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Chemical Structure of Wood Charcoal by Infrared Spectroscopy and Multivariate Analysis

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In this work, the effect of temperature on charcoal structure and chemical composition is investigated for four tree species. Wood charcoal carbonized at various temperatures is analyzed by mid infrared spectroscopy coupled with multivariate analysis and by thermogravimetric analysis to characterize the chemical composition during the carbonization process. The multivariate models of charcoal were able to distinguish between species and wood thermal treatments, revealing that the characteristics of the wood charcoal depend not only on the wood species, but also on the carbonization temperature. This work demonstrates the potential of mid infrared spectroscopy in the whiskey industry, from the identification and classification of the wood species for the mellowing process to the chemical characterization of the barrels after the toasting and charring process.

KEYWORDS: Wood charcoal; chemical composition; infrared spectroscopy; multivariate analysis; principal component analysis; projection to latent structures; white oak; red maple; sugar maple; silver maple; whiskey; maturation; mellowing process; toasting and charring process

INTRODUCTION

Charcoal is the carbonization product of organic matter exposed to high temperature, in the absence of air or oxygen. Wood charcoal has been manufactured for millennia for various applications, which currently include medical (*1*), agricultural (*2*), environmental (*3*, *4*), and food industries (*5*).

In the whiskey industry (*6*), charcoal utilization is part of the process. It contributes to the properties of whiskey in two separate processes: filtration and maturation. Used for Tennessee whiskey, the new spirit is filtered through charcoal before going into a cask. The whiskey is filtered through a charcoal layer of 10 feet thick before barreling, to leach out some of the fusel oils. This process, also known as the charcoal mellowing, distinguishes Tennessee whiskey from Bourbon. It is a slow and tedious process, requiring about 12 days for the whiskey to mellow slowly through the charcoal (*7*). The charcoal for filtration is produced from sugar maple wood (*Acer saccharum*). However, anecdotal evidence in changes of whiskey quality has been observed with changes in the maple species used to produce the charcoal.

Charcoal is used in another filtration process during the whiskey fabrication. Most bourbons are filtered before and after aging with activated charcoal. No flavor is imparted by activated charcoal, but when unfiltered whiskey gets too cool, it can develop a "chill haze" or cloudiness. Technically there is nothing wrong with cloudy whiskey; in fact, it is generally more flavorful than the filtered variety. This additional step is an aesthetic matter, because there may be a perception that the whiskey is spoiled in some way. As a consequence, distillers generally filter their bourbon before bottling it. Tennessee whiskey goes through the same quick filtration process after aging.

Charcoal is an extremely good filter and filters harsher components out of the whiskey. The most important component of the maturation process is the wooden cask. Freshly distilled spirits derived from the fermentation process are usually rather colorless and harsh in taste and possess an overpowering alcoholic flavor. However, if these products are permitted to age in wood, a unique transformation occurs such that a yellow to dark-brown color develops, the taste becomes smooth, and the flavor and aroma become complex and pleasing. Small changes during the maturation process have an enormous influence on the later taste of a whiskey. Aged whiskey gets all of its color and much of its flavors from the barrels. Bourbon whiskey is always aged in new, white oak barrels. The insides of the barrels are deeply charred. When the barrels are formed, the staves are heated to help them bend, and the heat caramelizes some of the wood sugars and tannins within each stave. This toasting stage of coopering forms the red layer, which not only

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Table 1. Percentage of Carbon from the Analysis of Thermally Treated Wood

species	ambient	250 °C	275 °C	300 °C	325 °C	350 °C
red maple	49.85	50.25	49.15	52.11	52.68	70.20
silver maple	49.28	41.69	50.43	52.95	60.12	71.16
sugar maple	49.46	49.63	48.27	68.60	65.00	72.04
white oak	49.60	49.00	52.11	68.55	65.34	71.60

