




Classification of the hot air heat treatment degree of larch wood using a multivariate analysis of near-infrared spectroscopy

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Abstract

In this study, hot air heat treatments of larch (*Larix kaempferi*) wood specimens were conducted at various temperatures (160–220 °C) and times (1–12 h) to classify the degree of hot air heat treatment using near-infrared (NIR) spectroscopy. NIR reflectance spectra were acquired from specimen cross-sections and were then preprocessed using the standard normal variate. Hierarchical clustering analysis (HCA) using the complete linkage and squared Euclidean distance was conducted to classify the three degrees of heat treatment. A principal component score plot of the NIR spectra was well grouped by the HCA grouping result, and the first component reflected the cluster analysis grouping well. A partial least squares discriminant analysis was performed to develop the discriminant regression model of the three heat treatment degrees. The R^2 and root mean square error of validation were 0.959 and 0.191, respectively. NIR is considered to be a good candidate to routinely measure the degree of hot air treatment for larch wood.

Keywords Larch · Wood heat treatment · Discriminant analysis · Multivariate analysis · Near-infrared spectroscopy

Introduction

Heat treatment is a wood modification technique that changes various physicochemical properties. When sawn lumber is exposed to high-temperature media, air, nitrogen, steam, or oils, ranging from 160 to 260 °C for several hours [1], the thermochemical conversion of the major components of the wood, including cellulose, hemicellulose, and lignin, changes the physical properties of the wood, such as the color, specific gravity, strength, decay resistance, equilibrium moisture content, and dimensional stability [2, 3]. Since wood is a complex compound of various chemical substances, chemical changes in wood are different according

to the time and temperature of the heat treatment [4]. It has been reported that permanent effects occur at temperatures between 185 and 230 °C for 2–3 h [5] or 150–240 °C for 0.5–4 h [6] for some species. These studies established that the treatment temperature and time highly affect the degree of thermal modification of wood and, hence, that quality control of heat-treated wood products may be accomplished by varying the treatment temperature and time.

In the last decade, heat-treated wood production has gradually increased to more than 159,000 m³ in the EU [7]. Heat-treated wood now has wide applications, for example, as decking, flooring, furniture, among other uses. The customer and producer both want guaranteed heat-treated products to use. However, the definition of the heat treatment intensity or heat treatment degree is ambiguous. The actual degree of treatment from high temperatures for a short time compared with low temperatures for a long time is unknown. Color measurement after heat treatment was proposed for heat treatment classification due to the visual darkening of heat-treated wood [8, 9]. However, there were limitations in predicting the mechanical properties using color changes of heat-treated wood due to the various complex chemicals of wood [10, 11].

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In near-infrared (NIR) spectroscopy, the high overlap of absorption bands means that there are no distinct peaks directly linked to specific major components in the cell wall. Thus, a multivariate statistical analysis, such as principal component analysis (PCA) or partial least squares regression (PLSR), usually generates powerful results for prediction and classification. NIR spectroscopy has been reported to produce good results for evaluating the mechanical, physical, chemical properties of wood [12, 13]. Recently, evaluations of the thermochemical changes using NIR spectroscopy have been studied [14–16]. Successful classification studies for various heat treatment degrees of heat-treated wood specimens using a clustering analysis have been reported.

In this study, the changes of the NIR spectra due to various heat treatment conditions were investigated. Additionally, heat-treated larch wood specimens were classified by NIR spectroscopy. The specimens, which were exposed to various temperatures (160–220 °C) and treatment times (1–12 h), were classified by hierarchical clustering analysis (HCA). The clustering was applied to scores and resulted in PCA.

