Spectral Range and Wood Surface Impacts on Equilibrium Moisture Content Estimation in Thermally Modified Beech Wood by FT-NIR Spectroscopy

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Abstract. Fourier transform near-infrared (FT-NIR) spectroscopy and partial least squares regression (PLS-R) were tested for the possibility of equilibrium moisture content (EMC) prediction in thermally modified beech wood (Fagus moesiaca C.). The samples were modified for 4h at temperatures of 170, 190 and 210 °C. After thermal modification, the samples were kept in a climatic chamber until EMC was reached. FT-NIR spectra (100 scans and 4 cm-1) were collected on the cross-section and radial surfaces at four points. PLS –R models were developed for four spectral regions: the first overtone, the second overtone, the third overtone and the combination band region. Applied thermal treatment caused a decrease of EMC by 42 % at 170 °C, by 53 % at 190 °C, and by 62 % at 210 °C. Principal component analysis (PCA) indicated that there is a difference both between treatments and between wood surfaces. The results of the spectra taken from the radial surface were, in all models, better than the spectra of the cross-section. Related to chemical changes, the first and second overtone region play an important role in the calibrations. The best prediction models for EMC of thermally modified beech wood were obtained from radial surface spectra in the first (Rp2=0.86, RPD=2.69) and second overtone region (Rp2=0.87, RPD=2.70). The obtained results could contribute to the development of predictive models in monitoring of EMC which could significantly improve the quality of industrial production of thermally modified wood.

1. Introduction
Thermal modification at temperatures up to 260 °C causes structural and chemical transformations which can significantly modify wood properties. These temperatures degrade the hemicelluloses which are the main factors of hygroscopicity in wood [1]. The lowered hygroscopicity leads to the reduction of equilibrium moisture content (EMC) and the level of this reduction depends on several factors: applied temperature and time, wood species, type of heating medium, etc. [2] reported that this reduction in beech wood averages at 30 % and [3] showed that, by using the same parameters of conditioning, beech wood showed a greater EMC reduction than spruce wood.

Manufacturing processes of thermally modified wood in the current wood industry involve various procedures such as regimes, sorting, moisture content monitoring, scaling and grading of wood.
products. In order to optimize these processes, it is necessary to have accurate real-time knowledge about thermally modified wood products properties and characteristics. Moisture content is one of the most important properties of wood because it affects the final quality of a thermally modified product. When wood adsorbs or loses water, significant changes in wood mechanical or physical properties occur. The techniques used to monitor moisture content in thermally modified wood must be fast, efficient and inexpensive. Current methods are mostly used in laboratories and are destructive, expensive and time-consuming.

Using an FT-NIR spectroscope, as a non-destructive method, has taken a significant role in determining the quality of wood and wood products. Apart from assessing the physical and mechanical properties [4, 5, 6], the FT-NIR method, along with PLS-R (partial least square – regression) analysis, was researched for predicting moisture content of non-modified and thermally modified wood. [7] reported a very high coefficient of determination (R2=0.99) between the predicted and measured values of moisture content in small samples of spruce wood. [8] however reported a much lower correlation (R2=0.58) while examining moisture content in red oak wood. [9] concluded that wood surface had an important role in assessment of moisture content. [10, 11] confirmed that reducing of spectral range did not significantly affect quality loss in their models. On the other hand, there are studies about the application of FT-NIR spectroscopy in assessment of moisture content in thermally treated wood. [12, 13] reported high values of statistical parameters for certain species of genera Eucalyptus (Eucalyptus globules and Eucalyptus urophylla) and Pinus (Pinus pinaster and Pinus ocarpa). [13] also reported that quality of their model in assessment of MC of kiln-treated wood was much lower compared with wood treated in autoclave.

Considering the importance of thermal modification and the assessment of its properties by using non-destructive methods, and also the fact that beech (Fagus moesiaca C.) is the most important industrial wood species in Balkan peninsula, the focus of this research was the assessment of EMC of thermally modified beech wood by using NIR spectroscope. A secondary goal of this paper was to show the influence of wood surface and of the reduced spectral range on the quality of models. The results could contribute to the development of predictive models in monitoring of moisture content which could significantly improve the quality of industrial production of thermally modified wood.

2. Materials and methods

2.1. Materials

For this research, five beech logs were cut from Goč mountain forest in western Serbia. Each log was cut into four radial boards 30 mm thick. In total, 20 boards without visible knots and deformations were cut. The boards were each cut into four samples (one modified and three for thermal treatment). The samples had clearly defined anatomical directions and had no visible defects. They were cut into 20x20x20mm samples used for assessing EMC.