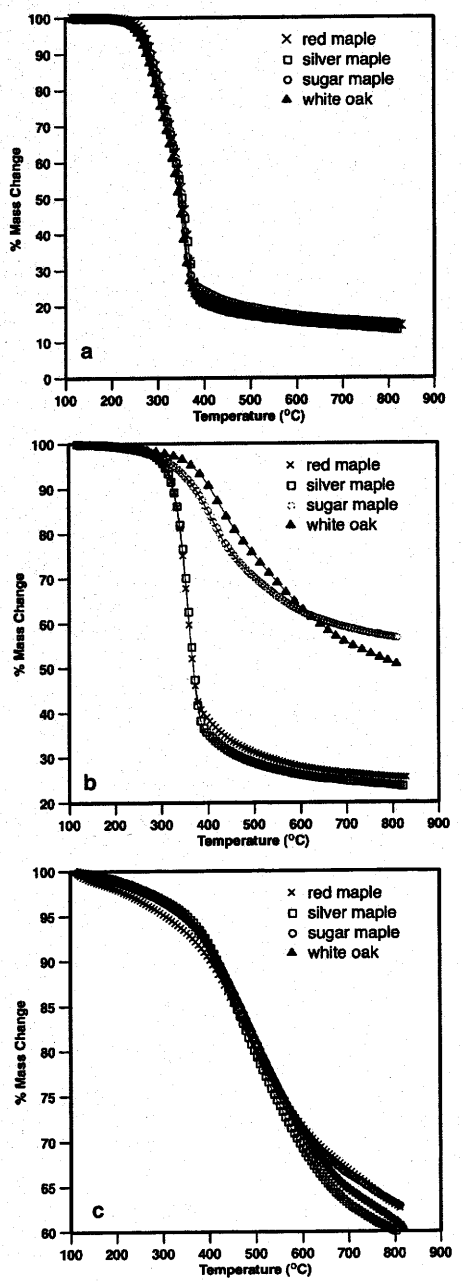

Figure 1. TGA of (a) ambient, (b) 300 °C, and (c) 350 °C conditioned wood specimens representing the change in mass when heated in a nitrogen atmosphere.

helps give color to the whiskey, but also imparts some extra flavors. After the barrels are assembled, their interiors are then charred over open flame, creating a layer of charcoal over the red layer. When the whiskey is in the aging houses, it filters through that charcoal as it expands and contracts with seasonal temperatures changes. Both the red layer and the charred interior are believed to add flavors to the whiskey.

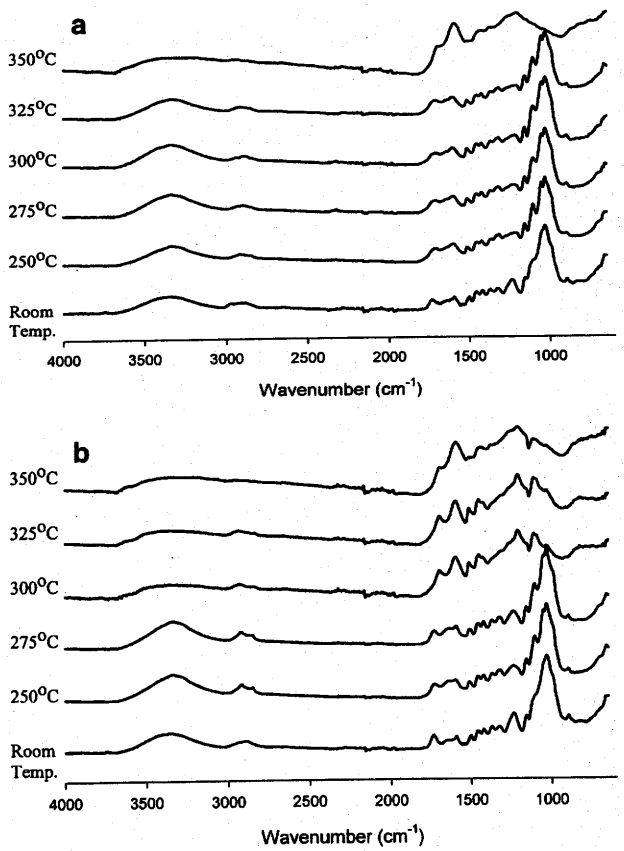

Figure 2. Mid infrared of red maple (a) and white oak (b) at various thermal treatments.

