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Application of an Fourier Transform-Infrared Imaging Tool for Measuring Temperature or Reaction Profiles in Pyrolyzed Wood

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FT-IR imaging was used to monitor the structural and chemical changes of wood particles under various pyrolysis conditions. The temperature or reaction profile inside pyrolyzed wood was obtained from a novel approach using chemical images coupled with multivariate analysis. Poplar sections 100 μm thick were pyrolyzed at 250−500 °C and the resulting FT-IR images were used as standards to determine the temperature in a poplar wood block (5 mm × 5 mm × 20 mm). Principal component analysis (PCA) and partial least-squares (PLS) regression were used to develop predictive models to map the temperature profile in the pyrolyzed wood. The results indicate that FT-IR imaging coupled with multivariate analysis is a powerful tool to study the heat transfer effects in the pyrolysis of thick wood particles. We believe that this is a unique and novel approach to visualize the chemical changes in heated biomass and thermal effects in other materials.

1. Introduction

Biofuels have received increased interest worldwide in recent years due to concerns about the limited oil reserves and climate change from green house gas emissions.[1] Pyrolysis and gasification are two of the most promising methods for the thermochemical conversion of biomass such as trees, agricultural residues, and waste organic materials toward a clean fuel source.[2,3] In particular, pyrolysis, i.e., thermal decomposition in the absence of oxygen, is always the first step in combustion or gasification processes where it is followed by total or partial oxidation.[2]

The pyrolysis of a biomass particle is complex since the governing phenomena are both chemical (i.e., volatilization and char formation) and physical (heat and mass transfer phenomena) and also depend on a wide range of factors including particle size and shape, pyrolysis temperature, heating rate, and residence time.[1,4−8] In general, wood pyrolysis has been divided into two major regimes, thermally thin and thermally thick, based on transient conduction within the wood particle.[1,5,6,8] Often, these two regimes are further divided depending on which is the slowest or rate-limiting step among chemical reaction, internal heat transfer, and external heat transfer creating four characteristic conditions for the pyrolysis process. Those four regimes are the pure kinetic regime (chemical reaction time ≫ heat transfer time), the thermally thin regime (external heat transfer time > chemical reaction ≫ internal heat transfer), the thermally thick regime (internal heat transfer time ≈ external heat transfer ≫ chemical reaction), and the thermal wave regime (internal heat transfer time ≫ external heat transfer > chemical reaction). The heat transfer process is an important element that needs to be understood to describe the pyrolysis phenomena and is especially important for thermally thick wood particles. In general, practical biomass feedstock sizes in an industrial pyrolysis processing, such as wood chips and pellets, fall in the thermally thick regime where the pyrolysis process is heat transfer controlled. This work presents a novel approach to study the pyrolysis process of thick wood particles, including the heat transfer effects.

Recently, real-time microscopic analysis of poplar wood sections undergoing pyrolysis has been conducted by Haas et al.[9] using light microscopy with a hot stage and transmission electron microscopy (TEM). The results from their study show that the structural complexity of unprocessed plant tissues used for thermochemical conversion of biomass to fuels impedes heat and mass transfer and may increase the occurrence of tar-forming secondary chemical reactions. Although this approach by Haas et al. has provided insight into physical and structural changes of biomass undergoing pyrolysis at microscopic scales, the microscopic techniques used in the study do not provide chemical information.

In the current study, Fourier transform-infrared (FT-IR) imaging is used as a tool to study both the structural and chemical compositional changes of biomass during thermochemical conversion. FT-IR imaging has been applied in the investigation of plant materials previously, including the structure of crystalline cellulose and the architecture of primary cell walls at a molecular level.[10−15] However, this is the first

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report to our knowledge of FT-IR chemical imaging used to monitor the structural and chemical changes of wood particles after pyrolysis.

Infrared spectra of each wood component have multiple overlapping IR absorption bands.[16] Chemical changes during wood pyrolysis add even more chemical components to the materials, resulting in a congested IR spectrum. Therefore, the assignment of single bands is very difficult and often unreliable. It is known that the reliability of complex spectral analyses can often be improved by applying statistical multivariate methods,[15,17–22] such as principal component analysis (PCA), partial least-squares (PLS), multivariate curve resolution (MCR), and artificial neural networks (ANN). In this study, PCA, MCA, and PLS methods were used for the analyses of FT-IR imaging data in order to objectively obtain the temperature or reaction profile inside the pyrolyzed wood particle as a function of the distance from the surface heated to 500 °C.

2. Experimental Section

2.1. Materials. The wood samples used in this study included cross sections of poplar (*Populus* sp.) sectioned to 16 or 100 μm thick using a Leica RM2255 rotary microtome (Leica, Wetzlar, Germany). Also used were poplar wood blocks (5 mm × 5 mm × 20 mm) that represent realistic feed stock sizes for a biomass refinery. The wood block was cut in half after pyrolysis using a coping saw to sample the center of the block and then was cross-sectioned to 100 μm thick on a Leica RM2255 rotary microtome for the FT-IR imaging study. All wood samples were analyzed at room temperature and humidity without any additional drying procedure. The moisture content of the wood samples was estimated to be ~5% based on ambient humidity.

2.2. Microscope Hot Stage Pyrolysis Experiment. The microscope hot stage used for pyrolysis reactions was an INSTEC HCS621G (Instec, Inc., Boulder, CO) with SCT200 temperature controller and WinTemp control software, manufacturer-modified for a temperature range of −196 °C (liquid N_2-cooled) to approximately 700 °C. In this work, the temperature of the reactor was varied from 250 °C up to 500 °C in 50 °C increments. Wood blocks or wood sections (16 or 100 μm thick) sandwiched between two quartz cover slides were loaded in the hot stage under the nitrogen atmosphere and slowly heated from room temperature to a set temperature with a heating rate of ~150 °C/min. The residence time of biomass in the hot stage was about 3 min.

