Quantification of Wood Thermal Treatment by Electron Paramagnetic Resonance Spectroscopy

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Dedication

To my grandmother, rest in power.

Abstract

The process of thermally treating wood can impart desirable properties such as an aesthetically appealing color, dimensional stability, and increased resistance to moisture and fungal decay. However, potential undesirable outcomes, such as increased brittleness, may arise with extensive thermal treatment. Due to this risk, it is extremely important to quantify the extent of heat treatment on a specimen for quality control. Previously, free radical content in thermally treated wood was discovered. We therefore set out to quantify the radical content of thermally treated wood samples utilizing electron paramagnetic resonance (EPR) spectroscopy and attempted to find out if this could be correlated with the extent of heat treatment. We heat-treated samples using a pilot-scale, in-house oven kiln (an industrially relevant process), as well as in the highly controlled and quantifiable environment of a thermogravimetric analysis (TGA) analyzer. With these wood samples, we measured the free radical content using EPR to determine the correlation between radical content and other factors such as: treatment temperature, treatment atmosphere, rate of formation, treatment time, and the effects of moisture. Our main goal was to find reliable methods for quantifying the extent of heat treatment in thermally treated wood by the use of EPR spectroscopy.

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Chapter 1

Introduction

1.1 Background on wood

Wood is one of the greatest renewable materials on earth and its uses are endless. There are two wood classes of trees, hardwood and softwood. Hardwood trees, scientifically referred to as a deciduous tree, is a tree that bears leaves.[1] Whereas softwood tree, or a coniferous tree, is a tree that bears cones or needles.[1]

It is easy to mistake the words “hardwood” and “softwood” as indicators of strength and structural integrity. However, the name of the wood has nothing to do with its actual performance as a structural material but can give clues to the weight and density of a wood’s composition. Hardwood generally has a denser composition and is heavier in weight than its softwood counterpart.[2] In fact, both hardwood and softwood are commonly used as construction material. Typically, softwood is more likely to be used in the creation of accent pieces, while hardwood is more commonly utilized in the composition of structural pieces. This is seen in the use of softwood during the construction of doors, furniture, and frames, while hardwood is typically utilized for walls, ceilings, and floors.[2]

As with any material, there are positive and negative factors to consider when deciding to use wood. Wood is a very strong material with a compressive strength (weight or stress in the form of pushing) that is much stronger than its tensile strength

(resistance of being pulled apart). Even more impressive is that wood's tensile strength is stronger than aluminum and glass, with some types being even stronger than concrete.[1] Compared to steel, wood becomes stronger as it is exposed to heat and loses its moisture content, whereas steel tends to expand and warp, decreasing its reliability and strength.[2] Despite these clearly positive attributes, wood is not always the best choice as a construction material and in applications. Commonly known for its vulnerability to water, wood is easily susceptible to rot and mold. Wood also tends to attract pests like insects or other invasive animals.[3]

To alleviate some of the downfalls of wood as a material and make it more attractive in use of structural applications, wood is often treated with different chemicals such as wood preservatives. Treating wood in this way can help to prevent rot, mold, insects, other pests, and environmental factors from harming the integrity of the wood. However, many of these chemicals are toxic to the environment and to humans. For example, one of the most common chemicals that is used in the chemical treatment process is creosote, a chemical wood preservative that has been closely linked to the development of cancer, liver failure and other ailments, and is widely considered toxic to humans.[1,4] To help wood be more fire-retardant, wood is also treated with various fire-retardant chemicals.

Human ingenuity has identified a technique of thermally treating wood that allows individuals to take full advantage of the many great properties of wood while simultaneously eliminating, or greatly reducing the costs or any concerns associated with chemically treated wood.

1.2 The process and application of thermally treated wood

An alternative to chemically treating wood, with significantly fewer risks of toxicity, is thermally treating wood. Thermally treated wood is placed under heat and pressure for a specific amount of time. Many of the same desired properties of wood persist without the use of chemicals and can be applied to both hardwood and softwood.

Wood is primarily made up of cellulose, hemicellulose, and lignin (Figure 1.2.1).[5] To understand the way these three interact with each other it is best to think of it as a brick wall, where cellulose is the bricks, lignin is the rebar, and hemicellulose is the mortar that helps bind it all together.[6] A closer image on a cellular level of how this interwoven network exists is in Figure 1.2.2[7] while an analogous structure of an actual brick wall is given in Figure 1.2.3.[8] Once wood is heated between temperatures of 160-220 °C, the breakdown of hemicellulose occurs, cellulose crystallization starts at temperatures above 160 °C, decomposition of lignin starts at temperatures above 280 °C, and decomposition of crystalline cellulose happens at temperatures between 300-340 °C.[8] It is suspected that free radicals are produced through thermal treatment. There is disagreement about, and perhaps many possibilities for, where the free radicals occur and how they form. ThermoWood concludes that the free radicals come from the thermal structural changes from lignin.[9] Whereas the U.S.D.A concludes that the radicals come from the thermal breakdown of cellulose molecules that do not convert into levoglucosan (Figure 1.2.4).[10]

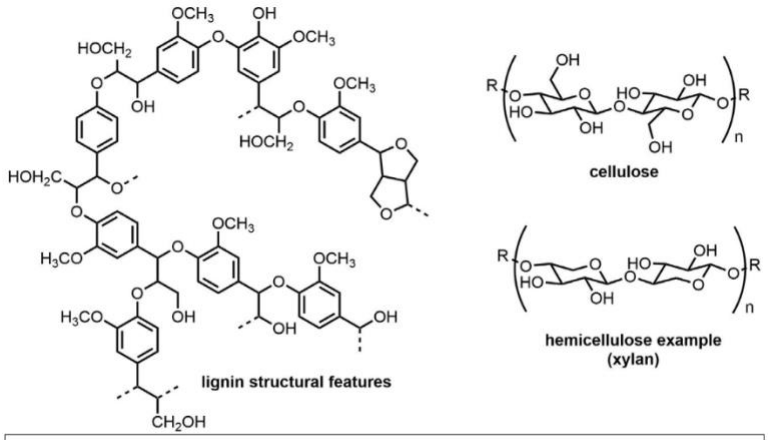


Figure 1.2.1 Three common molecules of wood, lignin (left), cellulose (top right), hemicellulose (bottom right).[5]

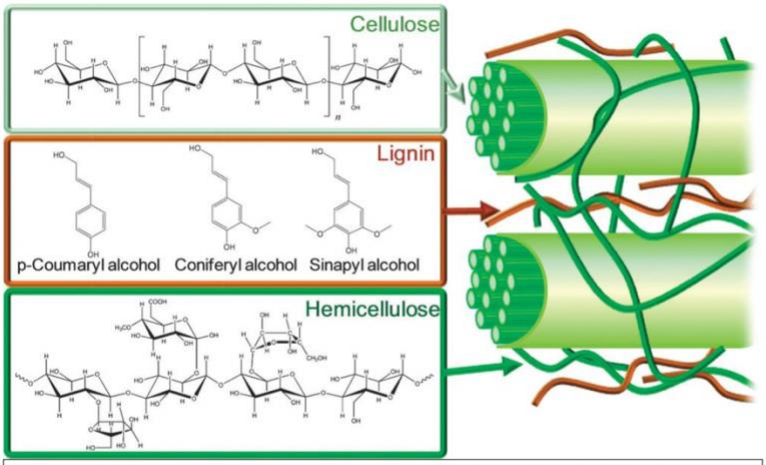


Figure 1.2.2 Structures of cellulose, precursors of lignin, and hemicellulose in descending order on left with representation of interwoven cellular structure on

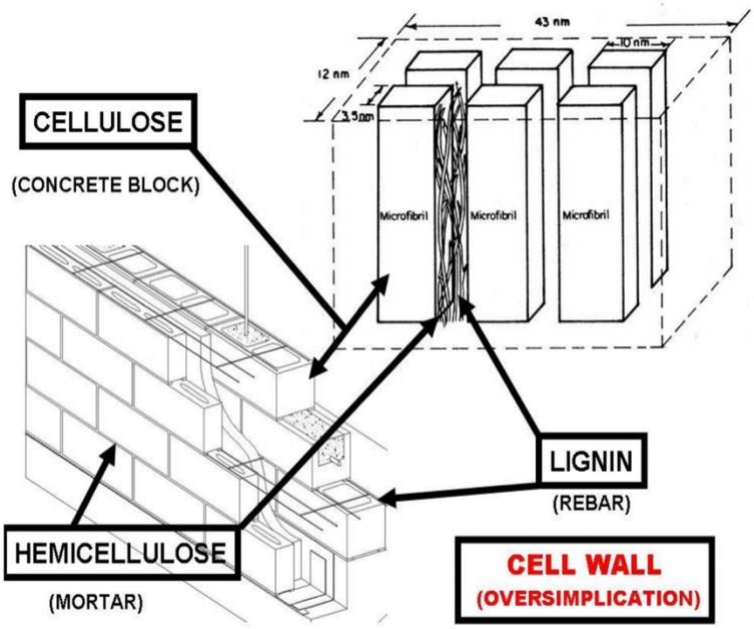


Figure 1.2.3 Analogous representation of the interwoven network of cellulose, lignin, and hemicellulose within wood.[8]

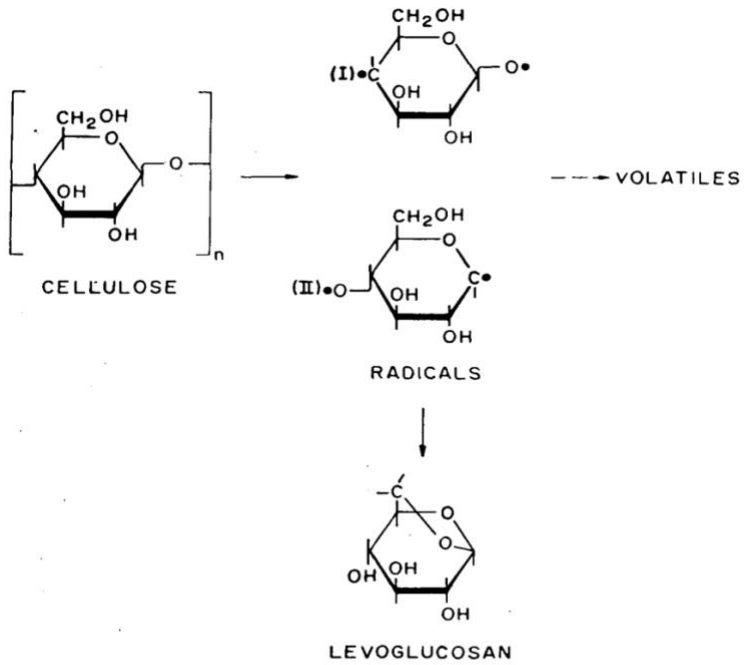


Figure 1.2.4 Mechanism of cellulose degradation resulting in Levoglucosan, volatiles and radicals.[10]

Cellulose forms a polymer chain on carbon one and carbon four (seen in Figure 1.2.4). When cellulose depolymerizes due to heat, radicals are left on both sides of the chain, in one or two different orientations. If the oxygen is left on carbon four, the radical stabilizes and the cellulose converts into levoglucosan.[10] If the oxygen is left on carbon one, the stereochemistry doesn't allow the conversion to levoglucosan, keeping a radical on carbon four while the oxygen forms and oxygen bond.

Through the development of the thermal treatment process, the wood industry has achieved an advancement that is safer for people and the environment. Individual companies use various techniques to produce different heat-treated wood products, with the intensity and type of treatment affecting the performance properties of their products. Temperature, wood species, moisture content, atmospheric conditions, and

time are a few variable components that are involved in the intensity of treatment.[8] New Option Wood, Thermo Treat, Firmolin, and ThermoWood are examples of popular wood companies with varying thermal treatment techniques.[6] The temperatures of treatment at each company range between 170 °C and 215 °C. Methods of thermal treatment vary between companies and are often unique within an individual company's process. For example, New Option Wood has two lines of wood treatment: Retification and Perdue. The Retification process utilizes a nitrogen rich atmosphere, and the Perdue process utilizes an oxygen rich atmosphere.[6] ThermoWood uses two processes called Thermo-S and Thermo-D which utilizes different temperatures and types of wood.[9] Softwoods are treated at 190 °C for the Thermo-S process and 212 °C for Thermo-D. Hardwoods are treated at 185 °C for the Thermo-S process and 200 °C for Thermo-D.[9]

There are disadvantages to the thermal treatment processes. Over or under treatment of wood can lead to problems with uniformity in product quality. If wood is undertreated, mold resistance, heat resistance, and an increase in structural strength, among other desired qualities, will not be fully achieved. However, if the sample is thermally treated too much, undesirable qualities will appear in the wood such as increased brittleness, decreased density, and a decrease in bending strength.[8] A process to precisely and accurately thermally treat wood was an important goal in this study in order for us to reliably prepare samples under varied conditions. Using a kiln or a thermogravimetric analyzer (TGA) are the two methods of thermally treating wood that we will use in this study.

The first question is, therefore, how do we quantify the thermal treatment of wood to achieve a more uniform material?