In this work, thermogravimetric analysis and infrared spectroscopy coupled with multivariate analysis are used to investigate the chemical structure of charcoal made from different maple species: sugar maple (*Acer saccharum*), red maple (*Acer rubrum*), and silver maple (*Acer saccharinum*). The second part of the study consists of using infrared spectroscopy to study the effect of thermal treatments on the chemical structure of white oak to have a better understanding of maturation process in toasted charred white oak barrels.

MATERIALS AND METHODS

In the current work, sugar maple (*Acer saccharum*), red maple (*Acer rubrum*), silver maple (*Acer saccharinum*), and white oak (*Quercus alba*) were heated in an inert environment to temperatures of 250, 275, 300, 325, and 350 °C for 2 h, along with an untreated control. Samples size was approximately 1 cm × 2 cm × 5 cm. The initial moisture content of the wood before heat treatment was 7.1% ± 0.6%.

Thermogravimetric analysis (TGA) was then used to determine the remaining amount of combustible material remaining in the charcoal. For this analysis, a sample of approximately 5 mg from each piece of charcoal was heated in a thermogravimetric analyzer (Perkin-Elmer) from 50 to 900 °C at 20 °C/min in a nitrogen atmosphere. The TGA tests were performed in triplicate on each piece of charcoal. The averages of the three tests were then used for the results.

