaccharides to volatile products (Hill 2006). In accordance with the findings of other authors (Výbohá et al. 2018, Čabalová et al. 2018) it can be assumed that the earlier degradation of hemicelluloses increases the proportion of lignin in Sessile oak wood relatively. According to Sun et al. (2019) increase of the relative content of lignin and extractives after degradation of hemicelluloses by thermovacuum treatment of eucalyptus wood results in decrease in O/C ratio. Because hemicelluloses have a low calorific value and lignin, on the other hand, a high calorific value, GCV values of Sessile oak wood increase due to degradation of hemicelluloses with increasing temperature and time of thermal treatment.

CONCLUSIONS

The effect of thermal treatment under various process conditions (at temperatures of 160 and 200°C , duration of 3 and 9 hrs) on the gross calorific value of Scots pine (*Pinus sylvestris* L.) and Sessile oak (*Quercus petraea* L.) wood were studied. The value of GCV of untreated Scots pine wood was higher than in the case of Sessile oak wood. It is because softwoods contain more lignin and resins than hardwoods and just these components increase the calorific value of wood. The different composition of Scots pine and Sessile oak wood also influences their behaviour during thermal treatment. With increasing temperature and thermal treatment duration, the mass loss of both tree species increased but at 160°C the mass loss was higher for Scots pine samples, while at 200°C for Sessile oak samples. Whereas the calorific value of Scots pine wood with increased severity of treatment decreased, in the case of Sessile oak it increased. Mentioned differences in Scots pine and Sessile oak wood behaviour using ATR-FTIR spectroscopy were explained. In the case of Scots pine wood with increasing temperature and time of exposure a decrease of resin acids was observed. The decomposition of these compounds contributes to decrease in GCV. In the case of Sessile oak wood, mainly at temperature of 200°C the degradation of hemicelluloses was observed that results in higher mass loss at this temperature. Reducing the hemicelluloses content of the wood, the lignin content increases relatively, resulting in an increase in the GCV.

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