2.3. FT-IR Imaging Experiment and Multivariate Data Analysis. FT-IR images were acquired using a Thermo Nicolet Image IR Imaging system (Thermo Scientific) composed of a Nicolet Nexus 870 step-scan interferometer and a Thermo Electron Continuum microscope configured for spectral imaging. The imaging detector was a Santa Barbara Focal Plane 64 × 64 mercury cadmium telluride detector. A 15× Cassegrain objective was used to image a sample area of approximately 400 μm × 400 μm, with a spatial resolution of ~10 μm. One or two NaCl windows (13 mm × 2 mm, International Crystal Laboratories) were used as a substrate for the samples. The spectra were collected in the wavenumber range of 900−3800 cm^{-1} using a transmission mode with a spectral resolution of 8 cm^{-1}. An average of 10 scans was used for each measurement and each image contains 4096 FT-IR spectra. Image processing was conducted using Spectral Dimensions Isys chemical imaging software.

Multivariate analysis was performed using The Unscrambler 9.0 (CAMO, Corvallis, OR). In this work, PCA, MCR, and PLS methods were used for FT-IR imaging data in the fingerprint spectral range of 900−1900 cm^{-1} to objectively identify the temperature or reaction profiles inside the biomass chars after pyrolysis.

3. Results and Discussion

In order to develop a new chemical imaging approach to study pyrolysis of biomass, we surveyed FT-IR spectra of poplar before and after pyrolysis using thin (16 μm thick) poplar cross sections that provided higher spectral resolution. Then, FT-IR spectra of a 100 μm thick poplar cross section after pyrolysis at various temperatures were obtained to measure the spectral changes in these standard samples. Finally, models using multivariate data analyses were built based on these standards and were applied to measure the temperature or reaction profiles inside a pyrolyzed block of poplar.

3.1. Pyrolysis of 16 μm Thick Wood Cross Sections. Initially, thin poplar wood cross sections (16 μm thick) were analyzed before and after pyrolysis at 500 °C using a hot stage reactor with a heating rate of ~150 °C/min and a residence time of ~3 min. Figure 1 shows the visible images and the infrared images of a poplar cross section before and after pyrolysis at 500 °C and the corresponding IR spectra of the regions indicated with the blue box. The color bars shown next to the FT-IR images in Figure 1b represent the color scheme used for all FT-IR images in this work. The signal intensity (absorbance at 1600 cm^{-1}) increases as the color changes from blue, green, yellow, to red. The blue holes in the images are empty lumen of vessel elements within a poplar wood section, while the red areas are where high concentrations of the cell wall materials exist. The legends in Figure 1b, F, R, V, and * refer to fiber cells, ray cells, vessels in wood sections, and new empty spaces that were created from the pyrolysis process, respectively.

Both visible and FT-IR images in Figure 1 show microscopic structural changes due to tissue expansion and collapse upon heat treatment, as observed in previous work.[9] We note that the samples were sandwiched between two NaCl windows to flatten the thin poplar section, resulting in slightly blurry visible images. The FT-IR image of poplar in the upper row in Figure 1b represents the distribution of lignin which is responsible for the intensity of the aromatic C=C stretching band[23,24] at ~1600 cm^{-1} in FT-IR spectrum in the upper row in Figure 1c. The FT-IR image of pyrolyzed poplar in the lower row in Figure 1b also shows the image at 1600 cm^{-1}, but now it originates from the distribution of the polyaromatic compounds produced during the pyrolysis process rather than that of lignin. That is, the broad band centered near 1600 cm^{-1}, which spans the range of ~1550 to ~1650 cm^{-1},

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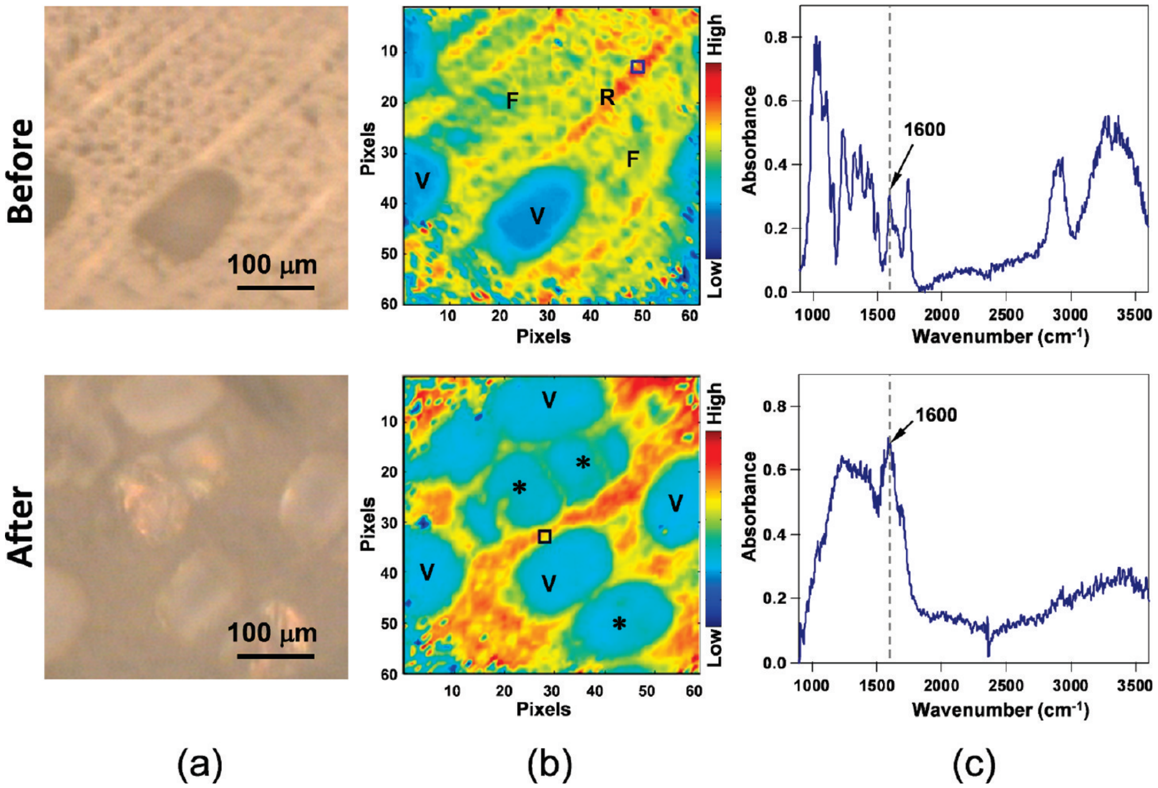