1.3 Quantification of heat treatment

Demand for thermally treated wood increased across the United States as the practice of thermally treating wood gained popularity. In a professional consumer perception survey administered by the Forest Products Management Development Institute at the University of Minnesota, thermally treated wood scored high on environmental performance, aesthetics, and durability compared to other wood products.[11] However, due to the variety of treatment procedures, there is a lack of product standards, process, and quality consistency among different producers.[6] This lack of consistency places unnecessary strain on the market for the rise in demand of thermally treated wood.[6]

As concerns rise for illegal logging and the use of toxic chemicals, the need for an industry standard is apparent.[6] A favorable aspect of thermally treated wood to the average consumer was the desirable look after treatment, or the aesthetic aspects.[11] Some companies, such as Menz Holz, use hot oil as a medium for heat transfer which functions as a stain or a lacquer. This process produces a better aesthetic with its end product that most consumers find attractive.[6] Menz Holz lists this process as both an oil treatment and a thermal modification process which veers away from traditional ways of thermally treating wood. Concerns arose for companies using methods outside of the

traditional ways of thermally treating wood due to the little knowledge of consumers and their acquisition of these products.[6]

To solve this problem, an industry standard needed to be found by measuring the extent of thermal treatment in a sample of wood. The key part was defining a standard range where acceptable thermally treated wood could lie. The standard range of thermal treatment would have an upper and lower limit of treatment. The lower limit would be where the wood is not treated enough. The upper limit is where the wood is treated too long leading to a brittle, unsound product. If the wood fell anywhere outside the limits, it would not be deemed to bear the name of thermally treated wood.

Initial tests were conducted by the National Resources Research Institute (NRRI) and by other contracted companies on how to measure the extent of heat treatment and to create a standard. Through preliminary research, it was found that thermally treated wood possesses free radicals (vide supra Chapter 1.2). The question now became can one see a free radical correlation to the extent of heat treatment? If so, can a known radical measuring technique like Electron Paramagnetic Resonance (EPR) spectroscopy be utilized to measure those free radicals?

1.4 EPR background

Electron Paramagnetic Resonance (EPR) spectroscopy, also known as Electron Spin Resonance (ESR) spectroscopy, is a useful technique to study free radicals. Free radicals, or unpaired electrons, can be highly reactive and are often used as a chemical

reaction initiator or for chain propagation, but can also be harmful, damaging our cells and causing illnesses.[12] Many of the foods we eat have free radicals in them and our bodies produce free radicals as well. Natural enzymes, like superoxide dismutase, and antioxidants, like vitamin C or E, eliminate free radicals in our bodies.[13]

EPR is a way to measure the quantity of free radicals in a substance and to figure out on what molecule the free radical exists. EPR measures the energy separation between an electron's two spin states of + and - 1/2 (spin up and spin down). An EPR experiment involves a few steps. First, the sample is placed in a magnetic field which separates the energy levels of the electron's two spin states. Next, the EPR instrument emits microwaves onto the sample and records the microwaves that come back. The spectrometer will then sweep a magnetic field and record the signal variation of the microwaves resonating back to the detector.

Some key factors of running EPR are magnetic field sweep, scan time, time constant, and number of scans. Magnetic field sweep is the actual gauss (G) range of the magnetic field that is "run" or "swept" in an EPR scan. It is important to have the field sweep large enough to capture all of the sample's signal.[14] Scan time is the time the machine takes to start at one end of the magnetic field and to sweep and scan to the other end. The time constant is how quickly the data can be detected and converted with the change in signal, on newer EPR spectrometers it can be referred to as the DGRC filter. Signal resolution and hyperfine peaks can be lost with an imbalance of the two. The more you increase the time constant the more you should also increase the scan time.[14] It is also important to have repetitive scans. With older EPR

spectrometers being retrofitted to computer exports, some runs are faulty. Running lots of scans and signal averaging is best to get a good signal to noise ratio in the data. There is a relative decrease in random noise to signal that is proportional to the square root of the total number of average scans.[14] Finally, if you want to quantify the amount of free radicals in a sample you must take the double integral of the data. The signal intensity is proportional to the radical concentration.[14]

1.5 Thermogravimetric Analysis Analyzer background

Thermogravimetric analysis (TGA) is a form of analysis used to study direct relationships between temperature, time, and mass. TGA allows the study of connected chemical relationships in different materials and chemicals. A few of these relationships are quantification of solvent loss, plasticizer loss, decarboxylation, pyrolysis, oxidation, and decomposition.[15] The accurate and precise control and measurement of temperature and mass are important. The atmosphere within the instrument can also be controlled with tanks of compressed gasses such as nitrogen and oxygen. The accuracy and controllability of TGA allows for testing thermal treatment of wood on a smaller scale to address questions and to find answers about the larger scale processes. An example of a TGA analysis can be seen below in figure 1.5.1.[15] The carbon content was found in a sample of ethyl cellulose by an increase in temperature and a

nitrogen/oxygen gas combustion switch. The change in weight after the switch is the carbon content.

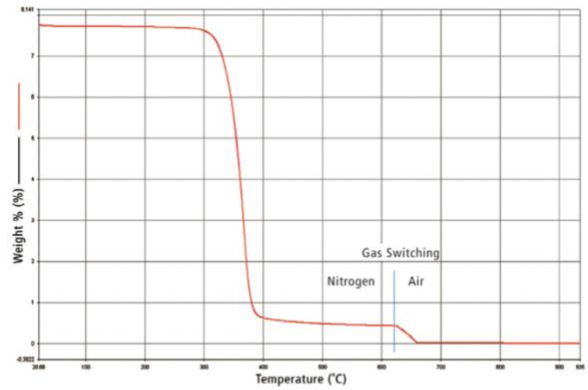


Figure 1.5.1 Showing a TGA data set of Weight % in respect to temperature of the decomposition of ethyl cellulose with a nitrogen/oxygen gas switch for combustion.[15]

1.6 Summary

The process of thermally treating wood creates a more reliable, aesthetically pleasing, healthier product that is in demand by consumers. However, the industry has not yet caught up to the growing demand, and this relatively new technique lacks industry standards. This could be problematic for consumers, as well as producers. A process for quantifying heat treatment should be created to determine the limits of an industry standard. One method to accomplish this is utilizing EPR spectroscopy. Using EPR spectroscopy, methods can be tested to see if there is a correlation between EPR free radical signal and the extent of heat treatment. To more accurately control heat treatment, a TGA analyzer will be utilized for its analytical grade control and measurement of temperature, weight, and atmosphere. By getting a deeper understanding and utilizing EPR spectroscopy, TGA, and thermally treated wood I will

attempt to answer the question: Can the quantification of wood thermal treatment be accomplished by a correlation in EPR spectroscopy? Our hypothesis is that radical content indeed increases with heat treatment and EPR can readily detect radicals. We need however, to determine how heat treatment and radical content varies with time at a given temperature, and at varied temperatures.

Chapter 2

Materials and Methods

2.1 Wood sample preparation

With wood being the pivotal focus of this project, it is important that sample preparation be done in a precise and accurate way to reduce unwanted variables. The wood for this project was taken freshly from outside and stored inside a temperature and humidity-controlled lab. Having fresh wood was key to this study because many types of wood that are store bought have been treated per the American Standard for Testing Materials international (ASTM international) methods. The most common treatment was the oven drying standard for commercial building lumber from ASTM international.[16] Wood samples from this source was therefore detrimental to this study for numerous reasons. Having pre-treated wood would hurt or skew the results. The fresh wood that was selected and used was balsam poplar (Populus balsamifera). This is a common northern indigenous tree found in most parts of Canada and northern Minnesota, Wisconsin, and Michigan shown in Figure 2.1.1.[17]

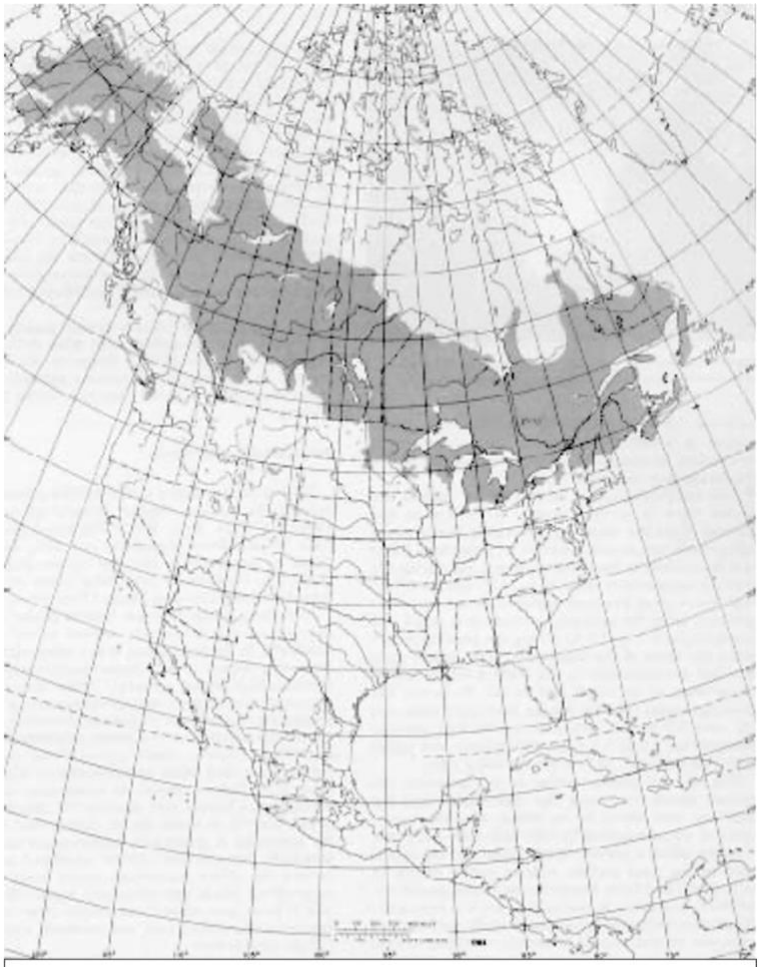


Figure 2.1.1 dark grey covering the native range of Balsam Poplar.[17]

For one initial test the wood was “chopped” and randomly cut. For the chopped sample of wood, it was chiseled away from a larger piece of wood with the back of a hammer and continued to be cut with a die cutter until pieces were small enough to fit inside a EPR quartz sample tube with an inner diameter of 3 mm. For the randomly cut samples the wood was cut multiple times and randomly with a pair of scissors until the size was just bigger than the chopped piece but still small enough to fit inside a sample tube.

For normal samples, a larger piece of wood was cut with a large utility knife (flat edge). It was cut with the grain out of the inner trunk of the log of the balsam poplar to a size of about 10 cm x 4 cm x 2 cm initially for yielding more than one sample. Next a smaller precision utility knife with flat #4 blades were used for precise small cuts for the remainder of the sample prep. It was imperative to use a fresh sharp blade to prevent miss- cuts, compression cuts, and uneven cuts, as free radicals can be generated by the physical manipulation of the sample, even before thermal treatment. Gloves were always used when handling and cutting samples to prevent skin oil transfer to wood. There are treatment processes that involve using oil in their treatment processes so it's important to try and avoid that.[6] The final dimension of the wood sample was 8 mm x 1.5 mm x 1.5 mm. A few initial tests had final sizes of 8 mm X 2 mm X 2 mm before the final dimensions of 8 mm x 1.5 mm x 1.5 mm were chosen. It was important to use accurate calipers that can measure to the tenth of a millimeter for accurate measurement. Once the piece had been cut to size, the sample was weighed. Each piece of wood of that size was around 6.0 mg to 9.0 mg in weight. For statistical needs the wood samples were kept within a size of 7-8 mg to avoid sample and result variance. If the wood weight fell outside of that range, the wood was examined under a microscope with calipers for dimensional issues. If it was under-weight the sample was unusable. If it was over-weight it was examined that one of the sides was a little too long, thick, or may contain a stray sliver on one of the sides. Additional cutting and weighing were needed for accurate size and weight. For the experiments the achieved weight range for all samples of wood fell between 7.25 - 7.75 mg.

2.2 Radical standard preparation

Different forms of radicals were used for parts of this project. The two main radicals were 1,1-diphenyl-2-picrylhydrazyl (DPPH) and 4-hydroxy-2,2,6,6-tetramethylpiperidine N-oxide (TEMPO). A 10 mM stock solution for each chemical was made using ethyl alcohol as the solvent of choice. The chemicals were weighed using an analytical balance and the stock solution was made in a falcon tube. Dilutions were made as needed from the stock solutions and ethanol. When testing these standards in the EPR, 57 µl of the solution was loaded using a pipetman into a quartz sample tube. A few minutes needed to pass by before any test because the solution would need some time to fully reach the bottom on the quartz tube.

2.3 TGA method

Thermogravimetric Analysis (TGA) was used for some experiments. The model of TGA analyzer that was used was the Discovery TGA 550. A pressurized oxygen tank and a pressurized nitrogen tank were needed depending on what study was being done. These were connected to the machine using a flow regulator gauge and plastic air tubing. A Bunsen burner or butane torch, a pair of small tweezer forceps, and TGA platinum hanging sample pans were also needed.

To use the TGA analyzer, the computer was turned on and the TGA analyzer from a switch on the back of the machine. Next, both gas tanks were opened, and the system was left to purge for 30 min before the sample run. The flow regulator flow rate

was set to stay under 20 psi. Next, the TGA software was opened, called Trios 550. The software was then checked to see that the balance flow of the gas was at 40 mL/min. The flow regulator was adjusted if the balance flow was incorrect. When this was confirmed, the prepared sample was acquired (vide supra wood preparation method). The platinum sample pan then needed to be clean from any contaminants. To do this a lit Bunsen burner or butane torch was utilized. The sample pan was held by the tweezer forceps and the pan was brought over the flame until red hot and then allowed to cool to room temperature. Once the platinum sample pan was clean and at room temperature, the sample pan was loaded (with no sample) onto the autosampler holder in an open position. In the software, a procedure file would be created within the design view. Here all parameters were set for the run which would include some of the following: the sample name, operator name, sample pan position number, study name, export file name (for data), export file name (for saving procedure), type of study (ramp, isothermal, custom, etc.) and additional parameters like selection of gas or the design of complex steps if needed. When testing wood, a procedure with the selection of gas was chosen, then a ramp step where the TGA was heated 10℃ per min to the selected temperature, with a final step of keeping the TGA isothermal for the selected amount of time.