Materials and methods

Larch (*Larix kaempferi*) wood was used for this study. Eighty-four specimens (7 temperatures × 12 h) were cut into 30 × 30 × 120 mm samples (longitudinal × radial × tangential direction). Before the heat treatment, the specimens were oven-dried at 105 °C. The heat treatment conditions were set at 160–220 °C every 10 °C for 1–12 h using a laboratory oven with an air circulation fan. After warming up the oven to the target heat treatment temperature, 12 oven-dried specimens, which were maintained 105 °C, were placed into the oven. A specimen was taken out from the oven every hour during the heat treatment and cooled in a desiccator (25 °C, 0% relative humidity) before acquiring the NIR spectra.

An NIR spectrometer (NIR QUEST 256-2.5, Ocean Optics, USA) was used to acquire the reflectance spectra from cross-sections of the specimens using a fiber optic probe. The optical probe had seven ring-arranged optical fibers. The outer six optical fibers illuminate the surface of the specimen with NIR rays, and the central optical fiber delivers the reflected rays to the spectrometer. The diameter of the illuminated beam was 3 mm. A 20-W tungsten halogen lamp (HL 2000-FHSA, Ocean Optics) was used. To enhance the signal-to-noise ratio, 15 scans were averaged over the wavelength range of 1000–2400 nm at each NIR acquisition point. Three NIR reflectance spectra were acquired for each specimen.

The Unscrambler 10.3 software (CAMO, Norway) was employed for spectral math preprocessing and multivariate analysis. All of the acquired spectra were preprocessed

by a 3-point moving average and standard normal variate (SNV) in sequence. HCA was conducted using the hierarchical complete linkage as the similarity evaluation between clusters and the squared Euclidean distance as the distance evaluation. Three distinct clusters were identified in HCA. PCA was conducted to extract the data structure. Then, the clusters were applied to score the results of the PCA for comparing the score distributions of the clusters. Partial least squares discriminant analysis (PLS-DA) was performed on the preprocessed spectra using the HCA result. PLS-DA is a discriminant analysis method in which a regression analysis is performed by assigning an arbitrary class value to clusters. In this study, the three clusters analyzed by HCA were assigned –1 (Cluster A), 0 (Cluster B), and 1 (Cluster C) to the class. Since we obtained three spectra from one specimen, we divided them into a 2:1 ratio and created a total of 168 calibration sets and 84 validation sets. In the development of the PLS-DA calibration model, severe outliers were excluded. The reliability of the discriminant model developed by PLS-DA was determined using the coefficient of determination (R^2) and root mean square error (RMSE).

Results and discussion

The heat treatment temperature applied in this study is above the thermal decomposition temperature of the main wood component. The mass loss of wood varies by species and heat treatment conditions, which allows a comparison between heat treatment conditions. Hemicellulose begins to be degraded by deacetylation at high temperatures, which acts as a catalyst to accelerate the degradation of polysaccharides [17–19]. In addition, dehydration removes the hydroxyl group [20]. This is due to the accelerated decomposition of polysaccharides in wood during the heat treatment. Zaman et al. [21] reported that the total amount of carbohydrates decreased with increasing heat treatment time during a 205–230 °C heat treatment, and the amount of glucose relative to the total carbohydrate amount increased. They suggested that the thermal stability of β -D-glucopyranose, which constitutes cellulose, is higher than that of hemicellulose. Our results show that the mass loss of specimens exposed to temperatures above 210 °C is higher than that of other specimens. The mass loss was only slightly increased below 200 °C (maximum 4.5%), with 210 and 220 °C heat treatments showing significantly higher mass loss (11.8 and 24.7% for 210 and 220 °C, respectively) according to time (Fig. 1). This result may be mainly caused by thermal conversion inducing carbonization or a reduction reaction during the heat treatment.