Figure 1. Poplar cross section before (upper row) and after (lower row) pyrolysis: (a) visible light image (360 μm × 360 μm), (b) FT-IR image (pixel = 6.25 μm) at 1600 cm^{-1} (aromatic C=C), and (c) FT-IR spectrum of a specific region of interest indicated as a blue box in part b. F = fibers, R = ray cells, V = vessels in wood, $*$ = empty spaces made from wood tissue expansion and collapse.

in the FT-IR spectrum of pyrolyzed poplar indicates a significant increase of aromatic content after pyrolysis due to the formation of graphitic like structures.[23,24]

Wood is mainly composed of the three polymeric components (cellulose, hemicellulose, and lignin) with minor components such as minerals and extractives.[1,2] During the pyrolysis process, the wood contains a mix of the chemical complexity of the original materials and the evolving char. Therefore, the FT-IR spectra of wood before and after pyrolysis have multiple overlapping IR absorption bands as shown in Figure 1c. Yet, they clearly show the dramatic changes in IR spectra, reflecting the significant chemical compositional changes in poplar after pyrolysis.

Hardwood such as poplar consists of ∼40−50% cellulose, ∼20−30% hemicellulose, and ∼20−30% lignin.[1,7,15] Cellulose is a homogeneous polymer composed of linearly linked β-(1→4)-D-glucopyranose units. Hemicellulose is a branched polymer that contains pentoses, hexoses, and/or uronic acids. The hardwood hemicellulose is mainly composed of xylan, which contains a backbone of linearly linked β-(1 → 4)-xylopyranosyl units. Lignin is a randomly linked, amorphous, high-molecular weight phenolic compound. Hardwood lignin contains syringyl propane units (phenolic groups having two methoxy groups) and guaiacyl propane units (with one methoxy group).[7,15]

The FT-IR spectrum shown in Figure 1c includes features corresponding to cellulose,[23,25] hemicellulose,[26] and lignin.[24,27]

Table 1. Band Assignments for the Infrared Spectra of Biomass before and after Pyrolysis

band position (cm^{-1})	assignments[23−28]
1000−1100	C−H, C−O deformation
1100−1300	aromatic ether (aryl-oxygen) stretch
1200−1300	conjugated ketone (phenyl-carbonyl) C−C stretch
1265−1275	methoxy group, e.g., aryl methyl ether C−O stretch
1325−1370	phenolic C−O stretch
1360−1470	aliphatic C−H deformation
1510	aromatic ring vibrations
1595−1600	aromatic C=C stretch
1620−1640	adsorbed water scissoring mode, C=C stretch
1650−1670	aryl C=O stretch
∼1700	unconjugated C=O stretch; C=O in phenolic esters/lactones
∼1730	ketone/aldehyde-type C=O stretch
1740−1750	carboxylic ester C=O stretch, uronic acid and acetyl groups of hemicellulose
∼1800	monomeric acid (acetic acid)
2860−2960	methyl and methylene C−H stretch
3000−3100	aromatic C−H stretch
3300−3430	O−H, N−H stretch

Detailed band assignments for the FT-IR spectra are summarized in Table 1. The most prominent bands in the wood IR spectra include ones at ∼1510 cm^{-1} (aromatic ring breathing), ∼1600 cm^{-1} (aromatic C=C stretch), ∼1620 cm^{-1} (adsorbed water/C=C stretch), ∼1660 cm^{-1} (C=C or aryl C=O stretch), 1730 cm^{-1} (ketone/aldehyde-type C=O stretch), and ∼1740−1750 cm^{-1} (ester carbonyl group C=O stretch). Among them, only a few bands originate from a single wood component. Specifically, the bands at ∼1510 and ∼1600 cm^{-1} are from the phenolic groups in lignin while the band at ∼1740−1750 cm^{-1} are from the ester carbonyl groups such as uronic acid and acetyl groups in hemicellulose.[26] In the IR

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range of 900−1900 cm^{-1} used in the current study, unfortunately, there was no isolated cellulose band that did not overlap with the bands from hemicellulose or lignin.

We note that in the FT-IR images the distributions of individual chemical species, such as cellulose, hemicellulose, and lignin, in poplar are shown to reflect the cell wall structure and seem relatively homogeneous across the wood sections at the spatial resolution (~10 μm) of the current FT-IR imaging method. In other words, the FT-IR images of poplar at 1600 cm^{-1}, 1740 cm^{-1}, or other vibrational frequencies looked almost identical. The same pattern was seen in the distribution of tars in pyrolyzed poplar (Figure 1b). With the relatively poor spatial resolution of this technique, it was not possible to reliably localize individual chemical components in the FT-IR images of poplar either before or after pyrolysis. Thus, our main effort was toward utilizing the FT-IR spectra of wood sections at different pyrolysis temperatures as finger prints or the standards of the pyrolyzed wood particles at each temperature.

3.2. Pyrolysis of 100 μm Thick Wood Cross Sections. The dramatic changes in IR spectra of poplar after pyrolysis at 500 °C suggests that FT-IR imaging can be used to differentiate the chemical changes in wood pyrolyzed at different temperatures. In order to quantitatively characterize the changes in the FT-IR spectra, standards were produced by pyrolyzing 100 μm sections of poplar from 250 to 500 °C in 50 °C increments. Sections of 100 μm were used instead of 16 μm sections because we intend to use the imaging data as standards to be compared with images from 100 μm sections of a pyrolyzed 5 mm wood block. Experimentally, it was not practical to section the brittle pyrolyzed wood block (chars) to thinner than 100 μm. During pyrolysis, the thicker wood sections are expected to trap more condensable vapors (tars) than thinner sections due to mass transport limitations. This property makes the use of thicker, 100 μm, wood sections more appropriate for the study of realistic biomass feedstocks for industrial-scale processing. Typically, wood chips are up to tens of millimeters thick, and sawdust is a few hundred micrometers in scale.[1,2] The down side of using the 100 μm sections, however, was that the spectral resolution was worse than that of the thinner ones.