Once the procedure was made it was then copied to the running queue. The sample pan was then tared using the software for accurate recorded weight. After the tare the sample was loaded onto the pan. One last check of the gas flow and overall procedure was performed and then the start button was pressed.

2.4 Oven kiln method

The oven kiln studies main tool was a Thermo Fisher oven. Other equipment was constructed in-house. To start the build of the sample holder or pilot kiln a 5-inch glass vial with a frosted ground glass 4.5-inch wide mouth opening was obtained. The wide mouth was important for taking the samples in and out of the vial. Next, 3 different sizes of stainless steel woven mesh sheets were used. One sheet has a small mesh size where the wood cannot fit through the bottom. The second mesh size was just large enough for the wood pieces to pass through. The third mesh size was about twice the size of the second. Each mesh sheet was cut to a diameter slightly smaller than the bottom of the glass vial. They were placed inside and orientated flat on the bottom of the vial. The finest mesh was added first to keep the samples from touching the bottom of the glass. Next, the second largest mesh was added to allow the samples to fit in a unique and individual position. Then the largest mesh was added to provide some space and depth for the sample to sit. Finally, the second largest mesh was added again to help aid in the positioning of the wood. The screens added together in this order allowed for correct sample tracking and separation.

The wood was cut and prepared per the wood sample preparation (vide supra wood preparation method). Once the wood was cut and prepared, the weight of each piece of wood was recorded, labeled, and kept separated. Once all samples were ready, each piece of wood was placed evenly spaced in the vial. Five to six pieces of wood were placed in each vial. A long skinny pair of tweezers was used to lower the wood

upright into the vial and between the steel mesh. For a 5 sample experiment the pieces of wood would be orientated by placing 2 next to each other on one side of the vial and the other 3 on the opposite side of the vial. When six pieces of wood were needed, 3 were placed on one side and 3 on the other side. All samples were kept as evenly spread out as possible with no samples near the outer glass and no samples near the middle. Once all samples are loaded, the outside of the glass was marked with a sharpie to identify each sample. Numbers were used to distinguish the samples from each other. To ensure the prevention of label fading with heat a few layers of marker ink were applied.

Once all samples were placed in the vial, the vial needed to be sealed. It has been thought that by sealing the vial, a slight pressure would be created by heating the sample, just as it occurs in industry. To keep the top of the vial secure, Apiezon H high temperature vacuum grease was used. This grease can withstand high temperatures (+240 °C) and pressures of enclosures.[18] The grease was spread around the lid on the frosted ground seal evenly in a thin layer. The lid was then placed on the vial and a slight twist motion was used as the lid was lowered onto the glass. This allowed the grease to be evenly spread on the frosted ground seal. Next a four-finger clamp was used to secure the lid to the base of the vial.

Once the vial was secure the thermometer data logger was set up. The thermometer has two detachable temperature probes that measure a range of -200°C to 1372°C with an accuracy of ±2°C. All data from the thermometer was stored in the data logger memory and was downloaded and backed up to a computer after each use.

In the thermometer setup mode, the data collection/frequency was set to 10 seconds (one data point recorded every 10 seconds). Next, one probe was fastened into the lower center grate on the oven and strung to the outside of the oven where it was then plugged into the thermometer. The temperature in the oven was then displayed. The glass vial with the samples were then placed on the lower center rack of the oven to be in a centralized place and close to the temperature probe to ensure accurate readings.

Once everything was in place, it was time to thermally treat the samples and a temperature was selected. For the experiments this was either 170, 180, 195, or 210 °C, temperatures commonly found in the industry.[6,9] The temperature knob on the oven was then placed close to the selected temperature (fine adjustment to follow). Once it was time to start, the oven was closed and latched, turned on, and the data logger was set to record. The start time was then recorded. On average it would take around 1 hr for the oven to reach temperature. Within that hour the temperature knob on the oven was adjusted to reach the goal temperature. The oven usually fluctuated between 2-4°C of the set temperature. After 1 hr of warm up and adjustments, the oven was then left at the desired temperature for 24 hr. Once the 24 hr had passed the oven was then switched off. The oven was naturally cooled for 1 hr before opening the oven, turning off the data logger, recording the times, and removing the vial. The times for warm up, "at temp", and cool down were recorded. The vial was then given a few minutes to cool outside the oven in atmospheric temperature and pressure. The clamp was then loosened and removed, and the lid removed by careful twisting, to prevent the lid from jumping off and jostling samples. Each sample was taken out with the long skinny

tweezers and placed in individual snap cap microcentrifuge tubes and labeled. The samples are then taken and weighed using an analytical balance to record the weight after the treatment process. The data was recorded for each sample.

The data logger was then plugged into the computer where all temperature data was downloaded and backed up. The data was then moved into an excel spreadsheet to be analyzed. The time frame where the oven was “at temp” (the 24 hr after the warmup time and before the cool down time) was examined for any anomalies. No abnormal spikes or drops in temperature confirms there were no power outages, no one opened the oven, or bothered the samples during the run. Once that was confirmed the temperature data during the 24 hr “at temp” was averaged for a more accurate reported treatment temperature.

2.5 EPR Data Collection

Two EPR spectrometer were used for this project, the Magnettech MiniScope 5000x and the Varian E-line century series EPR spectrometer. The Magnettech is a newer benchtop spectrometer model that allowed for quick and accurate sampling with more automated features. The Varian spectrometer is an older model that allowed for manual adjustments and better access for experimentation with varied sample configurations.

The Magnettech Miniscope was used for the majority of data collection in the last year of this project. To use this EPR, the computer was first turned on and the software called “EPR Studios Software” was opened. Next, the EPR was turned on by a

manual switch in the back of the spectrometer. In the software, the main control tab "initialize" was selected to start the warmup sequence. The warmup sequence took around 15 minutes each time. While this happened, the systems tab was selected, and the data logger turned on to record the cavity temperature. This monitored the cavity to ensure a steady temperature. If that was the first time the machine was turned on for the day/week it needed two or more hours to warm up, if the machine was left on it may only need 15 minutes.

Once the spectrometer warmed up it was then time to run samples. The "Recipe" tab was selected, and a new recipe was made or selected. Within a recipe was where the spectrum parameters can be tuned as well as the selection of multiple parameters such as: sweep range, center field, sweep time, modulation amplitude, frequency, accumulations, and power. The recipe was then saved after all parameters were set. The sample that was to be run was placed into a 4 mm quartz glass tube. For this size the "PH4" sample holder was used. The quartz tube was then slid into the sample holder until it was at 62 mm from the bottom of the sample holder to the bottom of the quartz tube. This ensured that the bottom of the sample holder was in the center of the cavity. When running wood samples, the sample holder was moved down to 67 mm. The depth from the bottom of the sample holder to the center cavity is 61.9 mm. The thickness of glass at the bottom of the quartz tube is 1 mm in height. The sample height of the wood is 8 mm. In order to center the wood sample in the cavity center, the following math was used to determine the 67 mm sample holder depth:

$$8\,mm\ \div 2\ =\ 4\,mm\ \ EQ.2.5.1$$

$$61.9\,mm\ +\ 4\,mm\ =\ 65.9\,mm\ \ EQ.2.5.2$$

$$65.9\,mm\ +\ 1\,mm\ =\ 66.9\,mm\ \approx\ 67\,mm\ \ EQ.2.5.3$$

Therefore, to completely center the sample, the quartz tube was placed at 67 mm and not 62 mm. Next the stainless-steel nut on the center of the EPR spectrometer was unscrewed gently, then the black cap was removed, as well as the stainless-steel cylinder. The sample was then lowered into the hole, the cylinder was placed over the sample, and the nut screwed back on securely but not overly tight.

Once the sample tube was in place, the main control tab was selected on the software. In the main control tab, the sample was given a name, and a recipe was selected from the saved list (that was created earlier). Next, a file destination was chosen for both the "path" and "output file" so that all data arrived and was saved in the same space. Finally, the time interval was selected (pause between samples), and repetitions (how many times the recipe will be run for that sample) were entered. Then the start button was selected to start the trial(s).

The Varian spectrometer was used for a lot of the preliminary tests (each section labeled with which spectrometer used). Because of the range of controls that you can manually adjust, it was important to understand what type of radical was being analyzed. The cooling unit was first turned on because the Varian spectrometer has a large electromagnet that needs to be cooled due to the heat that was produced. Next, the spectrometer was plugged in (thus turning it on), followed by turning on the computer. Once logged onto the computer "EWWIN 2015" software was opened. The

following buttons were pressed in a specific order to initialize and connect the spectrometer, the order was as follows: “Varian”, “Volt ramp”, “NI USB 600X”, “Init. Spec”. “Connected” was displayed when the steps were done correctly, confirming that the spectrometer was initialized and connected properly. Once the spectrometer was connected the “spectrometer setup” tab was selected. Here there were parameters that were able to be selected and changed, some were required, and others were just for records.

The parameters that were for records to be saved with the output file were receiver gain, time constant, modulation amplitude, microwave power, and microwave frequency. The required parameters were field center, field sweep, scan time, time between scans, time between spectra, data points per scan, number of scans per spectra, number of spectra per experiment, backup every scan, save to file, save to chart, file name, save as a sequence, starting sequence, ask for name of each file, and user name. Once all parameters were selected “check all” and “send parameters to spec” buttons were pressed in that order so that all parameters got sent to the spectrometer and the “send parameters to spec” button turned to green and displays “Parameters sent to Spec”.

Next the cavity must be tuned, most of which was controlled by switches and dials on the control panel. The microwave power was turned low to 40 dB and no larger than 30 dB. The sample of choice in a quartz tube was placed in the sample holder cavity. Next the magnetic field was turned on by turning the field dial from “off” to “0”, and the microwave generator was turned from standby to tune. It then took around 30

- 60 seconds for the spectrometer to warm up and kick on the klystron. The klystron dip on the oscilloscope screen was adjusted and centered using the frequency control knob. The reference arm was then turned on. The mode pattern on the oscilloscope was made symmetrical by adjusting the reference arm phase dial, then the reference arm was turned off. Next the mode was set to operate, the un-calibration light then turned on. Once the un-calibration light turned off (after a few seconds) the frequency control dial was adjusted until the "AFC OUT" meter read zero. The reference arm was then turned back to on. The detection current meter was then observed as the power was increased to 40 dB. After the power had been increased the phase dial was adjusted to maximize the detection current. Additional adjustments to the frequency control were done to keep the "AFC OUT" dial reading zero. Next the power was increased to 0.5 mW (26 dB) or whatever level the experiment called for. Again, the frequency control dial was adjusted to keep "AFC OUT" reading at zero.

The spectrum was then able to be obtained after the cavity was tuned. To assure the parameters were accurate and correct they were checked once more. Once confirmed, three buttons in consecutive order were selected in the EWWIN software to start the data collection. The three are: "reset", "parameters sent to spec" (making sure it was green), and "GO". The spectrometer will then start its sweep and the computer would record the data while displaying it on the screen. After each scan, the data was saved to a file automatically.

The parameter settings that were used for all runs unless otherwise noted were as follows: Power 0.5 mW, gain 3,200, modulation amplitude 1 G, phase 90°, center field

3348 G (334.8 mT for the MiniScope), field sweep 250 G (25 mT for the Miniscope). 2048 data points were taken on the Varian EPR and 4000 data points were taken on the MiniScope 5000x.

2.6 EPR Data Processing

After all data had been collected from the EPR, it then needed to be processed to compare samples. The Varian spectrometer saves its files as a ".fls" file format. The Magnettech MiniScope 5000x saves its files as a ".csv" file format. Both file types hold the same type of data within them. Within each file it displays the magnetic field in one column and signal in the other. The EPR data was processed to quantifiably determine the double integral or total area "under the curve" of the EPR spectrum. This was accomplished by either an excel template or by a program written in Python called Cruncher (which ultimately uses excel and presents the data in excel).

The main method that was used was the excel template. To start, the template was opened and in a second excel tab all scans that were taken for a specific sample were imported. Next, all of the scans were averaged using excels "=AVG" function (outliers or interrupted spectrum were not included, only applicable for the Varian EPR). The average spectral signal was loaded into the first excel sheet, and a graph was made of the spectra with magnetic field on the x-axis and signal intensity on the y-axis. If the spectrum was from the older Varian spectrometer it needed to be baseline adjusted due to the retrofitting of the Varian EPR to a modern computer. To do this a new column was made in the excel sheet. In this column a command was given to take the cell with

the signal and add it with one single cell with a “variable number”. Next that entire new column was added together (Sum) in a single new cell or an “objective” cell. Solver was then used to adjust the Variable number with the goal to draw the objective cell as close to zero as possible. Once this command was carried out it will have taken all of the data points and moved them down equally towards zero, therefore baseline adjusting the data. Once the baseline was adjusted, an integral was taken within the signal range. The second integral was then taken from the first integral. Equation 2.6.1 was used to calculate the integral in excel. From here the max number within the second integral column was set as the final value, to double check that the math was correct the last number was subtracted from the first in the 2nd integral column and the resulting number should be the same as the max. The same original sample of wood given by NRRI was measured each time EPR data collection happened. To account for instrument error, the data from different days of this sample was analyzed to find where the data started to vary (the tenths place). The significant placeholder for further calculations and data comparison was selected from the place of variance.

$$Integral_2 = \left((Gauss_2 - Gauss_1) * \left(\frac{Signal_2 + Signal_1}{2} \right) + Integral_1 \right) \quad EQ.2.6.1$$

An EPR measurement of an empty quartz sample tube would be taken using the methods above. The data was then processed as instructed above. This sample was called “blank”, otherwise known as the background, and would be subtracted from all data acquired in the same day of measurements. This would eliminate all unwanted background signals for a focus on just the sample.