The NIR region has highly overlapping, wide absorption bands as well as complex combination bands. This makes it difficult to analyze the NIR spectra and find information

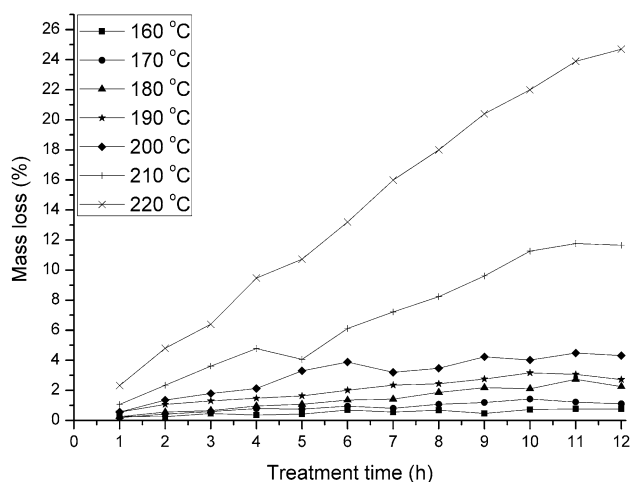


Fig. 1 Mass loss by heat treatment

from the raw spectra; however, mathematical preprocessing helps solve this problem. Figure 2 shows the standard normal variated NIR reflectance spectra of specimens treated at 160–220 °C for 12 h. At a higher degree of heat treatment (210 and 220 °C), preprocessed reflectance spectra were located at the relatively high position of 1400–2000 nm. The effect of heat treatment on a wood substance remarkably appeared at lower wavelengths in the NIR region. In the 1000–1350 nm region, the preprocessed reflectance remarkably changed as the heat treatment temperature increased. It is estimated that the change in the NIR absorption occurred due to thermal decomposition and the deacetylation reaction of hemicellulose as the temperature increased because the region is composed of the absorption of the second overtone of C–H stretching vibration at 1157 and 1171 nm as

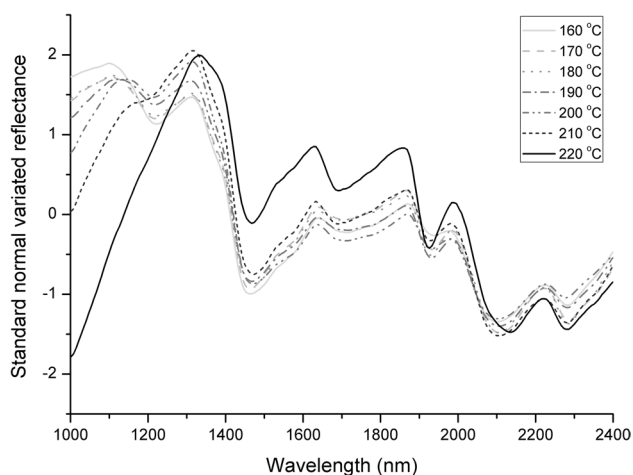


Fig. 2 Representative preprocessed reflectance spectra (three-point moving average, standard normal variate) of larch specimens by treatment temperatures (treatment time = 12 h)

well as the first overtone of C–H stretching vibration and C–H deformation vibration at 1350 nm. Figure 3 shows that the absorption at 1216 nm, known as C–H second overtone of stretching vibration, which gradually weakened with the increase in the degree of heat treatment.

Generally, it is known that cellulose has a high decomposition temperature. In our experimental results, the first O–H stretching of cellulose absorption at 1580 nm was reduced by heat treatment at 210 and 220 °C. Additionally, Savitzky–Golay (SG) 2nd derivatives decreased significantly at 1785 nm, where C–H showed first overtone of stretching when the cellulose was subjected to C–H stretching by the heat treatment at 220 °C. It was concluded that thermochemical conversion due to the decomposition of cellulose occurs at a temperature of 210 °C or higher.

Changes in lignin, which is known to be the most thermally stable of the main components of wood, were observed. The C–H stretching vibration in the aromatic ring of lignin at 1670 nm (Fig. 3) and 2134 nm (Fig. 4) increased, which meant that the heat treatment also affected the lignin compound. These results are similar to report of Mitsui et al. [22]. They indicated that acetyl groups reacted to lignin by heat treatment.