3.2.1. FT-IR Spectral Changes of Wood after Pyrolysis at Various Temperatures. Figure 2 shows FT-IR spectra in the fingerprint region and visible images of 100 μm thick cross sections of poplar at room temperature and after pyrolysis up to 500 °C. These images reveal the chemical and structural changes in poplar at each pyrolysis temperature. The IR spectra are shown in Figure 2a, and although it is not possible to assign all vibrational bands due to spectral overlap, compositional differences in the samples can be explained from some of the spectral features. In addition, these IR spectra will serve as standards to estimate the temperature inside a pyrolyzed wood block using PCA and PLS. The most significant changes in FT-IR spectra of 100 μm thick wood particles after pyrolysis under current experimental conditions (heating rate ~150 °C/min; residence time ~3 min) are as follows: (1) As the pyrolysis temperature increases, the intensity of a band at ~1740 cm^{-1} decreases while a new band at ~1700 cm^{-1} emerges. (2) A broad band at ~1600 cm^{-1} tends to be more prominent at higher temperatures. (3) A weak band near 1800 cm^{-1} appears in some spectra of wood at the temperatures above 300 °C. We note that FT-IR spectra in Figure 2 are area-normalized. Table 1 summarizes detailed band assignments for the FT-IR spectra with references.

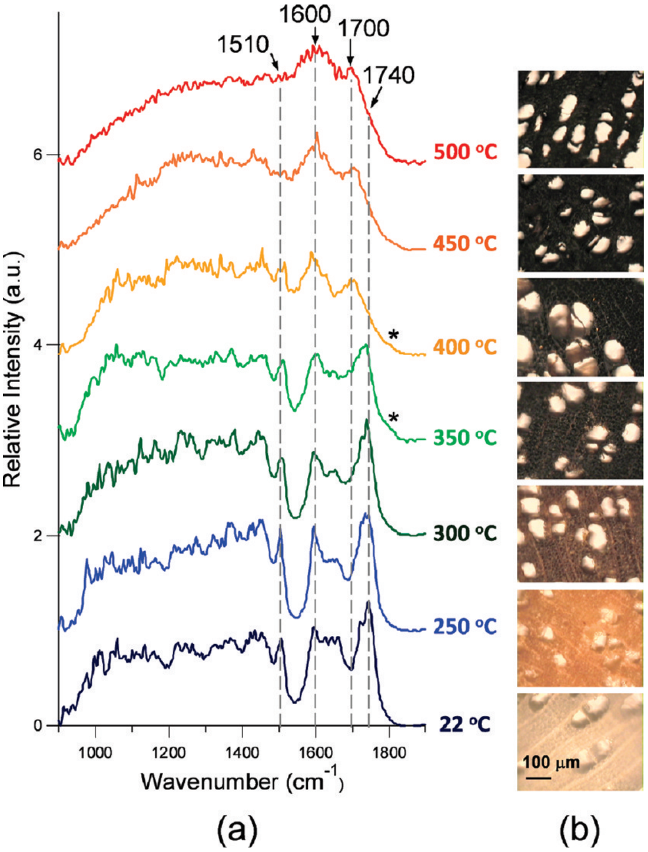

Figure 2. Pyrolysis of poplar cross sections: (a) FT-IR spectra of poplar and (b) light microscopic images (530 μm × 400 μm) of poplar sections (100 μm thick) at room temperature and after pyrolysis at temperatures ranging from 250−500 °C in 50 °C increments. The white spots are the lumen in the poplar cross sections.

These spectral changes at different pyrolysis temperatures can be explained considering the results from previous studies[7,28−32] on the pyrolysis of cellulose, hemicellulose, lignin, and wood particles. It is known that during a thermal treatment of wood, hemicellulose undergoes thermal decomposition first at ~150−300 °C producing acetic acids, then cellulose at 280−350 °C producing a tarry pyrolyzate containing levoglucosan, other anhydroglucose compounds, randomly linked oligosaccharides, and glucose decomposition products.[7,30] Thermal decomposition of hemicellulose occurs earlier than that of cellulose, due to the thermally unstable xylan-content in hemicellulose. This is also related to the low degree of polymerization (DP) of hemicellulose,being in less than 200, in contrast to high DP of the celluloses from wood in the range from 6000 to 8000.[16] Lignin is the least reactive wood component so it is more difficult to decompose. Major thermal degradation of lignin occurs over a broad temperature range of 280−500 °C.[1] According to a previous

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thermogravimetric study,[33] lignin decomposition seems to occur in two phases. First, initial degradation of lignin occurs between ~120 and ~300 °C from bond fragmentation in the phenyl propane side chains.[29,33] As a result, formaldehyde may be formed by fragmentation of the hydroxymethylene groups ($-CH_2OH$) present in the phenyl propane lateral chains. The secondary and the major phase of decomposition of lignin occurs between 300 and 480 °C by fragmentation of major chain linkages releasing monomeric phenol units into the vapor phase, followed by secondary degradation at the higher temperatures above 500 °C.[7,28,33]

More specifically, the phenomena relevant to the observed FT-IR spectra are as follows. Pyrolysis of hemicellulose involves the decomposition of the side units (4-*O*-methylglucuronic acid and acetyl groups) and the cracking of the main xylan chain.[16,30] Initially, carbonic acids (mainly acetic acid) are formed as a result of cleavage of the acetyl groups of hemicellulose.[30,31] In the FT-IR spectra of poplar shown in Figure 2a, a vibrational band at ~1740 cm^{-1} is mainly due to the ester carbonyl groups in hemicellulose.[26] Therefore, the decrease in intensities of the band at ~1740 cm^{-1} as the pyrolysis temperature increases represents the degradation of hemicellulose. Also, the formation of monomeric acids (mainly acetic acid)[23] seems to be the most plausible explanation of a small band at ~1800 cm^{-1} in Figure 2a (marked with asterisks) that was present in the IR spectra of some samples at high pyrolysis temperatures due to condensation of some of the volatile species inside the pyrolyzed wood.