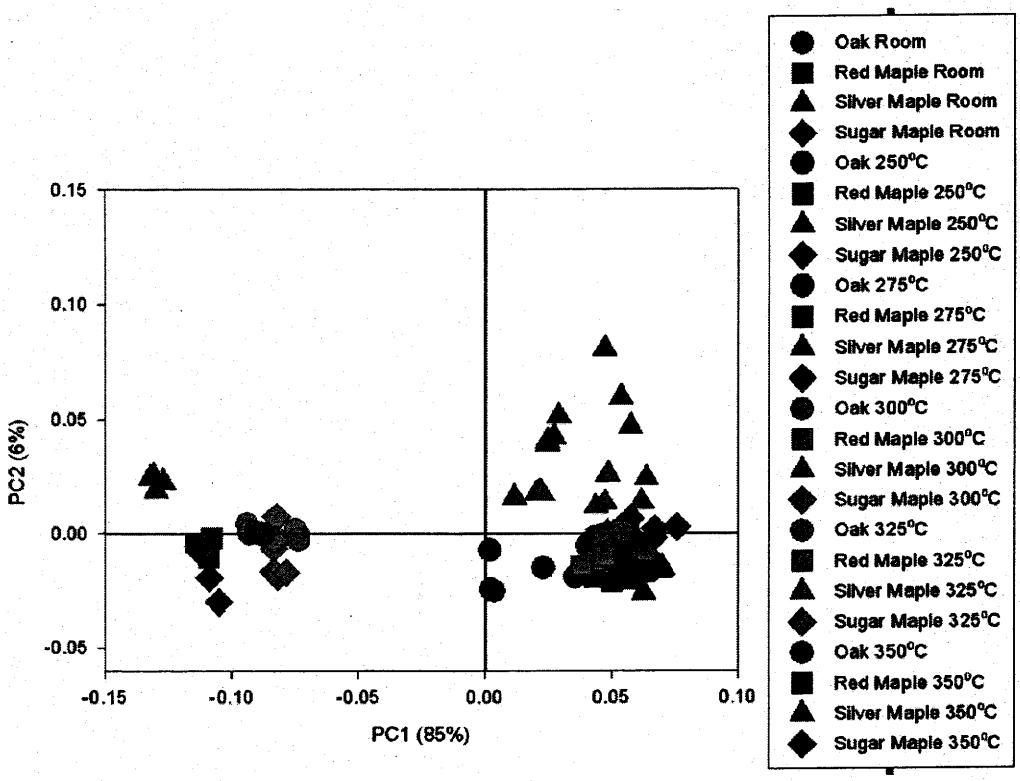

Figure 3. Scores plot of the first two PCs obtained by PCA of the mid infrared spectra measured on the heat-treated samples and control. Different symbols correspond to different wood species (● for white oak, ▲ for silver maple, ◆ for sugar maple, ■ for red maple), while the colors correspond to the different thermal treatments (black for room temperature, red for 250 °C, blue for 275 °C, magenta for 300 °C, aqua for 325 °C, and green for 350 °C).

Carbon and hydrogen percentages for each sample were determined by a commercial laboratory via CHN analysis (Galbraith Laboratories, Knoxville, TN), and the oxygen percentage was calculated by difference.

For the infrared measurements, small pieces from the samples were taken, ground in a mortar. The powder was placed on the ZnSe crystal of an attenuated total reflectance (ATR) accessory of a Perkin-Elmer Spectrum One FT-IR spectrometer. Spectra were collected over 4000–650 cm^{-1}, with the resolution of 4 cm^{-1} and 16 scans per sample. Sample contact area was a circle of about 1.5 mm in diameter. Four spectra were collected for each thermal treatment. The spectral data were imported into The Unscrambler software (ver. 9.1; CAMO A/S, USA), and the transmittance spectra were converted to absorbance spectra. Multivariate analysis was used to extract useful information from the spectral data set. Mainly principal component analysis (PCA) and projection to latent structures (PLS) were used. The absorbance spectra were normalized and subjected to a full multiplicative scatter correction (MSC) using the Unscrambler. These spectral data were then ready for the PCA and PLS analysis.

PCA is essentially a descriptive method (*8*). This method allows for visualization of the main variability of a data set without the constraint of an initial hypothesis concerning the relationship within samples, or between samples and responses (variables). The main goals of this procedure are to find relationships between the different parameters (objects and variables) and to detect possible clusters within objects and/or variables. PCA removes the redundancy (intercorrelation) in a data set, transforming it into a few loadings, which contain most of the valuable spectral information much while retaining most of the original information content. Each sample has a score on each principal component (PC). It reflects the sample location along that PC. Plotting these scores against one another can reveal patterns or clustering within a data set. Scores describe the data structure in terms of sample patterns and more generally show sample differences or similarities. Each score has an associated "loading", which provides information about the chemical differences between the samples.

PLS provides a model for the relationship between a set of predicator variables X (n objects, m variables) and a set of response variables Y (n objects, p response). It correlates known properties with the spectral data. If the spectral data contain information about the property of interest, a reliable calibration model can be constructed. In the FT-IR data set, there is only one response (Y), the temperature at which the samples were treated. The main idea here was to use the spectral data to determine the temperature exposure of the charred samples. The models were validated using a full cross validation approach (*8*). In this technique, a sample is left out from the data set and the model is calculated on the remaining data points. The value for the left-out sample is then predicted. The process is repeated with another sample of the calibration set, and so on until every object has been left out once. This approach was used to make sure that the developed models were not over-fitted. The number of principal components (factors) used for the models was selected by observing the response of the residual Y-variance to added factors. The models were completed when additional factors did not substantially decrease the residual Y-variance. PLS models generate also regression coefficients, or information on the chemical features that drive the calibration. The regression coefficients can be used to relate chemical features in the spectra to the properties of interest.