Interestingly, the peaks intensities, which were 1450 and 1920 nm known as water absorption bands, changed reversely. The peak intensity at 1450 nm decreased with the heat treatment degree, however, that at 1920 nm increased although heat treatment removed the water in wood. It was estimated that there might be a band affected by the heat treatment where overlapped with the water absorption band.

In this study, NIR reflectance spectra were obtained from the surfaces of larch wood specimens exposed to heat treatments under various conditions, and the possibility of

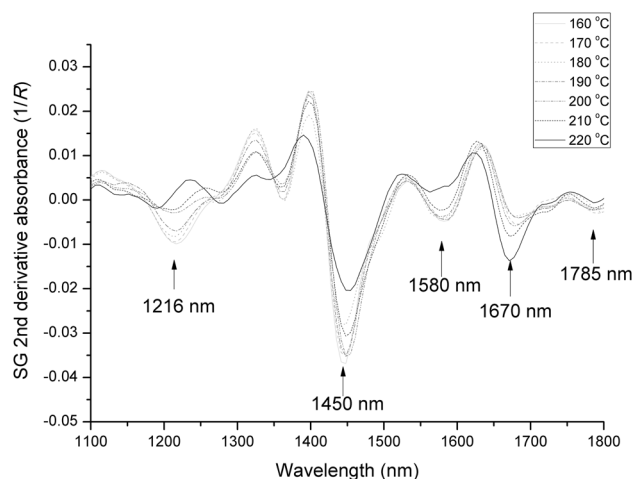


Fig. 3 Savitzky–Golay (SG) 2nd derivative absorbance (1/R) NIR spectra of heat-treated larch between 1100 and 1800 nm at various temperatures (treatment time = 12 h)

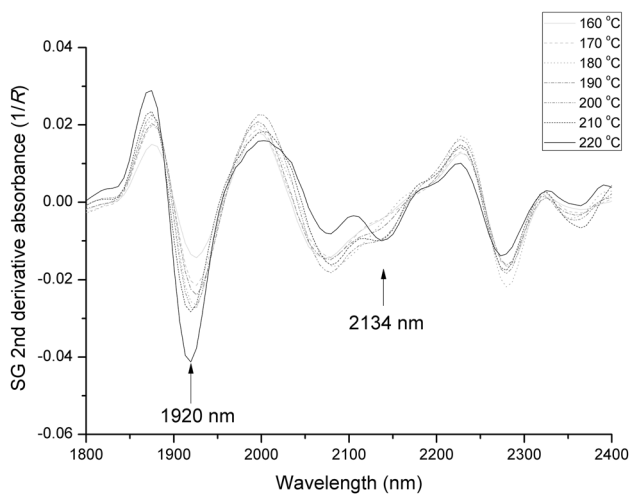


Fig. 4 Savitzky–Golay (SG) 2nd derivative absorbance (1/R) NIR spectra of heat-treated larch between 1800 and 2400 nm at various temperatures (treatment time = 12 h)

spectroscopic classification according to the degree of heat treatment of the specimens was analyzed by the application of HCA. HCA combines data into clusters starting with individual observations as clusters, successively merging the two closest clusters until left with only one cluster. HCA is used in various research fields because it visualizes clustering results, which are easy to interpret.

The variation of the NIR spectra of the larch woods due to various heat treatments showed various absorption peaks, as mentioned above. Thus, HCA based on the similarity of observations (NIR reflectance spectra) could be used as an effective tool to classify the heat treatment degree of wood.

Table 1 shows the results of the HCA of the reflectance spectra obtained from the specimens exposed to various heat treatment conditions and classified into three clusters (A, B, and C). Cluster A included all of the spectra

obtained from specimens heat-treated at 220 °C for 7–12 h. Cluster B included all of the spectra obtained from specimens heat-treated at 220 °C for 3–6 h as well as all of the spectra obtained from specimens heat-treated at 210 °C for 8–12 h. Cluster C included all of the other spectra of the other specimens.

