



Characterization of Wood Chemical Changes Caused by Pyrolysis During Flaming Combustion Using X-Ray Photoelectron Spectroscopy

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Abstract. As heat is applied to wood, thermal degradation, called pyrolysis, occurs. A majority of what is known about the pyrolysis of wood has been obtained using either extracted component polymers or wood pyrolyzed in an inert atmosphere. However, the physical and chemical reactions that occur during pyrolysis of wood are affected by the interaction of the polymers in whole wood as well as the oxygen present in the atmosphere. X-ray photoelectron spectroscopy (XPS) is a surface measurement technique that yields information on both the chemical composition of the sample and the chemical bonds among the elements and compounds that comprise it. Here, XPS was used as a tool to examine the number and type of carbon bonds in Douglas fir exposed to flaming combustion.

Keywords: XPS · Wood · Chemical composition · Pyrolysis

1 Introduction

When exposed to high temperatures, wood thermally degrades as a series of complex chemical and physical transformations. This thermal degradation is known to adversely affect structural properties of wood [1]. Yet, current knowledge of the chemical and physical changes that occur in wood during pyrolysis remains limited, particularly the knowledge related to the wood products for structural applications. Some concerns have been raised that the current understanding might not be conservative enough when calculating the structural load capacity post-fire [2]. A more thorough understanding of thermal degradation of wood is critical in maximizing wood's potential applications while maintaining a high degree of safety [3].

1.1 Chemical Changes in Wood Due to Pyrolysis

The polymeric components of wood are irreversibly altered as wood is exposed to high temperatures. The majority of what is known about thermal degradation of wood has been obtained using thermogravimetric analysis (TGA) on isolated polymeric components [4]. Dehydration takes place at temperatures between 105 °C and 200 °C [4]. Above 200 °C, the breakdown of the major polymeric components of wood begins. Hemicelluloses are the most thermally sensitive and begin to breakdown between 200 and 260 °C [4]. Cellulose thermally decomposes between 240 and 350 °C, and lignin thermally decomposes between 280 and 500 °C. There is a great deal to learn from the previous body of work based on TGA. However, thermal degradation of the isolated wood components is different from what occurs within bulk wood because, in wood, the entwined nature of the component polymers combined with the hierarchical structural of wood can alter the resulting effect of pyrolysis. Additionally, many of the kinetic parameters obtained by traditional TGA were conducted in non-oxidizing atmospheres and likely have limited applicability in terms of pyrolysis models used to describe structural wood fires (Fig. 1).

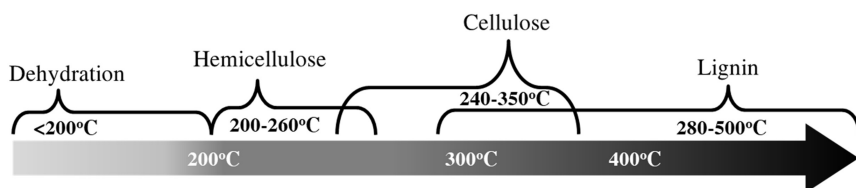


Fig. 1. Thermal stages of wood pyrolysis from TGA analysis. Redrawn from [4, 5].

The current knowledge of wood pyrolysis is mostly based on isolated wood polymers and is insufficient for understanding the formation of char in bulk wood material. In this work we present in-situ measurements of the elemental composition present in the pyrolysis zone and char layer of wood exposed to fire in atmospheric conditions.

1.2 X-Ray Photoelectron Spectroscopy (XPS)

XPS is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition, chemical state and electronic state of the elements that exist within a material. XPS works by irradiating a sample material with soft x-rays, which can penetrate the surface to a depth of 10 nm. Then, when the x-rays reach the sample's surface, photoelectrons are ejected from the sample and their kinetic energies (KE) are measured by an analyzer. The binding energy of the electrons is deduced from the KE and source photon energy. The resulting energies depend upon the element, the orbital from which the electron was ejected, and the chemical state of the element.

XPS has been used to study the surface chemistry of black cherry, red oak and pine wood surfaces [6], wood surfaces post heat-treatment in inert environments [7] and on

isolated wood polymers [8]. Based on binding energy and the types of bonds found in wood constituents, there is an agreement on the number and type of bonds to use for deconvolution of the C1s peak [7]. Since the peaks for the chemical states that exist within the C1s spectrum are close together, it is necessary to deconvolute to identify individual contributions. The deconvoluted peaks were used to qualitatively evaluate the elemental changes in the charred wood (Table 1).