A weight adjustment would be done if all samples being compared were thermally treated wood. Due to the lack in starting all samples at the same exact weight (but a controlled range) and some samples having a smaller ending weight this was done to better represent the data. Samples had an average mass loss of 11.9% from treatment start to finish. Equation 2.6.2 below shows what was used for the adjustments.

$$Adj.\,EPR\ radical\ signal\ area = \frac{\left(EPR\ radical\ signal\ area \times \frac{Heaviest\ weight\ before\ treatment\ of\ all\ samples}{weight\ before\ treatment}\right)}{weight\ after\ treatment} \quad EQ.\,2.6.2$$

The second way was by using a python code called Cruncher which was developed by Ryan Raskob and Jeffrey McVay Jr. This program does everything that was done manually in the excel template but eliminates the time it takes to import all of the data and format it correctly.

Once the final double integral number was collected it was called the “EPR signal area per sample”. A better way to display this data and compare it to other similar samples was to further divide that number by the mass of the sample to obtain the “EPR signal area per mg”. Once the method was solidified an empty quartz sample tube was scanned using the standard EPR settings, processed, and subtracted from each of the samples in the specific experiment.

Chapter 3

Initial tests

3.1 Rationale

The goal of the project was to use EPR to quantify free radicals in a thermally treated sample of wood, and therefore, the extent of heat treatment. To create a standard curve of radical concentration to EPR signal, control experiments were run with known free radicals to find a comparable standard. Simultaneously, experiments with wood were conducted following various processing methods and instrument parameters. The use of TGA was also explored as an accurate method of simulating industrial heat treatment.

3.2 TEMPO and DPPH Studies

Rationale:

In order to learn the workings of EPR and to better understand free radicals, it was necessary to work with known radical standards. One of the future goals of this project is to directly quantify the actual spin concentration or spin count in thermally treated wood. In order to accomplish this, a free radical with the same number and type of peaks as the wood needed to be found to directly correlate the two. It was decided to test two different free radical species seen in Figure 3.2.1[19,20]. The first

chemical tested was 1,1-diphenyl-2-picrylhydrazyl (DPPH) (CAS# 1898-66-4), a stable radical with a deep purple color. The second radical tested was 4-hydroxy-2,2,6,6-tetramethylpiperidine N-oxide (TEMPO) (CAS# 2226-96-2), a highly stable radical that is often used in organic synthesis reactions.[21]

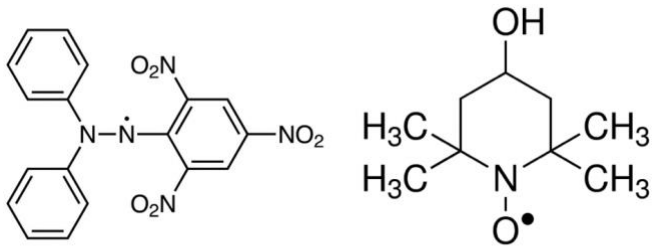


Figure 3.2.1 Chemical structures of 1,1-diphenyl-2-picrylhydrazyl (DPPH) on the left and 4-hydroxy-2,2,6,6-tetramethylpiperidine N-oxide (TEMPO) on the right.[19,20]

Each radical was made into solutions of 1, 2.5, and 5 mM concentration with 100% ethyl alcohol as its solvent. The samples were then run in the MS-5000 EPR utilizing the sample collection procedure in the methods section (vide supra Chapter 2.5). Quartz sample tubes were filled with 57 microliters of each solution, which provided the 8 mm total sample height. The calculation using Equation 3.2.1 was used to determine sample height. (Figure 3.2.2)

$$V = \Pi r^2 h \quad \text{Eq. } 3.2.1$$

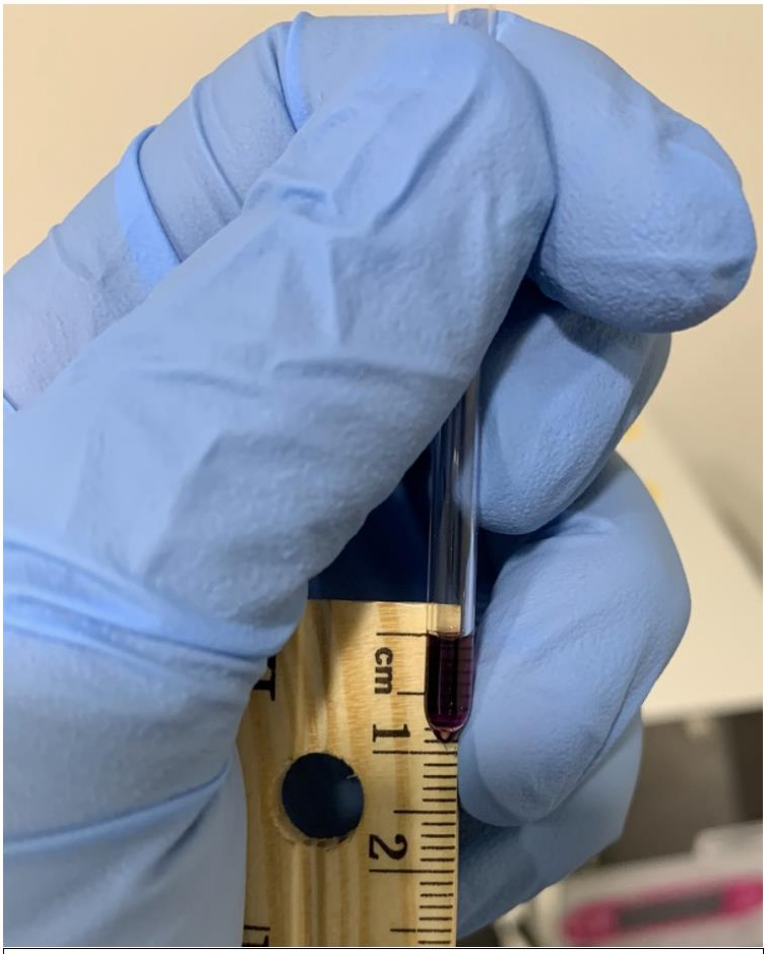


Figure 3.2.2 Quartz tube with 57µL DPPH Ethanol sample showing 8mm height from node to meniscus.

Results/discussion:

The Initial tests of DPPH showed a 5 hyperfine peak signal that can be seen in Figure 3.2.3. The initial tests of TEMPO showed a 3 hyperfine peak signal that can be seen in Figure 3.2.4.

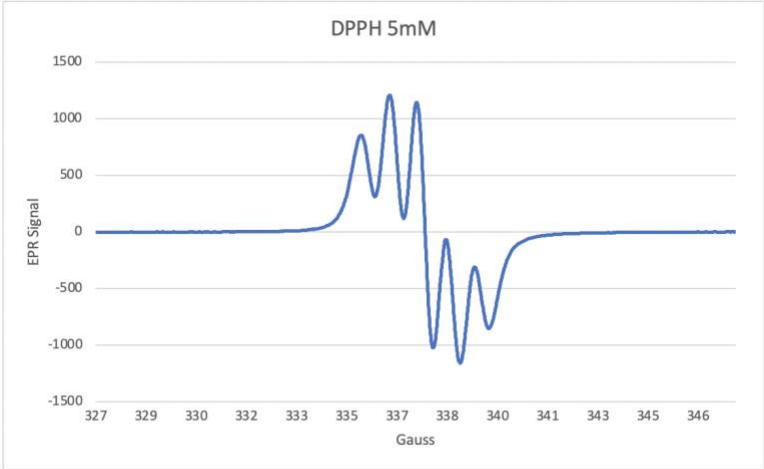


Figure 3.2.3 Raw EPR scan of signal to Gauss of a 5mM sample of DPPH.

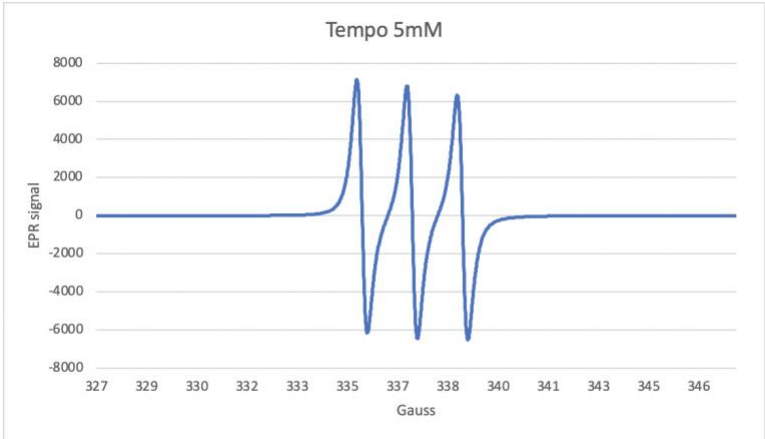


Figure 3.2.4 Raw EPR scan of signal to Gauss of a 5mM sample of TEMPO.

The double integral EPR signal area was calculated for each sample of 1, 2.5, and 5 mM sample of DPPH (Figure 3.2.5) and TEMPO (Figure 3.2.6). This data is also shown in Table 3.2.1. This showed a linear relationship between the concentration and EPR radical signal area (Figure 3.2.5 and Figure 3.2.6). Linear trendlines are fit in Figure 3.2.7.

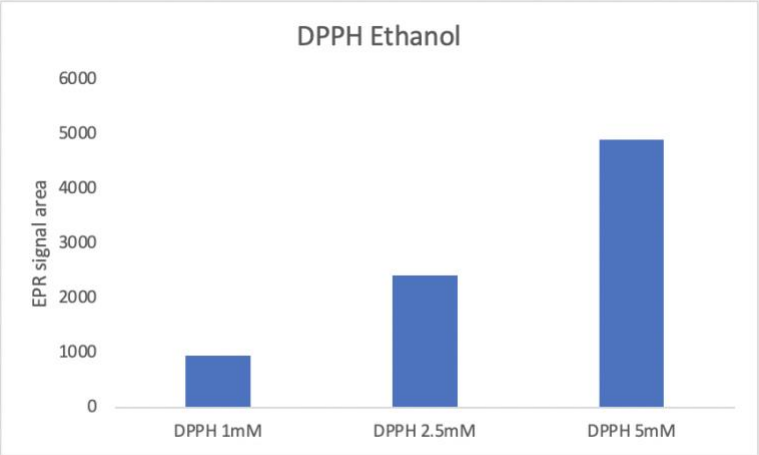


Figure 3.2.5 Graphical representation of double integral EPR radial signal area of 1,2.5, and 5 mM samples of DPPH Ethanol solutions from left to right.

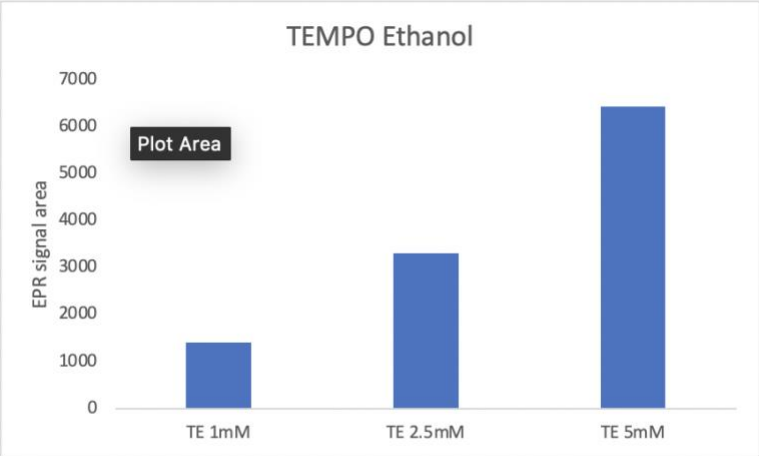


Figure 3.2.6 Graphical representation of double integral EPR radial signal area of 1, 2.5, and 5 mM samples of Tempo Ethanol solutions from left to right.

Table 3.2.1 Numerical EPR signal area data for Figures 3.2.4 and 3.2.5.

Sample and concentration	EPR signal area
TEMPO EtOH 1mM	1410
TEMPO EtOH 2.5mM	3300
TEMPO EtOH 5mM	6430
DPPH EtOH 1mM	940
DPPH EtOH 2.5mM	2410
DPPH EtOH 5mM	4900

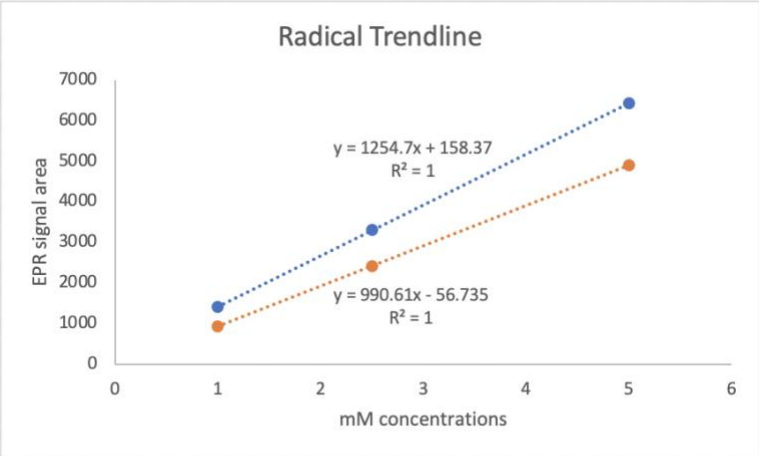


Figure 3.2.7 Trendlines shown with equations of DPPH radical in orange and TEMPO in blue.