An intense broad band near 1600 cm^{-1} (aromatic $C{=}C$) along with a band at ~1700 cm^{-1} ($C{=}O$ in phenolic esters) has been observed in the FT-IR spectra of pyrolyzed cellulose and lignin at 500 °C as well as in our FT-IR spectra of pyrolyzed wood samples (Figure 2a), indicating the significant increase of phenolic compounds and the formation of aromatic groups and/or aromatic hydroxyl groups as the char becomes more graphitic.[23,24]

Another interesting observation in FT-IR spectra of wood after pyrolysis in Figure 2a is that a noticeable decrease in the intensity of the band at ~1740 cm^{-1} occurs above 350 °C, a rather high temperature for the thermal decomposition of hemicellulose. In fact, the most dramatic IR spectral (or chemical) changes of the wood particles under our experimental conditions occur between 350 and 400 °C, showing rather slow response to the thermal treatments when compared to the previous thermal analysis works mentioned above. This phenomenon can be easily explained based on a recent thermal analysis study by Shen et al.[30] In their study, the major mass loss for cellulose and hemicellulose at heating rates from 5 to 60 °C/min was shown to shift toward higher temperatures at higher heating rates. For example, it shifted from 330 to 430 °C for cellulose and from 225 to 400 °C for hemicelluloses at heating rates from 5 to 60 °C/min, respectively. A higher heating rate results in a shorter time for the wood particles to react at a given temperature, so the thermal decomposition of wood appears to occur at higher temperatures due to a short residence time. In this work, the wood particles were pyrolyzed with a heating rate of ~150 °C/min so that the major thermal decomposition of cellulose and hemicellulose would be predicted to occur at ~400 °C or higher temperatures. This agrees with our results.

3.2.2. Structural Changes of Wood after Pyrolysis at Various Temperatures. Figure 2b shows visible images of the same 100 μm thick cross sections of poplar discussed above. As the pyrolysis temperature increases, pores in poplar cross sections continue to expand until ~400 °C, along with a gradual darkening of the wood particles. The wood tissue expansion is most likely due to expansion of wood components and/or due to escape of the gaseous products from the chemical reactions during wood pyrolysis. This observation is closely related to the most dramatic chemical changes between 350 and 400 °C in FT-IR spectra seen in Figure 2a. At temperatures above 400 °C, the chars collapse slightly and become brittle, yet they tend to hold most of their original tissue structure. Overall, the observations here are almost identical to the results from the previous work on the pyrolysis of 30 μm thick poplar sections using real-time light microscopy.[9] The only difference is that maximum tissue expansion appeared to occur at ~400 °C for 100 μm thick poplar sections in this work while at ~350 °C for 30 μm thick sections in the previous work. This minor difference is most likely due to the effects of the structural confinement or internal heat transfer inside the wood particles for wood sections with different thicknesses.

3.2.3. Multivariate Analysis of FT-IR Spectra of Pyrolyzed Poplar, "Standards". Principle component analysis (PCA) was used to quantify the spectral changes discussed above for pyrolyzed poplar. The separation between principal components with this approach depends on the extent of the spectral changes during pyrolysis at different temperatures. Figure 3a,b shows the results from the PCA analysis of the FT-IR spectral data set described above, poplar at room temperature and pyrolyzed from 250−500 °C in 50 °C increments. Typically 10 FT-IR spectra of poplar at each temperature were included in the PCA analysis. The score plot of the principal component 1 (PC1) against the principal component 2 (PC2) is shown in Figure 3a with score loading plots for PC1 and PC2 shown as blue and red lines in Figure 3b. These two components account for about 70% of the variability in the data. The data from each temperature in Figure 3a were color-coded as in Figure 2a and were clustered together nicely and separated well from other temperature groups. The only exception was the poor separation between room temperature and 250 °C, because there were little spectral differences between those two samples.

Multivariate curve resolution (MCR) analysis was applied to the FT-IR imaging data set for poplar at all temperatures in an attempt to decompose a complex FT-IR spectrum to several spectra of individual constituents. The results are shown in Figure 3c,d. MCR analysis could decompose FT-IR spectral data sets into three components, C1, C2, and C3. FT-IR spectra or loadings of the three components are shown in Figure 3c. The relative concentrations or scores of each component at different temperatures are shown in Figure 3d: The data points are averages over 10 measurements, and the error bars are standard deviations. As the temperature increases, a significant decrease in the concentration of C2 and an increase in that of C3 are observed. This trend implies that C2 represents raw wood materials, while C3 represents pyrolyzed wood. C2 contains strong vibrational bands at 1600, 1660, and 1740 cm^{-1}, which resembles the IR spectra of poplar at room temperature. C3 has similar structure to the IR spectrum of pyrolyzed poplar at 500 °C, but it shows better resolved spectral features of pyrolyzed wood, including prominent peaks near 1565 and 1620 cm^{-1}