RESULTS AND DISCUSSION

It was found that chemical transformations in the wood occurred at different temperatures depending on the tree species. TGA analysis of the wood samples indicates a different dependence on temperature (**Figure 1**). The thermal degradation of the unheated wood displays virtually identical behavior for all species and carbon/ash yields upon treatment (**Figure 1a**). This is also consistent with elemental analyses of the charcoal that has a final carbon yield of around 71% for all wood species (**Table 1**). Similarly, TGA analysis of charcoals produced at

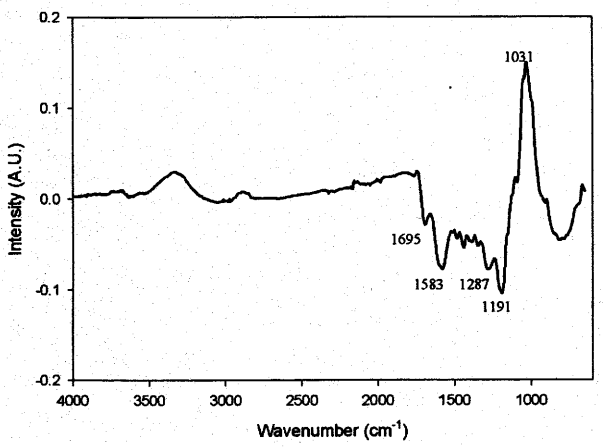

Figure 4. PC1 loadings plot.

350 °C display similar yields and thermal behaviors (**Figure 1c**). However, it appears that the kinetics of this degradation process proceeds at different rates for these wood species as can be observed by the elemental analysis at 300 and 325 °C (**Table 1**) and the TGA analysis at 300 °C (**Figure 1b**).

Fourier transform infrared spectroscopy was used to investigate the changes in the chemical composition of the samples with thermal treatment. **Figure 2a** and **b** shows infrared spectra collected for the heat treatments for red maple and white oak. Differences in the spectra with thermal treatment are observable. For the white oak samples, differences in the spectra are noticeable starting at 300 °C. For the red maple samples, changes in the spectra are observed at 350 °C. Before this temperature, no differences are really visible in the spectral data. In the sugar maple samples, like the white oak samples, changes are seen at 300 °C (figure not shown). Because of the number of samples, species, and heat treatments, multivariate analysis was used to compare the spectra and extract chemical information.

Principal component analysis was carried out on the set of the 96 pretreated spectra (4 species, 6 temperatures, 4 replicates). Based on the residual variance curve, the optimal number of PCs is 5. However, PC1 describes a considerable amount (85%) of the total variance and shows a particularly interesting trend, as it can be observed in the scores plot of **Figure 3**.

Two distinct clusters are obtained along PC1. On the left (negative along PC1) are the spectra of the samples with high thermal treatments, and the right part (positive along PC1) shows the low temperatures. PC1 is the most informative latent variable for the description of the thermal treatment of the samples, independent of the wood species. The loadings plot (**Figure 4**) shows the chemical features that are responsible for grouping the samples along PC1. The loadings show how well a variable (wavenumber) is taken into account by the model components. They can be used to understand how much each wavenumber contributes to the meaningful variation in the data, and to interpret variable relationships.

From this plot, it is possible to obtain information about the chemical aspects that are involved in the thermal process. The 1127−927 cm^{-1} loadings region is the most important region in discriminating the different heat treatments. The absorption bands in this wavenumber interval are typically assigned to the C−O stretching vibration in cellulose and hemicellulose. Additional vibrations appear in several regions of the loadings at 1191, 1287, 1583, and 1695 cm^{-1}. If a variable has a positive loading, it means that all samples with positive scores have higher than average values for that variable and all samples with negative scores have lower than average values for that variable. On the basis of this rule and the positive band at 1127−927