Conclusion:

It was concluded that a radical signal was found in both DPPH and TEMPO radical species. It was also concluded that there was a correlation between EPR radical signal area to concentration with linear best fit lines of y = 990.61x + 56.735 for DPPH and y = 1254.7x + 158.37 for TEMPO, an R^2 of 1, and a p-value of 0.01365234 between time points. This study will be compared to the wood samples to see if either of the radicals are similar to the wood for help creating a standard.

3.3 Quantifying Radicals in industrial thermally treated Wood from NRRI

Rationale

Prior research suggests that radicals can form in wood after thermal treatment.[9,10] By utilizing EPR, a correlation between free radical signal and heat treatment might be measured. To test this, industrially heat-treated and pre-cut pieces

of varying wood species that were treated at different temperatures were obtained from NRRI. Two different experiments on these specimens were performed to gain an understanding of the radial response and correlation.

For the first experiment, EPR was utilized to see if a sample of wood contained any detectable free radicals. It was hypothesized that a radical presence would be detected, but not as strong as a signal output as TEMPO or DPPH because unlike the two radical standards, wood composition is more than one structure or chemical compound. The confirmation of radicals in this initial sample piece of wood would allow the further testing of other heat-treated wood samples.

In the second experiment, additional pieces of wood were tested by EPR to test radical presence and to investigate a correlation between heat treatment temperature and EPR signal. It was hypothesized that there would be an increase in EPR signal with an increase in heat treatment temperature.

The source of initial wood samples and their preparation parameters, such as original size, time in kiln, and time at the stated temperature was not known. The Varian EPR spectrometer and standard setting were used (vide supra Chapter 2.5), with 2 scans per spectra, and 15 spectra per experiment. All data was processed per the EPR data processing description given in Chapter 2.6 Materials and Methods.

Results and discussion:

The original piece of wood that was acquired was treated at 180 ℃. The type of wood was red maple with dimensions of 2 x 2 x 8 mm. The raw signal from the EPR gave

a single derivative shape, shown in Figure 3.3.1. The double integral yielded the area shown in Figure 3.3.2 and numerical data shown in table 3.3.1. These results indicated that there was a significant radical presence in the wood shown in the form of EPR radical signal area.

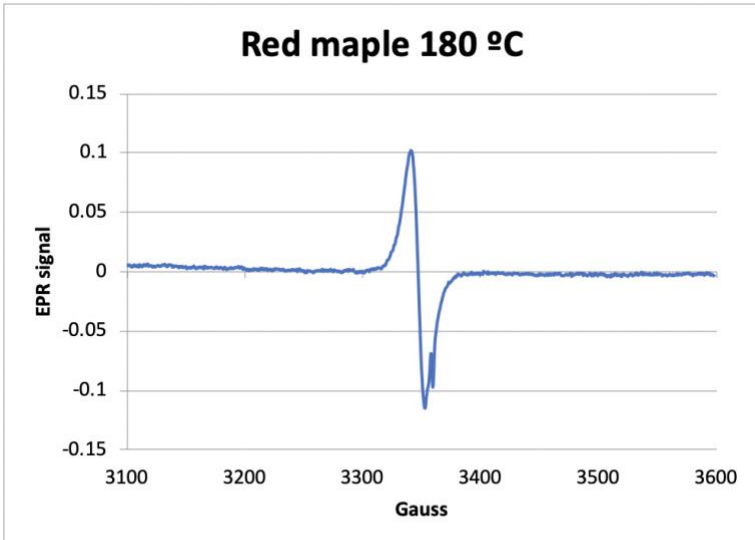


Figure 3.3.1 Raw EPR scan of signal verses Gauss of Red Maple treated at 180 °C from NRRI.

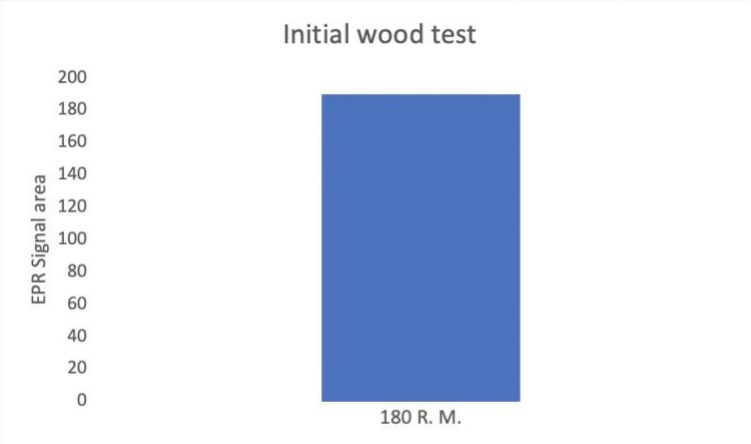


Figure 3.3.2: Graphical representation of the double integral area of the initial red maple wood that NRRI provided that was treated at 180°C.

Table 3.3.1 Numerical EPR signal area data from Figure 3.3.2	
Sample	EPR signal area
180 °C red maple	190

The clear presence of radicals in this sample allowed the project to progress forward to test other samples of wood. There were six additional samples. They were treated three different ways and were two separate species of wood. The treatment temperatures were untreated, 170 °C, and 180 °C and the types of wood were red maple and eastern hemlock. The averaged raw EPR signal scans are shown in Figure 3.3.3 (for red maple) and 3.3.5 (hemlock). The data for double integrals of the EPR signals of each of these samples is shown in Figure 3.3.4 (for red maple) and 3.3.6 (hemlock) with numerical data in table 3.3.2.

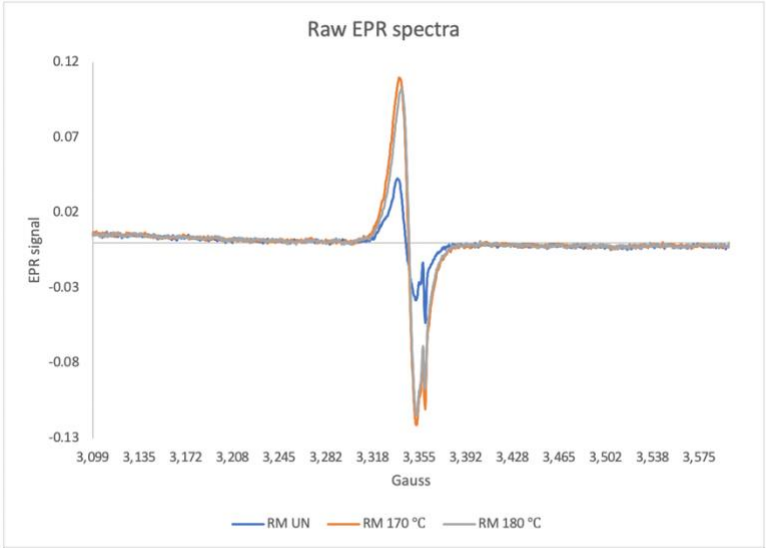
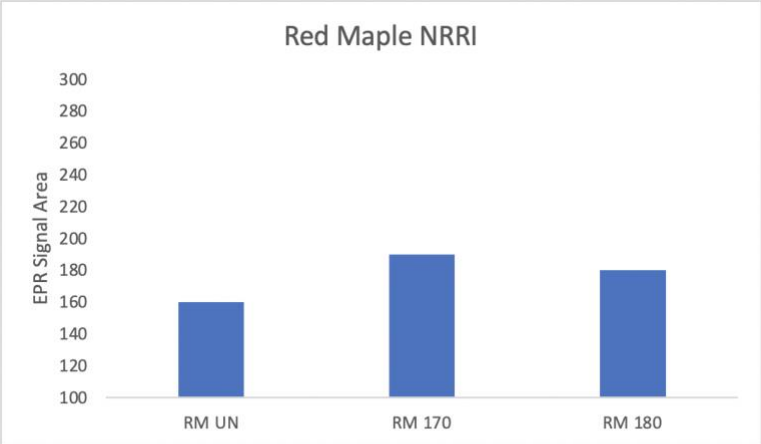


Figure 3.3.3 Averaged EPR signal data for Red maple untreated, 170 °C, and 180 °C.



Ch.3.3.4: Graphical representation of the double integral area of the Red maple wood samples treated by NRRI. From left to right is untreated, 170°C, and 180°C.

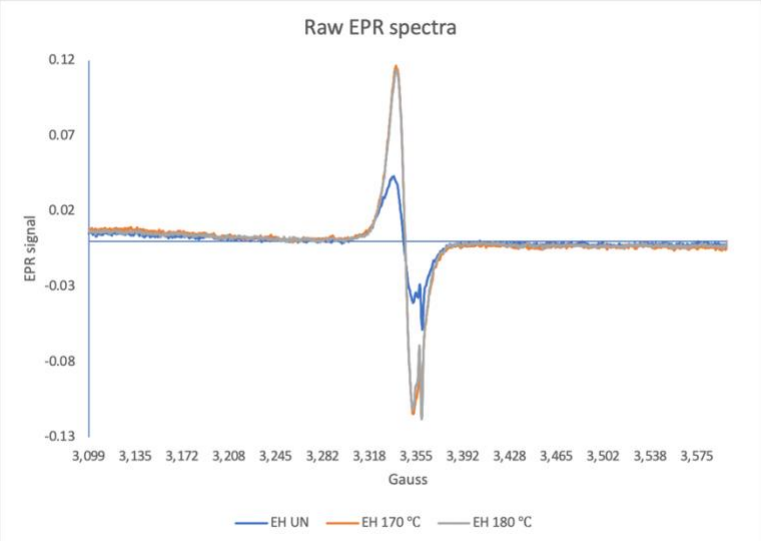
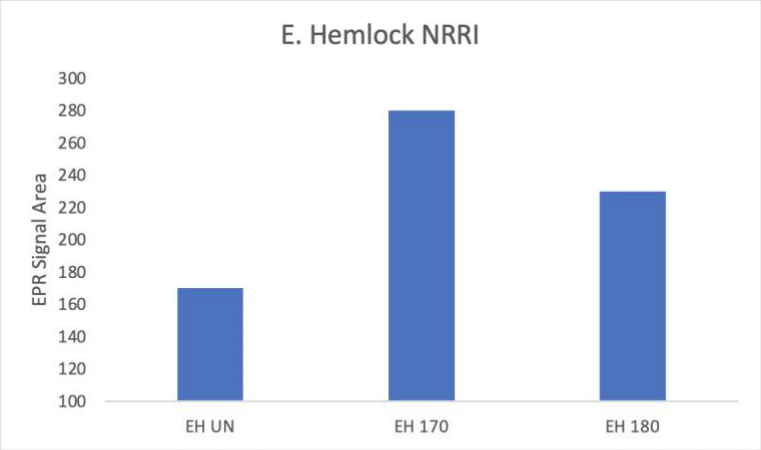


Figure 3.3.5 Averaged EPR signal data for Eastern Hemlock untreated, 170 °C, and 180 °C.



Ch.3.3.6: Graphical representation of the double integral area of the Eastern Hemlock wood samples treated by NRRI. From left to right is untreated, 170°C, and 180°C.

Table 3.3.2 Numerical EPR signal area data from Figures 3.3.4 and 3.3.6	
Sample	EPR signal area
Red maple untreated	160
Red maple 170 °C	190
Red maple 180 °C	180
Eastern hemlock untreated	170
Eastern hemlock 170 °C	280
Eastern hemlock 180 °C	230

A radical presence was found in all samples of the red maple scans shown in Figure 3.3.3. Interestingly enough, there was a presence of radical signal in the untreated piece (Figure 3.3.3). 170 °C and 180 °C both had a higher radical signal presence than the untreated wood sample, but the 180 °C treated sample had a lower not higher signal than the 170 °C piece.

Radical signal presence was also found in all samples of the eastern hemlock sample scans shown in Figure 3.3.5. Again, there was a higher radical presence at 170 °C and 180 °C. A decrease in signal area was seen in the 180 °C sample. This decrease in signal intensity is something that should be revisited. However, it is hypothesized that it was due to the sample preparations and thermal treatment methods not being

conducted in the same way. Since the details were unknown on how the samples were prepared it is hard to accurately say the cause in the decrease in signal from 170 ℃ to 180 ℃.

Conclusion:

In conclusion, the proof-of-concept of measuring radical signals present in the wood obtained from NRRI was supported, as shown in Figure 3.3.1 & 3.3.2. The confirmation of a signal in the additional pieces of wood, as shown in Figures 3.3.3-3.3.6 was also found. It was concluded that an irregular pattern of data at 180 ℃ is due to something in the preparation of samples. With an uncertainty of the methods used from NRRI for the treatment of the wood it's hard to narrow down what was the cause of the data irregularity. Prepping our own samples in-house might prove to provide better more quantifiable results and narrow down what variable caused the irregular data.

3.4 First TGA and EPR attempts on commercially obtained wood samples

Rationale

An initial pilot attempt was made to use Thermogravimetric Analysis (TGA) to thermally treat wood in order to test radical correlation with EPR. The key advantage of using TGA is the ability to control temperature and reaction environment to analytical accuracy. The mass loss can also be monitored to a high accuracy as well. This allows

the elimination of multiple variables in sample preparation and brings focus to specific changes from which conclusions can be drawn.