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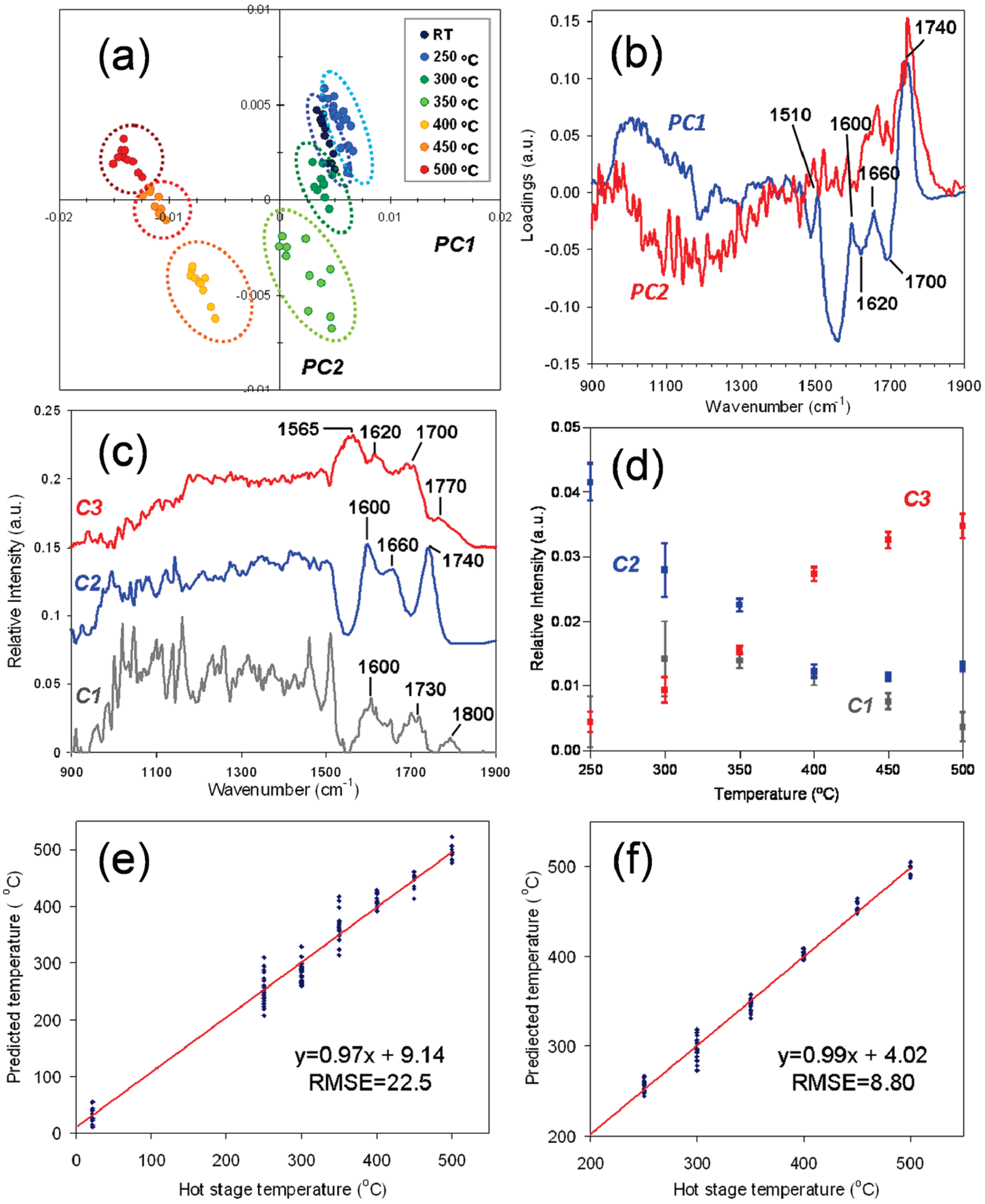

Figure 3. Multivariate data analyses of FT-IR spectra of 100 μm wood sections at each temperature: (a) Score plots of the principal component 1 (PC1) against the principal component 2 (PC2) and (b) score loading plots for PC1 (blue line) and PC2 (red line) from PCA analysis; (c) FT-IR spectra of the three components resolved from MCR analysis and (d) their relative concentrations at different temperatures; (e) a plot of the predicted temperature vs the real hot stage temperature for the pyrolysis of poplar from a PLS model that was built with FT-IR data at all temperatures and (f) one from a PLS model that was built with FT-IR data at 250−500 °C only.

that possibly originate from polyaromatic compounds formed during the pyrolysis. Meanwhile, the concentration of C1 shows a small increase at 250−300 °C and a decrease at 350−500 °C. This trend indicates that C1 represents some of the pyrolysis products formed at intermediate temperatures around 300−350 °C (e.g., a band at ~1800 cm^{-1} due to monomeric acids[23]).

Partial least-squares (PLS) regression was applied to the FT-IR data set to help quantify the variations with temperature. It is desirable to have good correlation between FT-IR spectra and temperature to build a reliable PLS model to predict the temperature of unknowns. Our FT-IR data had only one y-variable (the response variable), temperature, for the x-variables (the predictor variables), FT-IR spectra in the range of 900−1900 cm^{-1}, so the Unscrambler PLS-1 algorithm for one y-variable was used for the multivariate data analysis.

Initially, PLS regression analysis was done for the data set including FT-IR spectra of poplar at all temperatures including room temperature. The result is shown in Figure 3e as a plot of the predicted temperature vs the measured pyrolysis temperature. The correlation coefficient, the slope of the linear fit, was 0.97 and the root-mean-square error of prediction (RMSE), a measure of the average prediction error, was 22.49 °C. In other words, this predictive PLS model is expected to have an average temperature prediction error of ~22.5 °C for unknowns. The fact that the FT-IR spectra of poplar at room temperature and 250 °C were very similar suggested that the room temperature data might have