2.2. Thermal modification of wood and EMC testing

Thermal modification was carried out in a laboratory chamber (1 m3, ± 1 °C sensitivity, water vapor atmosphere), where samples were exposed to temperatures of 170, 190, or 210 °C. It took approximately twenty-four hours to heat the samples from room temperature to the treating temperature, after which the temperature was kept constant for four hours [6]. The chosen schedules are often used in industrial thermal modification of beech timber. After the thermal treatment, the samples that did not have visible cracks and defects were used for recording the FT-NIR spectra and moisture content assessment. There were a total of 180 specimens (90 unmodified + 90 thermally modified).

The unmodified and thermally modified samples were conditioned at 23 °C and relative humidity of 50 % until EMC was reached. EMC were determined by oven-drying method after conditioning.
2.3. Near-infrared spectroscopy and multivariate analysis

FT-NIR spectra were collected after thermal treatment with a Nicolet Nexus 670 FT-IR spectrometer equipped with a Thermo Nicolet Smart Near-IR UpDrift probe in the wavenumber range from 11000–4000 cm\(^{-1}\) using the default parameters. The FT-NIR spectra were acquired by an integrating sphere scanning an area of about 7 mm in diameter. For each scanning point, 100 scans (4 cm\(^{-1}\)) were collected and averaged into a single spectrum. Four spectra on the cross-section and radial longitudinal face of test samples were averaged to one average spectrum per face. The measurements were taken on a planed surface.

PLS-R analysis (Unscrambler 9.7) was applied in the prediction of EMC by FT-NIR spectroscopy. PLS-R calibration was done with two subsets (calibration set and validation set) with a maximum ten latent variables (LV). Samples for calibration and validation sets were divided manually. First, the samples were ranked in ascending order of their dependent variables and every third or fourth sample was taken into the validation set. Secondly, NIR variables were regressed against the values of EMC by cross-validation of five randomly chosen groups. Different data treatments were evaluated for the spectral data: first derivative (1stDer), second derivative (2ndDer), standard normal variate (SNV), normalization (norm.), multiplicative scatter correction (msc) and combinations of all. First derivative was obtained by using a 9-point filter and a second order polynomial as well as the Savitzky-Golay algorithm [14]. For the 2nd derivative, a 15-point filter and a second order polynomial were used. Outlier samples were identified by Student residuals and leverage value plot analyses. Model efficiency was then tested by the validation set. Beside the full FT-NIR region, PLS –R models were developed for four spectral regions: the first overtone, the second overtone, the third overtone and the combination band region [15].

The evaluation of the statistical models was done based on RPD (residual prediction deviation or ratio of performance to deviation), and two groups were created for model classification: preliminary screening, 1.5≤RPD≤2.0; and screening, 2.0<RPD≤5.0; The RPD was introduced by [16] several and is calculated as the ratio of two standard deviations: the standard deviation of the reference data for the validation set and the standard error of prediction (from cross-validation or test set validation).

In this paper, chemometrical properties of wood were examined by principal component analysis (PCA). PCA is one of the dimensional reduction techniques that reduce the difficulties in interpreting high and low-dimensional signals. When the data are distributed in a multidimensional space, it is possible to find an axis that can reduce the dimension most efficiently and to reduce the dimension of that axis. In other words, it is essential to find the optimal axis among several axes, and the exact axis can be obtained by the PCA [17,18].

3. Results and discussion

3.1. EMC of thermally modified beech

Table 1 shows the average values of EMC of unmodified and thermally modified beech wood, after conditioning, and the basic statistical parameters. Average EMC of unmodified samples was 9.56 % and this research confirmed that thermal modification decreases the hygroscopicity. Applied thermal treatment caused a decrease of EMC by 42 % at 170 °C, by 53 % at 190 °C, and by 62 % at 210 °C. The Tukey HSD test (with 95 % probability) indicated a significant difference (F=204.3 p<0.05) in EMC between the used temperatures. The decreases and variations of EMC are similar to those reported by [19] who also researched of beech wood.
According to [20], the reason for lower absorption water could be the altered chemical composition after heat treatment. Beside the changes of cellulose, extractives and lignin, high temperature range degrades hemicelluloses in the wood, the main component responsible for its hygroscopic character. This will cause reduction in moisture adsorption capacity, resulting in lower equilibrium moisture content (EMC), and radial and tangential swellings [20]. Other authors reported that reaction of lignin polycondensation [21] or the increase of crystallinity of cellulose chains [22] could also be the cause of lower EMC after thermal modification.