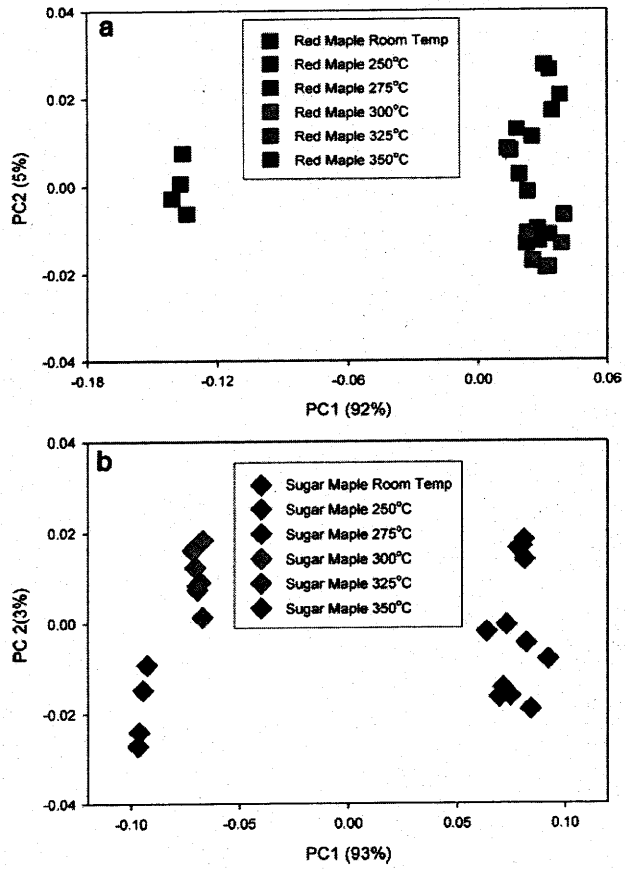

Figure 5. Scores plot of the first two PCs obtained by PCA of the mid infrared spectra measured on the heat-treated red (a) and sugar (b) maple.

cm^{-1}, one can conclude that the samples in the right cluster (low thermal treatment) have higher cellulose and hemicellulose content than the samples in the right cluster (high thermal treatment). Based on the negative bands associated with lignin at 1583 and 1195 cm^{-1}, all samples with negative scores (high thermal treatment) have higher than average values for these variables. These observations are consistent with the literature on the thermal degradation of wood (*9*). Between 250 and 300 °C, hemicellulose and cellulose are degraded, while at higher temperatures, the degradation of lignin occurs. Some differences due to the species are also observed from **Figure 3**. **Figure 5a** and **b** shows more clearly these differences. They represent the scores plot of the first two PCs obtained by PCA of the mid infrared spectra measured on the heat-treated red and sugar maple, respectively.

The samples cluster along PC1 depending on the thermal treatment. For red maple, the change in the chemical composition of the samples starts at 350 °C. Below this temperature, the chemical composition of the samples is closer to the untreated wood than to charcoal. For sugar maple, the change in the chemistry appears at a lowest temperature. The samples heated at 300 °C have already a composition similar to charcoal. The red maple and silver maple samples require more energy (higher temperature) to degrade than the sugar maple and white oak samples.

The principal component analysis of all of the species at all temperatures reveals that at 350 °C all of the samples are charcoal. Thus, the next step of our study was to classify the charcoal. The chemical composition (infrared spectra) of the charcoal was used. A PCA was run on all of the samples treated at 350 °C. **Figure 6a** and **b** shows the plots of the results from

Table 3. Correlation Coefficient (R) and Root-Mean-Square Error Calibration for the Different Wood Species and All Species Together

species	Nb of PCs	correlation coeff. R	RMSEC
white oak	3	0.989	5.5
red maple	4	0.959	10.4
silver maple	2	0.972	8.2
sugar maple	2	0.951	10.9
all species	4	0.883	16.6