Table 1. Chemical bond types present in wood and the component polymer attributions.

Bond	Binding type	Binding energy (eV)
C-C or C=C	Aliphatic carbon bonding from carbon contamination or Aromatic Carbon (abundant in lignin)	285.0
C-O	From alcohols and ether functional groups (abundant in cellulose)	286.4
O-C-O	From ketones	287.6
COOH	From carboxylic acid due to oxidation of an aldehyde group	289.2
π - π^*	From aromatic carbons in lignin (shake up)	291.5

2 Methods and Materials

2.1 Charred Wood

The wood specimen was obtained from one board of Douglas fir (*Pseudotsuga menziesii*) lumber with final dimensions of 100 mm $\times$ 100 mm $\times$ 21 mm. To measure the thermal wave through the Douglas fir specimen, we inserted 30-gauge, Type K thermocouples into the specimens through horizontal holes drilled at heights of 4 mm, 8 mm, 12 mm, and 16 mm below the top surface (Fig. 2a). Additional thermocouples were placed between the back of the sample and the retainer frame (i.e., at 21 mm) and on the specimen's top surface. The temperatures between thermocouples were calculated using a non-linear spline fit.

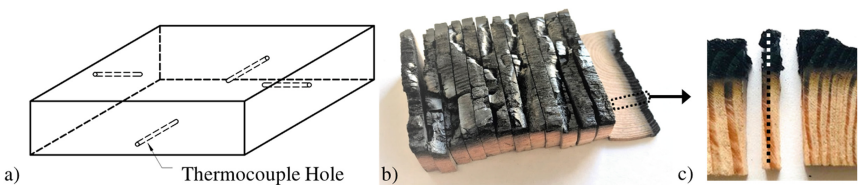


Fig. 2. (a) Schematic of wood specimen with holes for thermocouples, (b) charred wood specimen sliced into 4 mm sections and (c) sliver of charred wood with latewood for XPS analysis. The dotted line represents the line scan.

The radial face of the specimen was exposed to a constant heat flux of 50 kW/m^2 using a cone calorimeter (FTT iCone Mini, East Grinstead, West Sussex, UK) without piloted ignition. Prior to exposure in the cone calorimeter, the specimens were conditioned in an oven at 105°C for 24 h to drive off any moisture. The test was terminated by removing the specimen and extinguishing the fire with water when the temperature of the thermocouple at 21 mm reached 100°C .

The charred wood specimen was then cut along the transverse plane into 4 mm sections (Fig. 2b). To avoid edge effects caused by the cone calorimeter holder, a 4 mm slice from the center of the specimen was chosen and a latewood growth ring was selected for XPS line scans.

2.2 XPS Line Scan

For our experiments, the x-ray source was an aluminum $\text{K}\alpha$ micro-focused monochromator housed in a Thermo K-Alpha X-Ray Photoelectron Spectrometer. With this equipment, a line scan was carried out with a total of 72 spots, each with a spot size of $30 \mu\text{m}$. Each initial scan had an analyzer pass energy of 200 eV to obtain the survey spectra between zero and 1230 eV. Higher resolution scans were obtained with an analyzer pass energy 50 eV to increase the spectral resolution. For the $\text{C}1\text{s}$ scans, the binding energy range surveyed was 179–298 eV. To avoid the effects of surface impurities, the surface was etched for 20 s with an Argon ion beam before the XPS measurement. The line scan was set up on a small wood sliver (Fig. 2c), measuring approximately $16 \text{ mm} \times 1.3 \text{ mm} \times 1.8 \text{ mm}$. The line scan started at the unexposed/uncharred edge of the specimen and ended at the exposed/charred edge.

3 Results

The XPS survey spectra at two spots in the line scan are depicted in Fig. 3. The $\text{C}1\text{s}$ (around 285 eV) and the $\text{O}1\text{s}$ (around 532 eV) photoelectron peaks were clearly resolved. While Auger electrons are resolved above 1200 eV, photoelectron peaks from other atoms were minor, showing the wood consists mainly of carbon and oxygen. The intensity of the $\text{C}1\text{s}$ and $\text{O}1\text{s}$ peaks decreased with an increase in exposure temperatures as the readings moved towards the exposed edge of the wood.