Cluster B was present at 210 and 220 °C. Specimens with a mass loss ratio of 8.2–11.8% under the 210 °C heat treatment condition and specimens with a mass loss ratio of 6.4–13.2% under the 220 °C heat treatment condition were included in the B cluster. B clusters were present at 210 and 220 °C. Comparing the lowest mass loss ratio for each heat treatment temperature belonging to cluster B, the criteria were 8.2% for the 210 °C heat treatment and 6.4% for the 220 °C treatment. This means that even if the specimen is subjected to a long heat treatment at a low temperature, a similar effect to the short, high temperature heat treatment can be obtained, but the mass reduction rate is high.

PCA was applied to compress the data structure of the NIR spectra acquired from heat-treated specimens. In PCA, principal components (scores and loadings) are ordered by the amount of spectral variation. In our data, the first and second principal components (PC1 and PC2) contained 88 and 6% of the spectral variation of the specimens, respectively. Figure 5 shows the score scatter plot and loadings of PC1 and PC2. The HCA clustering result was applied to the score scatter plot of PC1 and PC2 (Fig. 5). Clusters A, B, and C were predominantly grouped by PC1, and there was little effect of PC2. Cluster A was located at the left side of the PC1 coordinates, cluster B was in the middle, and cluster C was at the right side. The scores of PC1 showed a negative value with the increase in the degree of heat treatment. The regions where the loading of PC1 was high enough to affect PC1 scores were mainly 1000–1300 and 1500–1900 nm considering

Table 1 Results of the hierarchical clustering analysis of near-infrared (NIR) spectra acquired from various heat-treated larch wood specimens

Time (h)	Temperature						
	160 °C	170 °C	180 °C	190 °C	200 °C	210 °C	220 °C
1	C(3)	C(3)	C(3)	C(3)	C(3)	C(3)	C(3)
2	C(3)	C(3)	C(3)	C(3)	C(3)	C(3)	C(3)
3	C(3)	C(3)	C(3)	C(3)	C(3)	C(3)	B(3)
4	C(3)	C(3)	C(3)	C(3)	C(3)	C(3)	B(3)
5	C(3)	C(3)	C(3)	C(3)	C(3)	C(3)	B(3)
6	C(3)	C(3)	C(3)	C(3)	C(3)	C(3)	B(3)
7	C(3)	C(3)	C(3)	C(3)	C(3)	C(3)	A(3)
8	C(3)	C(3)	C(3)	C(3)	C(3)	B(3)	A(3)
9	C(3)	C(3)	C(3)	C(3)	C(3)	B(3)	A(3)
10	C(3)	C(3)	C(3)	C(3)	C(3)	B(3)	A(3)
11	C(3)	C(3)	C(3)	C(3)	C(3)	B(3)	A(3)
12	C(3)	C(3)	C(3)	C(3)	C(3)	B(3)	A(3)