3.2. Estimation of EMC by FT-NIR spectroscopy

Obtained values of coefficient of determination and RPD in the prediction test (Rp2) ranged from 0.75 (RPD=1.80) in the spectra recorded on cross-section surface by using the absorbance of wavelengths in third overtone range, to those recorded in radial surface in the entire NIR range (Rp2=0.89, RPD=2.92) – Table 2.

Table 1. Equilibrium moisture content of thermally modified beech wood after conditioning (t=23 °C; φ=50 %)

| Statistical indicators | EMC (%): Unmodified | 170 °C | 190 °C | 210 °C |
|------------------------|---------------------|--------|--------|--------|
| N                      | 90                  | 30     | 30     | 30     |
| x (%)                  | 9.56                | 5.56   | 4.52   | 3.68   |
| SD (%)                 | 0.28                | 0.39   | 0.34   | 0.32   |
| Min (%)                | 8.82                | 4.6    | 3.8    | 2.62   |
| Max (%)                | 10.09               | 6.64   | 5.42   | 4.54   |

N – number of samples; x – average value; SD – standard deviation; Min – minimum; Max - maximum

Table 2. Summary statistics of the calibration and prediction models for EMC of thermally modified beech wood samples

| FT-NIR region | Wood surfaces | Pre-treatment | Calibration | Prediction |
|---------------|---------------|---------------|-------------|------------|
|               |               |               | No. of samples | SEC | SECV | R² | No. of samples | SEP | R² | RPD |
| CbR           | CS            | norm          | 51           | 0.48 | 0.53 | 0.8 | 27           | 0.55 | 0.79 | 2.1 |
|               | RA            | msc           | 51           | 0.38 | 0.41 | 0.87 | 28          | 0.45 | 0.85 | 2.57 |
| FoR           | CS            | msc+1         | 52           | 0.43 | 0.46 | 0.85 | 28          | 0.53 | 0.8 | 2.17 |
|               | RA            | norm          | 51           | 0.35 | 0.38 | 0.89 | 27          | 0.43 | 0.86 | 2.69 |
| SoR           | CS            | snv           | 51           | 0.43 | 0.47 | 0.85 | 27          | 0.5 | 0.85 | 2.32 |
|               | RA            | raw           | 51           | 0.34 | 0.37 | 0.89 | 27          | 0.43 | 0.87 | 2.7 |
| ToR           | CS            | msc+1         | 51           | 0.55 | 0.6 | 0.76 | 28          | 0.64 | 0.75 | 1.8 |
|               | RA            | snv           | 52           | 0.46 | 0.5 | 0.82 | 27          | 0.56 | 0.8 | 2.05 |
| Full range    | CS            | 1st           | 51           | 0.39 | 0.43 | 0.86 | 28          | 0.46 | 0.85 | 2.52 |
|               | RA            | 2nd           | 52           | 0.28 | 0.3 | 0.93 | 27          | 0.39 | 0.89 | 2.92 |

Key: FoR-first overtone region, SoR-second overtone region, ToR-third overtone region, CbR-combination band region, CS–cross-section, RA– radial section, R²-determination coefficient of calibration set, SEC-standard error of calibration, SECV-standard error of cross-validation, Rp² (value calculated to show the ability of the calibration to account for the variation in the validation set)-determination coefficient of validation set, SEP (the measure of the calibrations ability to predict wood properties in samples not used in the calibration set)- standard error of prediction and RPD (the ratio of two standard deviations: the standard deviation of the reference data for the validation set and the standard error of prediction from cross-validation or test set validation) - residual prediction deviation or ratio of performance to deviation

In both wood parts, the highest statistical parameters were obtained by using the full NIR range. As for individual reduced regions, the best prediction models for EMC on cross-section of thermally modified wood were obtained from spectra in second overtone range (Rp2=0.85, RPD=2.32), while on radial surface it was the first (Rp2=0.86, RPD=2.69) and second overtone range (Rp2=0.87, RPD=2.70–Fig. 1). Obtained values of statistical indicators were mostly in the line of the published values of prediction of EMC of oven treated eucalypt and pine [13]. [12] tested the possibilities of application of NIR in prediction of EMC of eucalypt and pine treated at atmospheric pressure with

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presence of air. The authors reported values of coefficient of determination in calibration samples for eucalypt-0.94 and for pine-0.93 and these values are significantly higher as compared to the data obtained in this research. On the other hand, statistical indicators obtained with coniferous species were somewhat better considering that they have a more homogeneous structure.