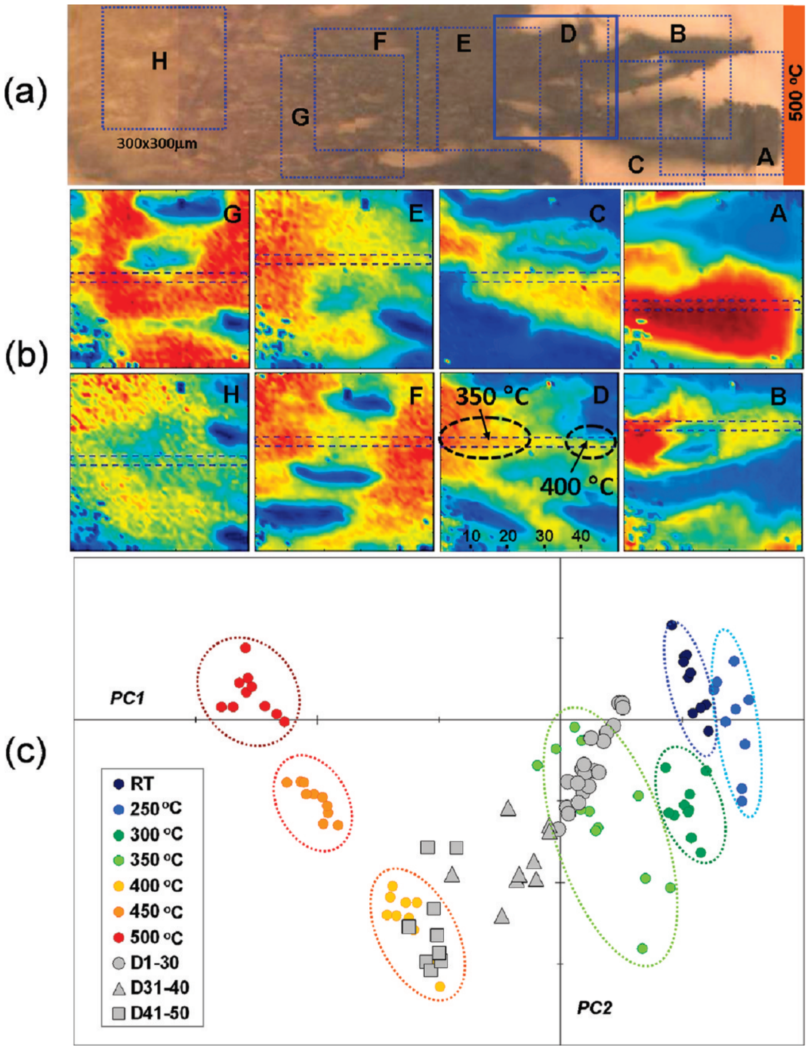

Figure 4. Determination of the temperature gradient inside pyrolyzed poplar using FT-IR images and PCA analysis. (a) A visible image of pyrolyzed poplar at 500 °C with the areas outlining the eight FT-IR image regions marked as blue boxes. (b) Eight individual FT-IR images plotting the intensity at 1600 $\mathrm{cm^{-1}}$ with the areas chosen for PCA analyses (marked as dotted rectangular boxes). (c) The PCA data analysis result for the FT-IR spectra from the dotted box (1 × 50 pixels) in image D of part b together with the data set from the standards used in Figure 3.

adversely affected the correlation between FT-IR spectra and temperature in the PLS model. Therefore, we excluded the room temperature data for PLS analysis to see if the FT-IR data set for 250−500 °C provide a better PLS model. As expected, the PLS analysis result from the FT-IR data set without room temperature data, shown in Figure 3f, produced a better predictive PLS model with a correlation coefficient of 0.99 and RMSE of 8.80 °C. This second model was used to predict temperature profiles inside the 5 mm thick poplar char sample.

3.3. Measurement of Temperature Profiles Inside a Pyrolyzed 5 mm Wood Block. In order to study heat transfer during the slow pyrolysis of thermally thick wood, a poplar wood block (5 mm × 5 mm × 20 mm) was pyrolyzed using a hot stage and sectioned to 100 μm thick for FT-IR imaging. The temperature profiles inside the pyrolyzed wood block were obtained as a function of the distance from the heated surface using the novel approach of chemical imaging coupled with multivariate data analysis. The PCA analysis and the PLS model described above for the temperature range of 250−500 °C were used to measure the temperature profile experienced by the wood inside the block.

3.3.1. Temperature Measurements Using FT-IR Imaging and PCA Analysis. As shown in Figure 3a, the PCA multivariate analysis method is an effective tool for grouping or clustering the FT-IR spectra of poplar at each temperature separately from those at other temperatures. Thus, the same PCA data analysis method was applied to determine the temperature profile inside the 5 mm poplar block after pyrolysis at 500 °C.

Figure 4a shows the visible image of the cross section of the pyrolyzed poplar wood block at 500 °C. The orange rectangle on the right is where the heat was applied to the sample. The pyrolyzed poplar sample was very brittle near the heated surface, and the ragged shape on the edges of the pyrolyzed wood section resulted from sectioning the charred surface. The pyrolyzed poplar section shows a gradual color change from a black color near the char surface where the heat was applied to a lighter brown color away from the char surface, indicating heat transfer limitations. The peach color in Figure 4a is due to the background where the char flaked away during sectioning.

FT-IR images of the pyrolyzed poplar section were collected in eight different regions marked with blue boxes in Figure 4a in order to cover all the areas of interest. The corresponding

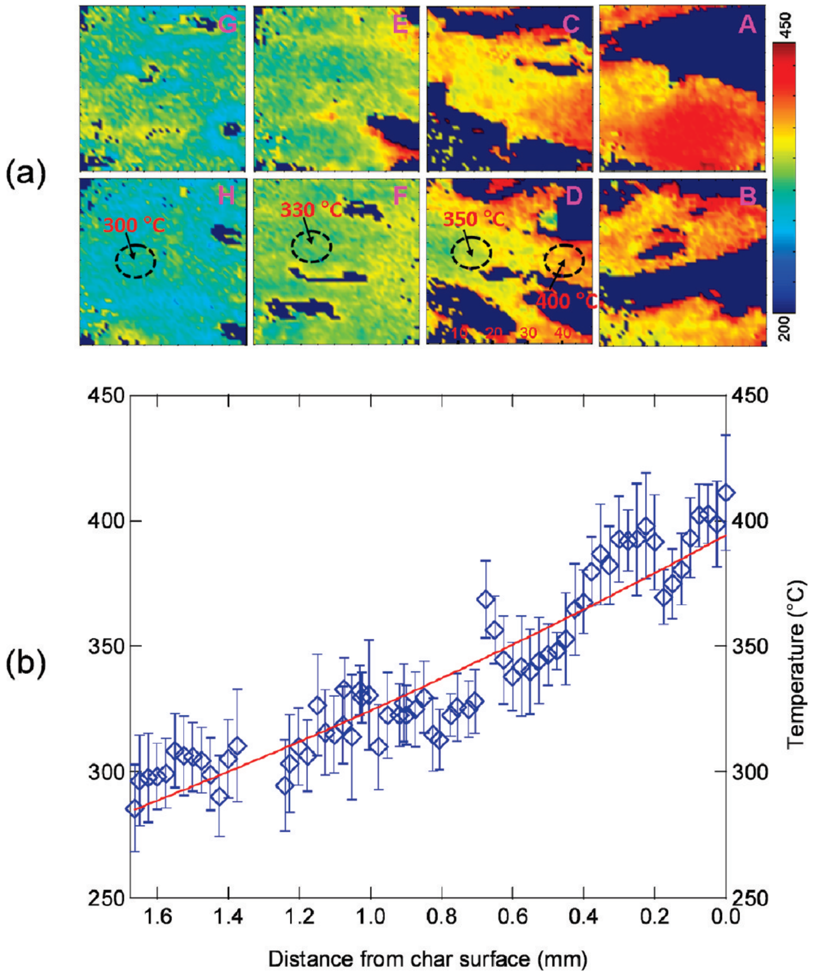

Figure 5. Temperature measurements inside a pyrolyzed wood block using FT-IR imaging and PLS regression. (a) Images showing the temperature experienced by a section taken from the middle of a block of poplar that had been heated on one edge to 500 °C. The regions labeled A−H correspond to those shown in Figure 4a. (b) A temperature profile inside the poplar block as a function of the distance from the char surface (blue diamonds) and the corresponding simple exponential fits (red line).