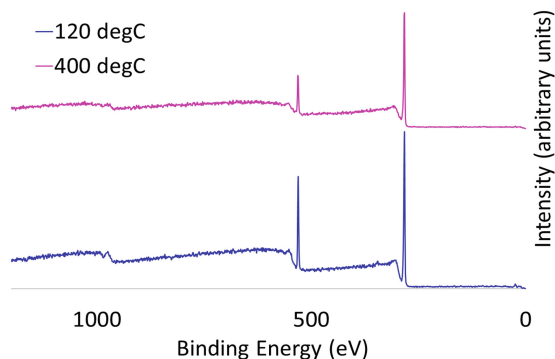


Fig. 3. XPS survey spectra at two spots within the wood sliver.

The C1s spectra was chosen to investigate the chemical structure of the charred wood due to the difficulty of O1s peak extraction that results from complex shift behavior [9]. To determine the type of chemical bonds present and their contribution to the total spectra, the C1s high resolution spectra was deconvoluted using an automated peak fitting routine [10] with a Pseudo-Voigt function [11] with a Shirley background correction [12]. Figures 4a and b shows the deconvoluted C1s spectra at the same spots as the survey spectra in Fig. 3. As shown in Fig. 4, the extracted peaks within the C1s spectra are changing with exposure temperatures. The intensity of all peaks decreases with an increasing temperature. Further analysis to quantify these changes are underway.

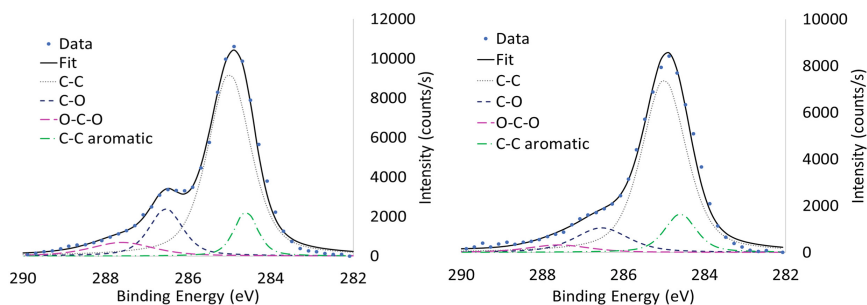


Fig. 4. Deconvoluted XPS high resolution C1s peaks at (a) 120 °C (b) 400 °C.

To take into consideration potential changes in the electrical resistivity from the unmodified wood to the charred regions, we used an internal reference that set the C-C peak at 285 eV for all spots within the line scan. The amount the peaks were shifted with respect to 285 eV is known as the charge compensation. The charge compensation changes from the uncharred wood through to the charred region (Fig. 5). This represents a reduction in electrical resistivity as the wood polymers thermally degrade and carbon is left behind [7].

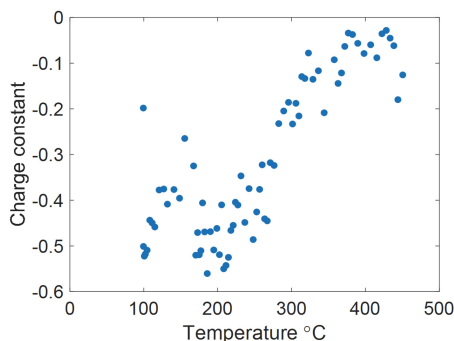


Fig. 5. Change in charge compensation through the charred wood slice from the unexposed edge at 100 °C to the charred edge at 450 °C.

4 Concluding Remarks

Current knowledge regarding the chemical and physical changes that occur in wood during pyrolysis is limited. This project utilizes XPS to examine the type of carbon bonds in Douglas fir exposed to flaming combustion in an effort to better understand the thermal degradation of the polymers in bulk wood.

Here, a change in the amount of material being irradiated is deducible from the survey spectra in addition to a noticeable change in electrical resistivity. Further data analysis of the deconvoluted C1s peak is required to quantify the relationship between the chemical structure of the wood polymers and the exposure temperatures in bulk wood.

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