![Figure 1. Calibration plot for EMC of thermally modified beech wood using NIR variables from second overtone region](image)

Table 2. shows that wood surface affected the quality of models predicting the EMC. Much better parameters in all wavelength regions were obtained by recording the spectra on radial surface. [8] found that models built to estimate moisture content of red oak (Quercus spp.) lumber from spectra collected on cross-section were better than models based on spectra recorded over tangential or radial sections. These authors reported that better prediction models obtained from cross section or longitudinal (radial or tangential) sections could also be due to the distinct anatomical differences within the growth rings. The difference between longitudinal and cross-sections can also be due to surface roughness differences, which relate to particle size differences and influence radiation scattering [15]. This can result in spectral changes such as baseline offset as well as slope and band shift [15]. According to [22], the roughness of the cross-section is higher than the roughness of the tangential and radial section. Also, cross-sections consist of transversal sections of tracheid cells, which have a longitudinal axis that is parallel to the direction of the NIR incident radiation. Therefore, the NIR radiation can travel further into the wood, causing an increase in absorbance [15].

3.3. Spectroscopic characterization and principal component analysis

Showed results of the influence of spectral range on the quality of statistical models were in line of the published results of [9]. Their research reported that the first and second overtone regions were the most informative and that they had a low noise level. Recorded FT-NIR spectra of unmodified and thermally modified beech wood indicate that absorbance increases with temperature (Fig. 2). This is caused by the darker tone of the wood [24]. The biggest change in absorption was found in the second overtone range, on -CH groups at 8300 cm\(^{-1}\) and in first overtone region on -OH groups at 7100 i 5150 cm\(^{-1}\). However, the raw spectra do not give enough information about spectral changes relative to applied treatment. Because of that, FT-NIR spectra were analyzed in the second derivative mode (2nd; not shown). The differences in spectral lines and absorption at 5800 and 5865 cm\(^{-1}\) indicate a degradation of carbohydrates and a deacetylation of poliosa. Differences before and after treatment were found on -OH groups in amorphous (7000 cm\(^{-1}\)), semi-crystalline (6775 cm\(^{-1}\)) and crystalline (6460 cm\(^{-1}\)) regions of cellulose. This result is caused by degradation of -OH groups under high
temperatures. Differences observed at 5980 cm\(^{-1}\) i 6900 cm\(^{-1}\) show the modification of lignin [15]. The obtained 2nd spectra are in line with the results of [5,6,24] for beech wood.

![Normalized FT-NIR spectra of beech samples from radial surface after thermal modification](image)

**Figure 2.** Normalized FT-NIR spectra of beech samples from radial surface after thermal modification

In this paper, PCA were carried out with original spectra obtained in the radial and cross-section surfaces of the thermally modified wood, to carry out a preliminary evaluation of the behavior of the spectra and possible separation of the specimens according to differences temperature and wood surfaces. Three clusters indicated that there is a difference between treatments as a result of different level of chemical changes (Fig. 3). The two main components together account for 100 % of the variability of the analyzed data, 91 % are explained by the main component 1 (PC1) and 9 % are explained by the main component 2 (PC2). Also, there is a difference between the cross section and radial surface at all temperatures, which is a consequence, beside of the anatomical structure, and the different colors of the wood surface [21].

![PCA score plot of normalized NIR spectra recorded on cross-section (CS) and radial (RA) surface of thermally modified beech samples](image)

**Figure 3.** PCA score plot of normalized NIR spectra recorded on cross-section (CS) and radial (RA) surface of thermally modified beech samples
4. Conclusions
The applied thermal modification reduced hygroscopicity of beech wood for 42 to 62%. The obtained results show that it is possible to predict EMC of thermally modified beech wood by using NIR spectroscopy and PLS regression. The anatomical structure and color of the wood surface lead to different models of FT-NIR spectra taken from cross section and radial surface. Statistical parameters were better in predicting EMC on radial surface. According to PCA analysis, there is a difference between treatments as a result of different level of chemical changes. Beside full FT-NIR range, very good models were also obtained from reduced wavelength ranges in different overtone regions. In general, according to statistical indicators, most models could be used for screening (2.0<RPD<5.0). This is particularly visible in first and second overtone regions – regions with most important chemical compounds susceptible to modification of wood under high temperatures. The possibility of using a reduced (“narrow”) spectral range from radial surface enables using a smaller, faster and cheaper spectrometer for monitoring EMC of thermally modified wood.

The obtained results can be useful for the wood industry as it provides accurate estimates of the equilibrium moisture content of thermally modified wood, assisting in the definition of regime parameters, optimizing industrial processes and the consumption of raw material.

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