Focused attention was placed on developing a way to prepare wood samples for the TGA treatment and EPR analysis. The wood was chopped, cut randomly, and prepared to approximate dimensions of 2 x 2 x 8 mm. Wood was acquired from the hardware store. The wood species was balsam poplar. Six samples were prepared, one was prepared by the chopping method (vide supra Chapter 2.1), one was prepared by the random cutting method (vide supra Chapter 2.1), and 4 pieces were cut to the dimension of 2 x 2 x 8 mm using the standard wood preparation method (vide supra Chapter 2.1). The chopped and random cut samples were untreated. For the treated sample tests, four wood samples were thermally treated from room temperature to 180 ℃ at a rate of 10 ℃ per minute, and then held two samples isothermal under nitrogen and the other two samples under an oxygen atmosphere for 12 hr each. It was hypothesized that there would be a clear radical signal presence in the thermally treated wood with a minimal signal in the untreated wood.

The Varian EPR spectrometer and standard settings were used (vide supra Chapter 2.5), with 2 scans per spectra, and 2 spectra per experiment. All data was processed per the EPR data processing description given in Chapter 2.6 Materials and Methods.

Results and discussion:

All six samples were tested using EPR. This includes the two untreated samples (chopped and random cut), the two prepped pieces under nitrogen at 180 ℃, and the two prepped pieces under oxygen at 180 ℃. All six samples possessed radicals; the double integral radical signal area can be seen in a visual representation in Figure 3.4.1. The untreated samples were 2.3% and 4.7% away from the average double integral EPR signal area of the treated pieces. (Table 3.4.1)

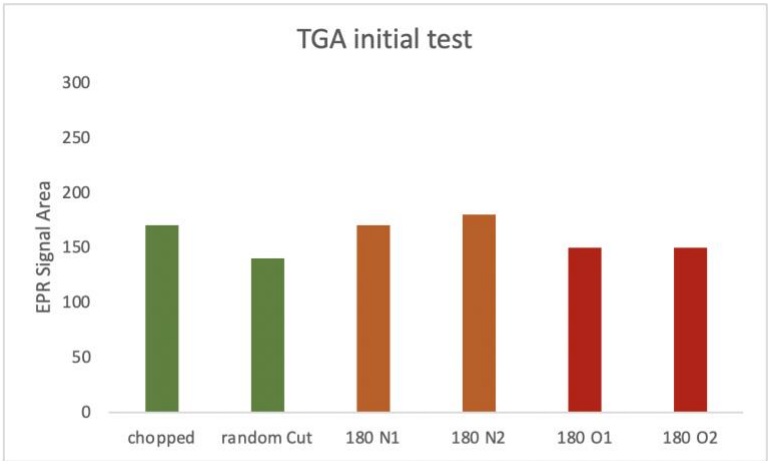


Figure 3.4.1: Store bought Balsam poplar used in the initial tests on the TGA. From left to right the samples are untreated chopped, untreated random cut, 180 ℃ Nitrogen sample 1, 180 ℃ Nitrogen sample 2, 180 ℃ oxygen sample 1, 180 ℃ oxygen sample 2

Table 3.4.1 Numerical double integral EPR signal area values.

Sample	EPR signal area
Chopped	170
Random cut	140
180 ℃ N1	170
180 ℃ N2	180
180 ℃ O1	150
180 ℃ O2	150

From the data shown in Figure 3.4.1 free radical presence in the wood treated at 180 ℃ was supported. The wood treated in this experiment didn't produce as high as a signal from the wood studied from NRRI (vide supra Chapter 3.3), which is believed to be the result of only treating the wood in the TGA for 12 hr verses a range between 16-35 hr of treatment for the NRRI wood. Also, it was noticed that the untreated wood gave a radical signal just as large as the other samples. After further investigation, it was found that construction lumber that is sold at commercial businesses are commonly oven dried per ASTM standards at 103 ℃.[22] This would explain why there is a similar EPR signal between untreated and TGA heat treated wood samples due to this wood being treated with heat previous to this study.

Conclusion:

In conclusion, radical presence in the samples treated at 180 ℃ in oxygen and nitrogen atmosphere was supported. Heat-treating wood for 12 hr gave less EPR radical signal than the heat-treated industrial samples provided by NRRI. Therefore, the next trial would be treated longer, for 24 hr. There was also a confirmation of radical presence in the untreated chopped and random cut wood. This was due to commercial construction lumber wood being kiln dried per ASTM standards. To move forward, fresh wood that was not treated would be used. This would allow a more accurate control on the measurement of untreated wood to compare to treated pieces, and therefore give a better correlation of heat treatment to radical signal.

3.5 Chapter Conclusions

Initial testing was imperative in learning more about EPR spectroscopy and pressing towards the goal of this project of determining the extent of heat treatment by EPR. Many discoveries were made through this process. First, more understanding about how the EPR works through the testing of DPPH and TEMPO standard radical species. It also allowed an understanding of the relationship of EPR signal to concentration. Second, an EPR radical signal was found in an industrially thermal treated sample of wood that NRRI provided. This was an important finding confirming radical presence in thermally treated wood. This finding helped the transition to treat wood utilizing thermal gravimetric analysis and the use of EPR to measure the free radical content. The initial tests brought great insight towards the main goal. It also developed great questions that once investigated and answered would help towards the main goal as well.

Chapter 4

Exploring and tuning experiment parameters

4.1 Rationale:

After the initial success of the tests performed utilizing EPR, it was time to move on to the next stages of this project. A variety of questions arose throughout the initial testing phase: 1. Why was there a high EPR radical signal area for the untreated wood? 2. How does size of a sample play a role in EPR radical signal? 3. How does sample weight play a role in EPR radical signal? 4. What is the most effective way to maximize signal to noise? 5. What is the best way to account for moisture and the most efficient way for all samples to contain the same moisture level? 6. Why was there an absence of trend in the wood from NRRI and is there something that can be done to find one? Addressing and fixing these problems is crucial to move forward to develop a standard method of testing for future experiments.

4.2 Problem #1: "untreated" wood signal: Why was there a high EPR radical signal area for the untreated wood and ultimately no trend in EPR signal to treatment temperature?

Rationale:

The first study using TGA in Chapter 3.4 found that the untreated wood samples had a close EPR radical signal area to the heat-treated samples. In order to move forward, the need to figure out why the EPR radical signal area of

the two untreated samples were 2.3% and 4.7% away from the heat-treated samples was to be addressed. To address this, it was decided to run the same test utilizing fresh wood samples from outside. What was not known at the time of the initial test is that commercially purchased wood is often kiln dried.[22,23] It is hypothesized that utilizing fresh wood would generate a lower EPR radical signal area for the untreated samples in comparison to the heat-treated samples.

Fresh, untreated balsam poplar was obtained from the outdoors to make sure that it had no kiln heat treatment. A large amount of fresh poplar that had been cut for firewood was obtained, which had been air dried for >6 months. From the experiments in Chapter 3.4 above, it was learned that an extended TGA run time of 24 hr for each sample might yield radical signals closer to the industrial heat-treated wood, described above in Chapter 3.3. It is hypothesized that these TGA conditions, which more closely resembled the industrial condition, would also give a radical signal that more closely emulated industrial samples. In addition, temperatures of 195 ℃ and 210 ℃ were selected to probe additional radical generating temperatures in order to identify any trends that may persist. It is hypothesized that the EPR signal area would increase with the increase in treatment temperatures.

For this round of thermal treatment using TGA, seven total wood samples were prepared. One sample was left untreated while the other six samples underwent thermal treatment, two at each temperature of 180 ℃, 195 ℃, and 210 ℃. Within each temperature set, one sample was run under an oxygen environment, while the other was in a nitrogen environment. Each sample of

wood was cut to the same sample size as before of 2 x 2 x 8 mm. It was hypothesized that there would be a trend with an increase in signal as the temperature increased.

The Varian EPR spectrometer and standard settings were used (vide supra Chapter 2.5), with 2 scans per spectra, and 15 spectra per experiment. All data was processed per the EPR data processing description given in Chapter 2.6 Materials and Methods.

Results/discussion:

After running each sample for 24 hr in TGA under nitrogen, EPR measurements indicated a radical presence in all samples (Figure 4.2.1). For the samples that were treated under nitrogen, an increase was observed in EPR signal with the increase in treatment temperature shown in Figure 4.2.2 and numerical data in Table 4.2.1. All samples also had a radical presence higher than the untreated piece.

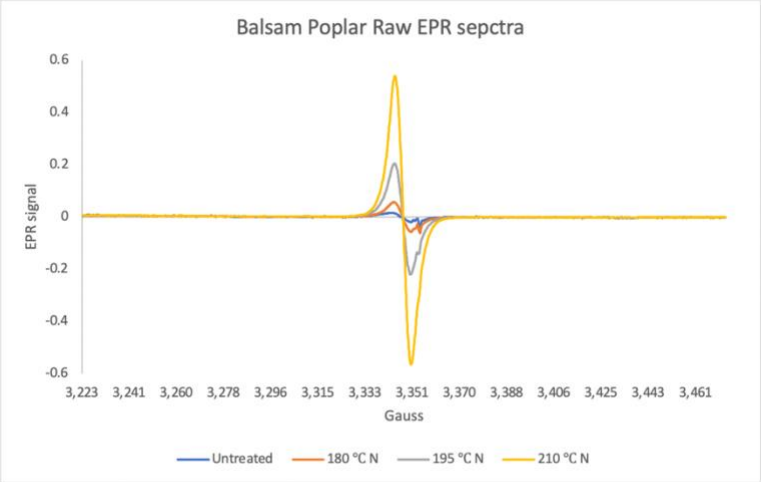


Figure 4.2.1 Averaged raw EPR signal of balsam poplar wood untreated and treated by TGA under nitrogen at temperatures of 180 °C, 195 °C, and 210 °C.

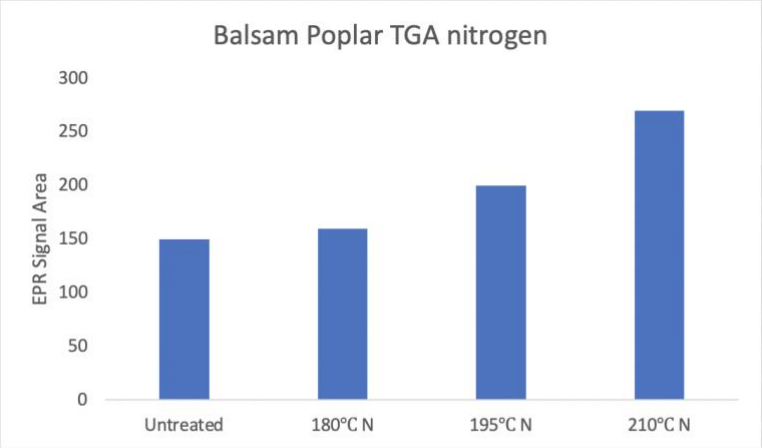


Figure 4.2.2 Fresh Balsam poplar tested for 24 hours under a nitrogen atmosphere under different temperatures in the TGA. From left to right the samples are untreated, 180 °C, 195°C, and 210°C.

Table 4.2.1 Numerical EPR signal area data from Figure 4.2.2	
Untreated	150
180°C O	160
195°C O	200
210°C O	270

After running each sample for 24 hr in TGA under oxygen, EPR measurements indicated a radical presence in all samples (Figure 4.2.3). The

wood samples that were run under oxygen atmosphere conditions also displayed a trend, but not as strongly as the samples treated under nitrogen. The trend under oxygen displayed an increase in EPR signal with the increase in treatment temperature except for 210 ℃ that gave a lower signal (Figure 4.2.4). Numerical data can be seen in Table 4.2.2.

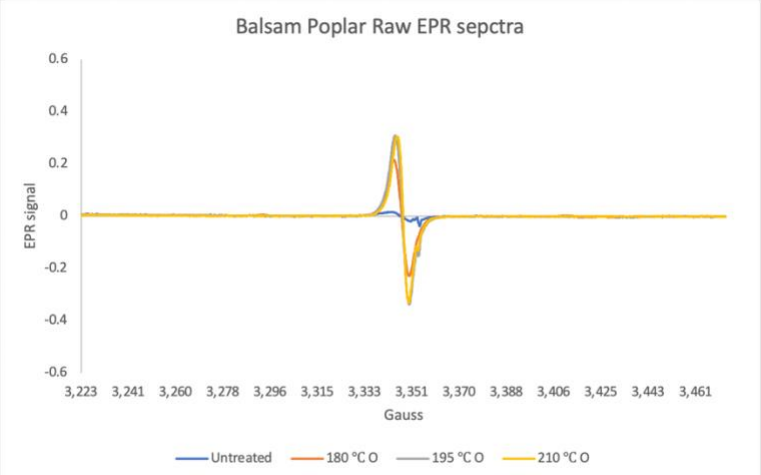


Figure 4.2.3 Averaged raw EPR signal of balsam poplar wood untreated and treated by TGA under oxygen at temperatures of 180 °C, 195 °C, and 210 °C.

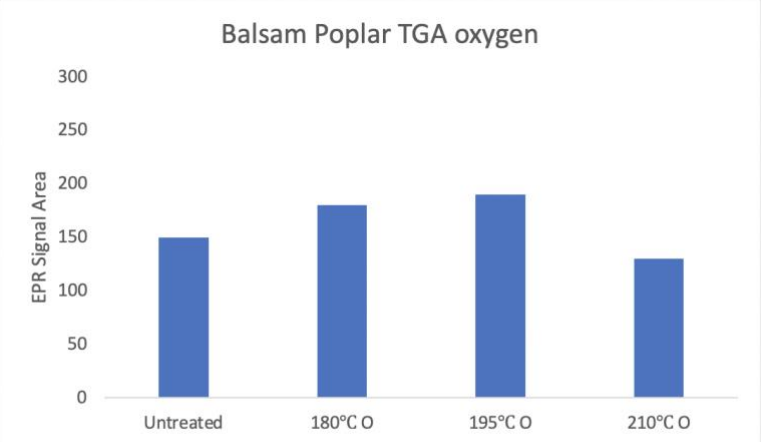


Figure 4.2.4 Fresh Balsam poplar tested for 24 hours under an oxygen atmosphere under different temperatures in the TGA. From left to right the samples are untreated, 180 °C, 195°C, and 210°C.