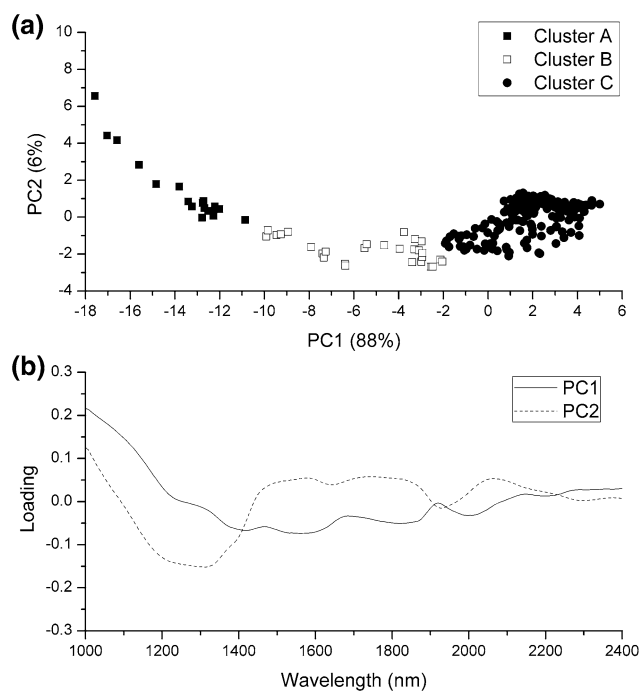


Fig. 5 Principal component analysis of the preprocessed spectra: **a** score scatter plot of the first (PC1) and second (PC2) components grouped by the HCA results, **b** loading plot of PC1 and PC2

mean-centered spectra. Therefore, it was concluded that those regions led the clustering by the heat treatment.

A PLS-DA was performed based on the HCA results. The prediction reliability of the calibration model (7 out of 168 outliers) and validation result by the PLS-DA are shown in Table 2.

The calibration model was optimal when it included two factors, which resulted in an R^2 and root mean square error of calibration (RMSEC) of 0.959 and 0.192, respectively. In the validation set, R^2 and root mean square error of validation (RMSEV) were 0.959 and 0.191, respectively. Each specimen is discriminated according to the class value predicted by the PLS-DA model. In this case, the range of -1.5 to -0.5 is class A, -0.5 to 0.5 is class B, and 0.5 to 1.5 is

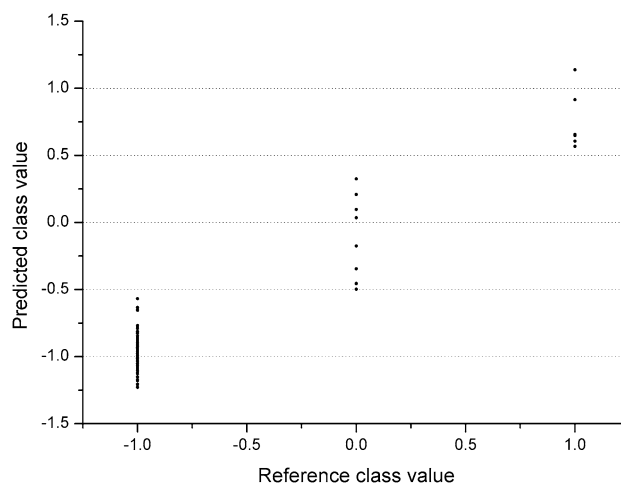


Fig. 6 The results of reference versus predicted class values of the validation set using the PLS-DA calibration model

class C. As a result of the validation shown in Fig. 6, each specimen was distributed within the range of the class value and showed an accurate prediction performance.

Conclusion

NIR reflectance spectra of larch wood were acquired after heat treatment between 160 and 220 °C for 1–12 h to classify the degree of heat treatment. The changes in the NIR of heat-treated larch wood were found at 1216, 1580, 1785, 2134 nm, which correlated with cellulose, hemicellulose and lignin. A hierarchical complete linkage clustering analysis using preprocessed (smoothing and SNV) NIR spectra resulted in three distinct clusters (A: 220 °C 7–12 h, B: 220 °C 3–6 h and 210 °C 8–12 h, and C: the others). When the clustering result of HCA was applied to score the scatterplot of PC1 and PC2, the samples were well-grouped. The PLS-DA model resulted in high reliability ($R^2 = 0.959$, $RMSEV = 0.191$) in the classification of the degree of heat treatment.

Table 2 Regression results of partial least squares discriminant analysis (PLS-DA)

Regression results						
Number of factor	Calibration			Validation		
	Elements	R^2	RMSE	Elements	R^2	RMSE
2	161	0.959	0.192	84	0.959	0.191

R^2 coefficient of determination, $RMSE$ root mean square error

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