FT-IR chemical images for the aromatic C═C stretching band at 1600 cm^{-1} are shown in Figure 4b. We note that each FT-IR image can cover approximately 400 μm × 400 μm, but only an area of ~300 μm × 300 μm was used for data analysis to avoid bad data points from dead pixels on the periphery of the FPA detector. The images in Figure 4b contain several bad data points due to dead pixels in the imaging system that are noticeable at the lower left corners in the images, but those data were not included in data analysis. The data used for PCA analyses were selected from the areas marked with dotted rectangular boxes in each image in Figure 4b to ensure that the data sets include the pyrolyzed poplar, not the background. The eight images, labeled A−H, from the char surface toward the inner part of the wood block correspond to the visible light images in Figure 4a.

Figure 4c presents an example of PCA data analysis that shows how the temperature inside the wood particle at each position can be estimated. FT-IR spectra were selected from the area with a dotted rectangular box (1 × 50 pixels) in the image "D" and are labeled as D1 to D50 from left to right. These IR spectra were included in the PCA analysis with the standards, the data set used in Figure 3. The resulting score plot of PC1 against PC2 in Figure 4c provides a guide to determine the temperatures of the selected positions in the sample. The scores for the standards at each temperature showed the same pattern as in Figure 3a. Although the variation of PC2 may look higher than that of PC1 in Figure 4c, in fact, they are almost same (refer to Figure 3a that includes the scale of the variations). The selected IR spectra from the wood block, D1−D50, were divided into three groups, D1−D30, D31−D40, and D41−D50, in order to more easily visualize the data. The first group D1−D30 (gray circles) overlaps with the standards for 350 °C. The second group D31−D40 (gray triangles) falls in between the standards for 350 and 400 °C. The third group D41−D50 (gray squares) overlaps with the standards for 400 °C. Therefore, we can assign the temperatures of the selected areas, i.e., 350 °C at the region D1−D30 and 400 °C at the region D41−D50, as shown in the IR image "D" in Figure 3b. The temperature at the region D31−D40 is obviously between 350 and 400 °C but less well-defined. It appears that the PCA method can be used to estimate the temperature inside the block or how much heat was transferred to that position. However, this method suffers from rather high error of temperature prediction, up to 50 °C with our current standards sample data. Errors in the temperature estimation using the current method can be improved by adding FT-IR data at more temperatures with smaller increments than 50 °C. However, this method poses other problems like that it relies on a subjective decision on how to assign the temperature because many data points do not perfectly overlap with the standards but fall in the middle. Also, it is cumbersome and time-consuming to compare each data set with the standards manually. Therefore, PLS regression was applied to our FT-IR imaging data to get the temperature profile inside pyrolyzed wood.

3.3.2. Temperature Measurements Using FT-IR Imaging and PLS Regression. We used the PLS model shown in Figure 3f to create a temperature or chemical reaction profile of the pyrolyzed 5 mm poplar block. Figure 5 summarizes the results from the temperature measurements using PLS regression. Figure 5a shows images of the same regions shown in Figure 4. However, in this case, the images project the values of the predicted temperatures from the PLS modeling. The temperature prediction by PLS regression was based upon a projection of the PCA scores onto the PLS model in Figure 3f. Thus, the images plot the temperature experienced by the biomass or the chemical composition that remains after pyrolysis. The color bar on the left of Figure 5a shows the color scheme that was used in the images. For ease of visualization, the background data points where the char flaked away during sectioning were colored with dark blue, corresponding to 200 °C. Images of the temperature profiles were colored with a range representing 200 °C (dark blue) to 450 °C (dark red) to maximize the color contrast.

Figure 5b shows the temperature profile of pyrolyzed poplar at 500 °C as a function of the distance from the char surface. Each data point (shown in blue diamonds) represents the average value of the temperatures across the sample at the same distance from the char surface. The temperature variations, standard deviations, in the pyrolyzed wood at each distance from the heat source were shown as error bars in Figure 5b. The temperature profile could be fitted using a simple exponential, and the fitted curve is shown as a red line ($y = 392\ e^{-0.19x}$, $R^2 = 0.85$), which represents the overall temperature profile inside the pyrolyzed poplar wood block. The structural inhomogeneity of wood results in variations in temperature across the pyrolyzed poplar even at the same distance from the char surface because the wood experiences different heating limitations parallel to the heated surface. This phenomenon is easily observed in the images of the temperature profiles in Figure 5a.

Overall, the results from the current study show that the FT-IR imaging technique coupled with multivariate data analysis has great potential as a tool to study the heat transfer effects in the pyrolysis of thick wood particles in real pyrolysis reactors. The authors believe that it is possible to calculate the rate of heat transfer and the thermal conductivity of the poplar wood using the FT-IR imaging data if the pyrolysis experiment is performed in a reactor with a fast heating rate. This work was conducted using a pyrolysis reactor with a slow heating rate, so it is not possible to calculate the thermal conductivity of the sample from current FT-IR imaging data with good accuracy. We believe that this is a unique and novel approach to visualize the chemical changes in heated biomass and may be applicable to reactions in other materials. In addition, this approach to measure the temperature inside pyrolyzed biomass is based on measurements of the chemical composition of the samples, not a thermocouple response, providing a full picture of temperature profiles inside the sample rather than discrete measurements at selected positions in the sample. Therefore, this new approach is expected to provide an opportunity to study thermal effects in many applications where the temperature measurements were hindered by the difficulty of the installation of thermocouples inside samples

4. Conclusions

FT-IR chemical imaging was applied to monitor the structural and chemical changes of thick wood particles under various pyrolysis conditions for the first time. The pyrolysis process of a biomass particle is complex since the governing phenomena are both chemical and physical. The heat transfer process is an element that needs to be understood to describe the pyrolysis phenomena and is especially important for thermally thick biomass samples. The results from the current study show that the FT-IR imaging technique coupled with multivariate data analysis has great potential as a tool to study the heat transfer effects in the pyrolysis of thick wood particles in real pyrolysis reactors. We believe that this is a unique and novel approach to visualize the chemical changes in heated biomass and may be applicable to reactions in other materials.

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