Table 4.2.2 Numerical EPR signal area data from Figure 4.2.4	
Untreated	150
180°C O	180
195°C O	190
210°C O	130

The utilization of fresh balsam poplar wood allowed for a smaller signal within the untreated wood in comparison to the treated wood samples. In addition, running the samples for 24 hr in TGA instead of 12 hr yielded larger EPR radical signals, and results more like those from industrial samples. The radical presence in the oxygen samples were smaller than nitrogen. For both nitrogen and oxygen atmospheres, there was an upward trend in radical content as treatment temperature increased with the exception of the 210 ℃ sample treated under oxygen. Two important observations were made. First, under oxygen the wood samples were visibly charred in the TGA. The higher the temperature of treatment and the presence of oxygen lead to withered burned samples. It therefore was believed the smaller signal at 210 °C under oxygen is due to an extent of oxidation with fresh oxygen that allows the wood to carry out the chemical reactions to a greater extent. It also was believed that this is the reason for the smaller signal in all the oxygen samples compared to the nitrogen samples.

To further examine the hypothesis of focus, it is imperative to compare this data and that of Chapter 3.4 to see the difference in trend (Figure 4.2.5 & Table 4.2.3).

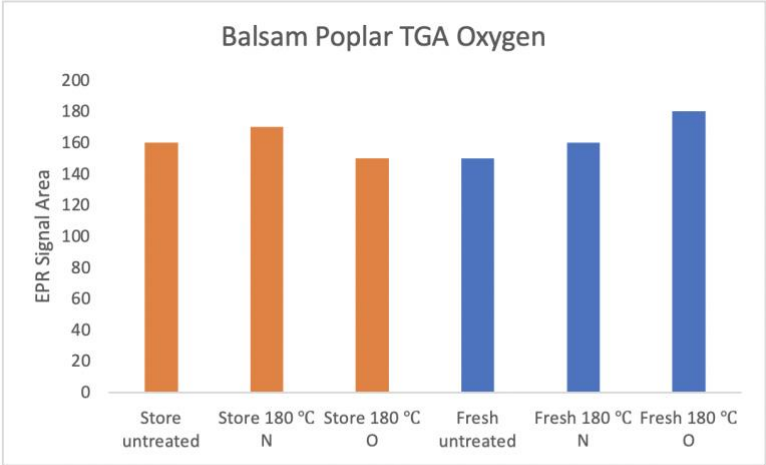


Figure 4.2.5 In orange from left to right is the original store-bought wood untreated, TGA treated at 180°C under nitrogen, and TGA treated at 180°C under Oxygen signal averages. In blue from left to right is fresh wood untreated, TGA treated at 180°C under nitrogen, and TGA treated at 180°C under Oxygen signal averages.

Table 4.2.3 EPR radical signal area averages of store bought, and fresh wood thermally treated using a TGA analyzer.

Sample	EPR radical signal area
Store bought untreated	160
Store bought 180 °C nitrogen	170
Store bought 180 °C oxygen	150
Fresh untreated	150
Fresh 180 °C nitrogen	160
Fresh 180 °C oxygen	180

A clear difference can be seen in Figure 4.2.5 for the differences in EPR radical signal area. The store-bought wood samples, shown above in orange, had the untreated sample signal area in between the signal area of the nitrogen and oxygen atmospheres. On the other hand, the fresh-wood samples showed a higher signal for both treated pieces in comparison to the untreated piece. The distance between untreated samples and heat-treated samples was 12.7% and 2.3% for fresh wood and store-bought wood respectively (Table 4.2.3). With no

commercial oven drying, the fresh-wood samples allowed for a better representation of the treated samples and the control sample.

Conclusion:

In conclusion, thermally treating the balsam poplar wood samples for 24 hr and using freshly acquired wood led to a more reliable trend between the correlation of thermal treatment to EPR signal area. A lower signal in all oxygen samples in comparison to nitrogen could be an indicator that the oxidation of the samples under that condition could have an effect. With fresh oxygen being supplied into the instrument this allows the chemical reaction of oxidation and depolymerization of the wood structure to continue longer than the nitrogen experiment. Thus, leaving a smaller size and weight sample afterwards, and potentially fewer radicals.

When comparing the fresh wood and the store-bought wood tests, the problem at hand can be resolved. The data set from the fresh wood had larger EPR radical signal than the untreated pieces, whereas the store-bought wood that was oven-dried did not. The findings of this study answered the question about the untreated sample and confirmed the hypothesis. This study also helped to remedy the gap of EPR radical signal of untreated to heat treated sample from 2.3% to 12.7%. For further experiments, the wood used for tests will be fresh balsam poplar wood, and the utilization of store-bought samples will not be further used.

Lastly, upon further investigation the wood sample for 210 ℃ oxygen was found to be smaller in size post-run due to the charring that occurred under oxygen. When comparing all of the samples by weight and by size, sample size and sample weights were varied across all samples treated and analyzed. This led to the next major adjustments to the studies, to investigate the size of wood sample, the positioning of the quartz sample tube inside of the resonating cavity, and the weight of the wood in relationship to EPR signal and comparable data.

4.3 Problem #2: Size: Will a consistent size of samples provide better data and comparability?

Rationale:

To improve reliability in the TGA treatments and resulting EPR data, it was hypothesized this could be done by having all wood samples prepared to a similar size and weight. The samples should be weighed before and after the heat treatment in order to improve the correlation between heat treatment and radical content, and also might explain the inconsistent data point observed with the 210 ℃ sample treated under oxygen (vide supra Chapter 4.2). It was also speculated that the microwave excitation from the EPR could pass all the way through the wood sample, therefore probing all radicals, or that only the surface radicals were being detected. It therefore was decided to explore how size and surface area effects results when measuring EPR on wood samples.

To explore this speculation further, it was decided to accurately cut a piece of wood (fresh balsam poplar) to the dimension of 1.5 x 1.5 x 8 mm in size

to study different sizes and its correlation to EPR signal. Calipers were used to verify the dimensions. The sample was treated in the TGA at 195 ℃ for 24 hr under nitrogen conditions. The sample was then measured in the EPR four different ways. The first time, the sample was run as normal in the EPR quartz sample tube. The piece was then cut directly in half making the length 4 mm instead of 8 mm. For the second run, just the bottom half was scanned. For the third run the bottom half was removed and the top half was scanned, the orientation was kept the same as when it was a run as a full sample. Finally, for the fourth run, the pieces were put back in their original orientation for the upper and lower pieces. It was hypothesized that the microwave radiation would pass through the wood and irradiate all radicals in the sample. Therefore, it was expected the first (full piece) and last sample (top and bottom half together) would have a similar signal area to each other, while the second (bottom half) and third (top half) sample would have a similar signal area to each other, as well as having half the signal to the first and fourth sample.

The Varian EPR spectrometer and standard settings were used (vide supra Chapter 2.5) with 2 scans per spectra, and 15 spectra per experiment. All data was processed per the EPR data processing description given in Chapter 2.6 Materials and Methods.

Results/discussion:

After running the sample for 24 hr in the TGA, EPR measurements showed a radical presence in all samples. The results can be seen in Figure 4.3.1 and Table 4.3.1.

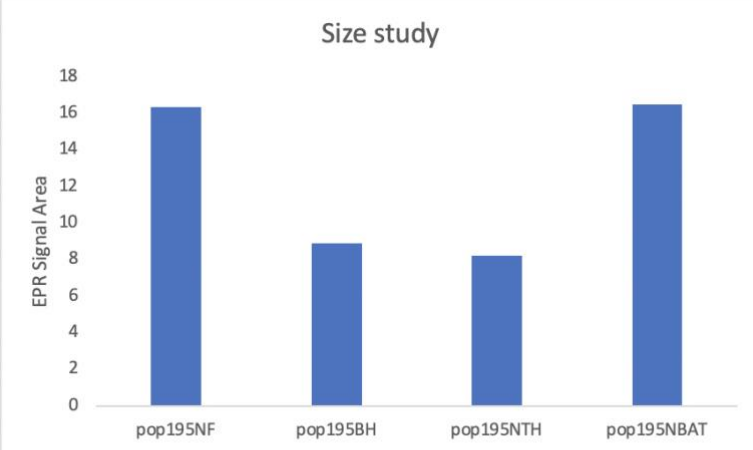


Figure 4.3.1: Fresh balsam poplar treated in the TGA for 24 hours under Nitrogen conditions. Far left was a full piece, the second from the left is the bottom half, the third from the left is the top half, and the last was the top and bottom half together in the same orientation.

Table 4.3.1 Samples with their numerical EPR radical signal area data.

Sample:	EPR radical signal area
Full piece	16.32
Bottom half	8.86
Top half	8.19
Top and bottom half together	16.5

The area under the EPR radical signal for the full piece of wood had a value of 16.32. The bottom half of the wood sample gave an EPR radical signal with an area of about half (8.86), 54.3% of the full piece sample. The top half of the wood sample had a similar EPR radical signal area of 8.19, 50.2% of the full

piece. Finally, the scan of the top and bottom pieces together in the same orientation had an EPR radical signal area of 16.5, 101.1% of the full piece. Both half piece samples gave a reading that was close to half of the original full piece, and the top and bottom pieces together in the same orientation gave close to 100% of the original piece signal. Based on this data it is clear how important the actual size of the sample is when it comes to running EPR and it became clear that the microwaves were exciting all radicals in the wood, not just those on the sample surface.

Conclusion:

To conclude, the hypothesis was supported that the EPR radical signal area was cut in half when the size of the wood was cut in half. The second hypothesis was also confirmed that the scan of the upper and lower halves together would have an area that was the same as the full uncut piece. Based on these results, it was decided all future wood samples would be cut to the same size of 1.5 x 1.5 x 8 mm, thus also making the position and height of the wood the same in the resonating cavity amongst all samples. These extra changes should help reduce variability in samples.

4.4 Problem #3: weight: Will a consistent weight of samples provide better data and comparability?

Rationale:

In Chapter 4.2 fresh wood was thermally treated using TGA. There was a failure in trend with the samples treated in an oxygen atmosphere (Figure 4.2.4). The wood sample treated at 210 ℃ had an EPR radical signal that fell out of trend and was lower than the samples treated at 180 ℃ and 195 ℃. When addressing this problem, the data, methodology, and samples were carefully examined. It was found that the piece had shriveled to a significant smaller size after treatment, thought to be the effect of oxidation.[24] It was also observed that all pieces, though they were close, were not precisely the same size or weight. In Chapter 4.3 it was concluded that all samples needed to be cut to the same size, with an improvement in precision. This is due to the sensitivity of the instrument and the resonating cavity.[25] To better represent the data, it was decided to also adjust the final EPR radical signal area by its starting and ending weight for all samples so a more precise representation and comparison of the samples would be shown. With this added step, it was decided to also make sure all samples size and weight were close to each other before treatment to prevent an increase in error (vide supra Chapter 2.1 wood sample prep). Equation 4.4.1 shows the formula for weight normalization that was used. It was hypothesized that there would be a better trend with the EPR radical signal area with the adjustment in weight.

$$\text{Adj. EPR radical signal area} = \frac{\left(\text{EPR radical signal area} \times \frac{\text{Heaviest weight before treatment of all samples}}{\text{weight before treatment}}\right)}{\text{weight after treatment}} \quad \text{EQ. 4.4.1}$$

Results/discussion:

The data from Chapter 4.2 was taken and adjusted per Eq.4.4.1. The data is now represented as EPR signal area per milligram of wood. The data from the original EPR signal area to the new EPR signal area per milligram of wood was compared (Figure 4.4.1 and Table 4.4.1). A trend could now be seen with the correct adjustment to weight.

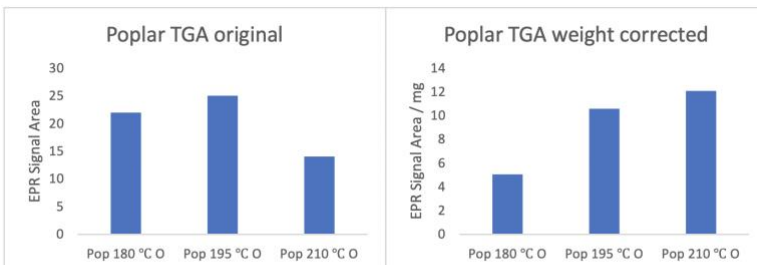


Figure 4.4.1 TGA thermally treated wood at 180 °C, 195 °C, and 210 °C consecutively under oxygen atmosphere. Original EPR signal area data from ch.4.2 on the left and EPR radical signal area per mg on the right.

Table 4.4.1 Numerical EPR data from Figure 4.4.1

Sample	EPR Signal Area	EPR signal Area / mg
Pop 180 °C O	20	N/A
Pop 195 °C O	30	N/A
Pop 210 °C O	10	N/A
Weight corrected pop 180 °C O	N/A	5.1
Weight corrected pop 195 °C O	N/A	11
Weight corrected pop 210 °C O	N/A	12

Conclusion:

The failure in trend with the experiment from Chapter 4.2 was corrected by appropriate weight adjustment. With the use of Eq.4.4.1 not only was the

problem fixed, but it better represents the actual radical signal and content in each sample of wood by representing the signal to its weight. For correct data representation, all samples for future studies will be compared by EPR signal area per milligram using Eq.2. To minimize adjustments in data, all samples will be cut to the same size of 8 mm x 1.5 mm x 1.5 mm and weigh between 7 and 8 mg (vide supra Chapter 2.1 sample preparation).