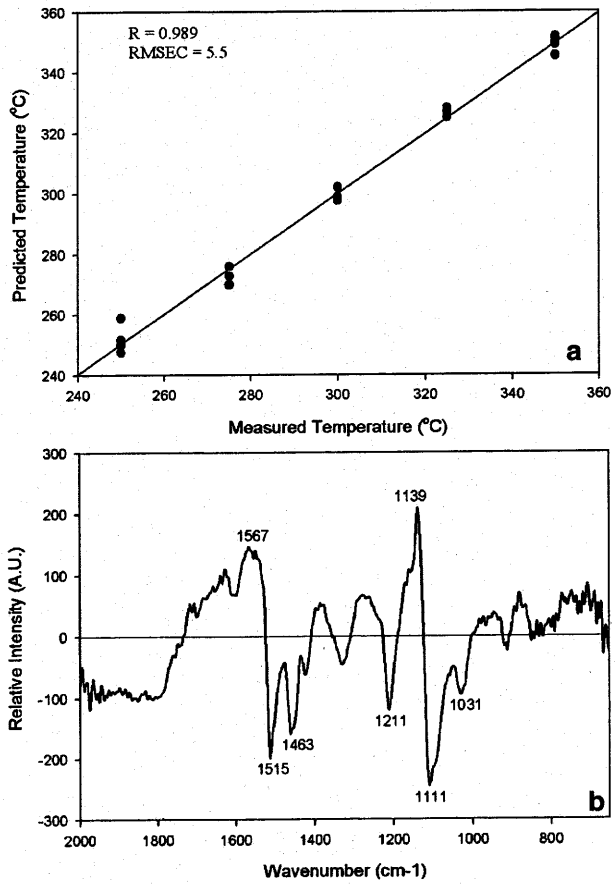

Figure 8. Results of PLS model for oak samples showing (a) the correlation between the measured temperature and predicted temperature with FT-IR spectra and (b) the regression coefficients.

responsible for differentiating sugar maple and red maple. Because these two species have similar characteristics, a third PC with only 4% of variation is necessary to distinguish one from another.

PLS regression was applied to the spectra to correlate temperature to the spectral data. A PLS model was calculated for each species and for all of the species together. **Table 3** shows the correlation coefficient (R) and the root-mean-square error of calibration (RMSEC) for the models built for each species and all samples together independent of the species. The PLS results for white oak will be discussed because of the importance of building a model that can predict the temperature in the barrel based on the chemical composition of the staves after the toasting and charring of the barrels. **Figure 8a** and **b** shows the results of the PLS analysis for the white oak set. A very good correlation was found (R = 0.989) between the measured temperature and the temperature predicted from the FT-IR spectra. This correlation shows that there is a direct and linear relationship between the chemical composition of the sample and the thermal treatment. The regression coefficients that indicate the nature of the chemical changes suggest that the three main components of wood are taken into account to build the model. Several significant variables (wavenumbers) in the fingerprint region (1800−600 cm^{-1}) can be identified in the regression coefficient plot (**Figure 8b**). The assigned peaks are conjugated C−O stretching at 1567 cm^{-1}, aromatic skeletal vibration at 1515 cm^{-1}, C−H deformation in lignin and carbohydrates at wavenumber 1463 cm^{-1}, syringyl ring and C−O stretching in lignin and xylan at 1211 cm^{-1}, C−O−C vibration in cellulose and hemicellulose at 1139 cm^{-1}, aromatic skeletal and C−O stretch at 1111 cm^{-1}, and C−O stretch in cellulose and hemicellulose at wavenumber 1031 cm^{-1}.

This work shows that FT-IR spectroscopy is a powerful tool for monitoring chemical changes in wood due to thermal treatment. FT-IR spectroscopy is therefore an excellent technique for quality control of charcoal in both applications in whiskey manufacturing. FT-IR spectroscopy can be used to classify wood species and confirm that the right species, sugar maple, is used to filter the distilled spirits in the mellowing process. It can also be used to monitor temperature and changes in the chemistry of the barrel during the toasting and charring process. In the maturation process, because the thermal treatment modifies the accessibility of the spirit to the wood, monitoring the chemical composition and wood structure across the stave is indispensable. The charring of the barrels creates a sequence of thermally degraded wood materials that extends into the stave.

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