4.5 Problem #4: Signal to noise: If a signal is present in a blank sample holder, should it be subtracted to achieve a better signal representation?

Rationale:

After the many preliminary tests, focus was turned towards the theory behind EPR and harnessing this to increase the chances of achieving quality data. One method to improve data would be to achieve a better signal to noise ratio similar to when radical species like DPPH and TEMPO are run. This would allow for a better understanding of the differences between the samples. After further research on the theory of EPR it was hypothesized, due to common resonator properties, that a small signal could be observed with no sample.[26] It is common for EPR spectrometers to have iron in the cavities, which can be observed through a sharp noise signal. If a signal containing no sample is observed and not accounted for it would provide difficulties in trying to represent a sample. Therefore, the data from running just the quartz sample tube with no sample would need to be measured and quantified. This signal would have an absence of analyte, and therefore could serve as a blank or background signal.[27]

The signal from the empty measurement would be removed from the signal containing a sample, otherwise referred to as a blank or background. This ultimately would provide a deeper look at the true representation of a sample.

The Varian EPR spectrometer and standard settings were used (vide supra Chapter 2.5), with 2 scans per spectra, and 15 spectra per experiment. All data was processed per the EPR data processing description given in Chapter 2.6 Materials and Methods.

Results/discussion:

The quartz sample tube was scanned in the EPR and a radical presence was detected (Figure 4.5.1). For comparison, a sample of wood that was heat treated at 180 °C utilizing an oven kiln was also measured by EPR (Figure 4.5.2). The same sharp radical impurity is observed on top of the wood radical signal.

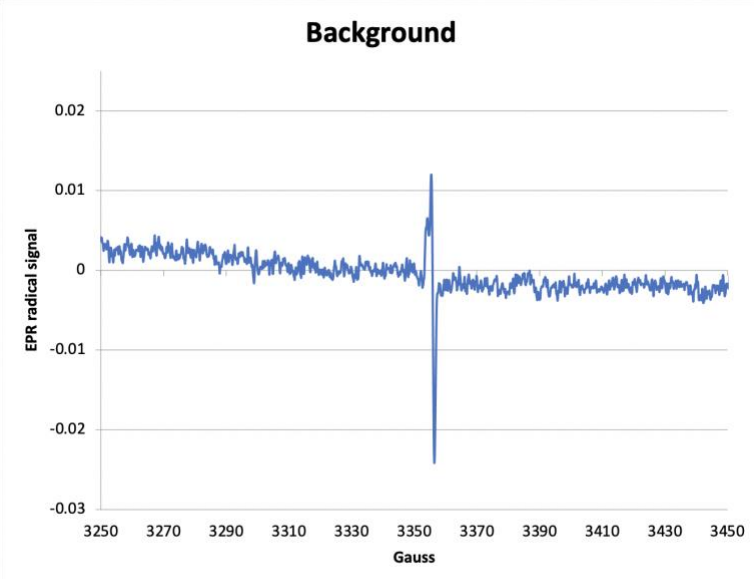


Figure 4.5.1 Raw EPR signal from empty quartz sample tube and resonating cavity.

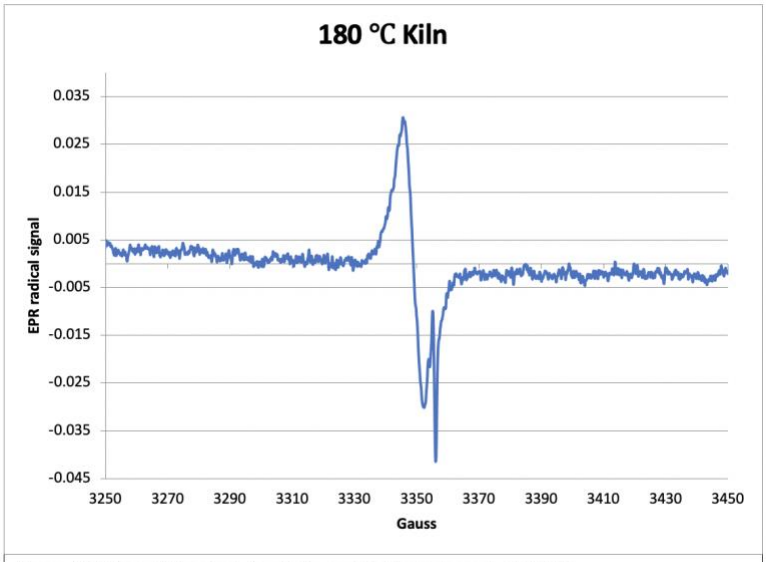


Figure 4.5.2 Raw EPR radical signal of oven kiln treated wood at 180 °C

A background signal was confirmed in running an empty quartz sample tube shown in Figure 4.5.1. The peak is seen at 3356 gauss. In Figure 4.5.2 the same background peak can be seen at 3356 gauss. Because the radical presence of wood is not as large as TEMPO or DPPH the empty sample signal becomes a significant signal due to its size comparison. A test was performed by subtracting the EPR radical signal area of a blank measurement from a treated sample to see if it would make a difference in data. The difference between having the empty quartz sample tube signal removed from the EPR radical signal area ("blank delete") and it being included is seen in Figure 4.5.3 and Table 4.5.1 with the data from Chapter 4.3.

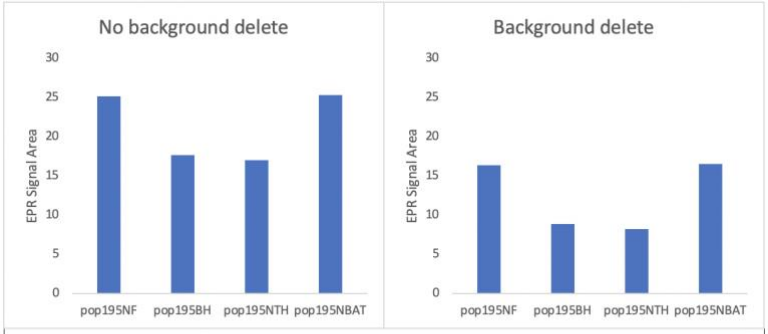


Figure 4.5.3 Data from the Size study in Ch.4.3. In both graphs the samples are fresh balsam poplar treated in the TGA for 24 hours under Nitrogen conditions. The samples are a full piece, bottom half, top half, and top and bottom half together in the same orientation from left to right. The left graph is the normal data and the right graph is with the background iron cavity and quartz sample tube subtracted from the EPR radical signal Area.

Table 4.5.1 Numerical EPR signal area data from Figure 4.5.3	
sample	EPR signal area
pop 195 °C N Full background delete	16.32
pop 195 °C N Bottom half background delete	8.86
pop 195 °C N Top half background delete	8.19
pop 195 °C N bottom and top background delete	16.5
pop 195 °C N Full	25.11
pop 195 °C N Bottom half	17.65
pop 195 °C N Top half	16.98
pop 195 °C N bottom and top	25.29

An EPR signal area is proportional to the radical concentration.[28] For example, if you measure a full sample of a substance that has an EPR signal area of ten and only half of that sample is measured, you should have an EPR area of five (vide supra Chapter 4.3). Figure 4.5.3, shown above, displays the data represented when you don't remove that blank measurement (left graph) and when you do (right graph). In the left graph the halved piece (signal of 17.65 and 16.98) does not have half the signal as the full piece (signal of 25.11). Whereas, in the right graph there is half the signal for the halved piece (signal of 8.86 and 8.19) in comparison to the full piece (signal of 16.32).

Conclusion:

Figure 4.5.1 shows the confirmation of the hypothesis of there being an EPR radical signal presence running an empty quartz sample tube. With this confirmation, the next step was to test for a better representation of data with the blank subtracted from each sample. The confirmation of this data can be seen in Figure 4.5.3. Samples after this test will have a blank run and subtracted to give a better visualization of the actual sample for a more accurate representation of the results. This is crucial especially when studying wood samples due to their smaller EPR radical signal.

4.6 Problem #5: Moisture and equilibrating samples: Can no moisture or the same moisture content in all samples be achieved?

Rationale:

EPR utilizes and directs microwaves down the wave guide onto samples and records the signal of microwaves coming back from the resonating cavity when the magnetic field is swept during a scan. Due to wood's natural property of water retention and possessing a moisture content, its effects on EPR signal needed to be studied. Water molecules absorb microwaves and rotate when microwaves are directed at and around them, similar to the way food is warmed in a microwave oven.[29] Due to the moisture in wood an attenuation in signal may be observed based on the different moisture content levels. With the effect it can have on EPR, it is important to eliminate moisture in all samples or to make sure

all samples have the same moisture content. There are two main ways to measure moisture content in a sample of wood. The first method is the utilization of a moisture meter that is either a pin or pin-less type.[30] The pin meter needs to be inserted into the wood while the pin-less meter rests directly on top of the wood, requiring a larger, flat piece of wood. However, due to the small sample sizes needed for these tests, this method is not an effective way to measure moisture content. The second method is to utilize ASTM oven-drying to calculate the moisture content. However, this method requires an additional heat treatment of the wood, and therefore contradicts the study.

With both of the previously known moisture content measurement methods being ineffective, a different method needed to be produced. The idea originally was to be able to account for moisture and the signal attenuation per sample with the thought that all samples would not contain the same moisture level. Finding a way that all samples contain the same level of moisture would be the next best solution available. To try to achieve this, Drierite (anhydrous calcium sulfate) and a desiccator were utilized. Using a desiccator and a drying, or moisture absorbing agent, are typically used to eliminate moisture in an chemical environment.[31] Drierite is a drying agent used for the efficient drying of organic liquids and solids, air, industrial gasses, and refrigerents.[32] The utilization of this product will allow increased control of moisture content and equilibrium of the samples within the desiccator. The samples will be evenly distributed within the desiccator and suspended using a cardboard matrix and microcentrifuge tubes (Figure 4.6.1). The wood is stored in room temperature

and atmospheric moisture conditions before treatment. With these storage condition in mind, and heat treatment being the source of treatment, it is assumed that not much moisture in the wood after treatment. A loss of moisture is actually expected. Because of this and the smaller size of the desiccator the sample are left inside to equilibrate for 24 hr before measurement on EPR.

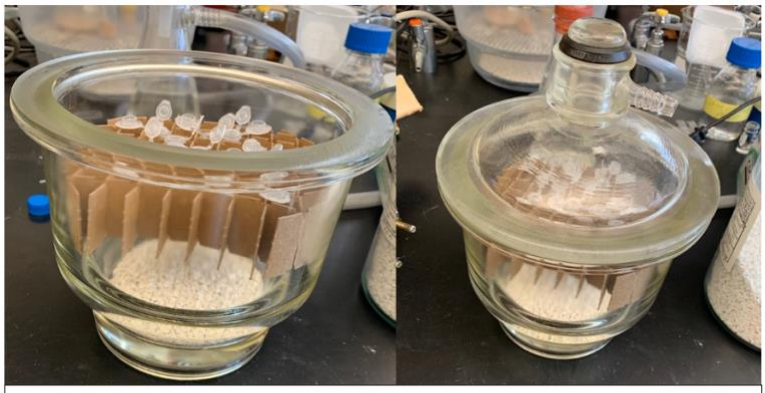


Figure 4.6.1 Desiccator with cardboard matrix and microcentrifuge tube suspension, with Drierite filled in bottom cavity. Closed and sealed on the right and open on the left.

Conclusion:

To account for the possible variable of signal attenuation due to moisture in the samples, the moisture content will be controlled and equilibrated instead of directly measured. This will be done by using a desiccator and Drierite. Practicing this method, all samples will be placed in the desiccator at the same time and enclosed for a selected amount of time to ensure that all samples are at the same moisture content before measurement. Therefore, any attenuation to the signal will be negligible because it will be the same across all samples.

4.7 Problem #6: No trend in NRRI wood: Why would there be no trend in the samples provided by NRRI?

Rationale:

When looking deeper at the initial collection of EPR data (vide supra Chapter 3.3) of the wood treated by NRRI, a way to acquire more reliable data was needed. There was a lack of a trend in Figure 3.3.4 and 3.3.6. When looking closer at their methods, some adjustments needed to be made to produce better samples. An attempt was made for access to their pilot kiln to test samples. A problem of obtaining access, training, and transportation to the site arose. After further thought, trying to make a pilot kiln in-house was the next best plan of action.

The oven kiln that NRRI used had internal thermometers inside of a chamber to keep track of and adjust temperatures. An inquiry about NRRI methods was asked and information of note was learned. Inconsistent treatment times, temperatures, and no known source of the wood was found. Without knowing if the wood was commercially dried before acquisition and an inconsistency in treatment times, it was hard to accurately compare the wood.

An attempt will be made to achieve a better method of treatment by implementing a consistent and a smoother rise to temperature, set temperature, and cool down temperature. This will be easier to accomplish with an oven that is smaller in size, that has a calibrated heating element, possesses a data logger for a second temperature reading to increase accuracy, and to record time and

temperature stamps. It is hypothesized that the control of temperature could be achieved at a more accurate degree.

Results and discussion:

The oven kiln data was collected from NRRI from the original samples of Red Maple and Eastern Hemlock. The reported temperatures were 170 ℃ and 180 ℃ for each wood species. Temperature was plotted in respect to time (Figure 4.7.1). Two probes were used in the collection of temperature.

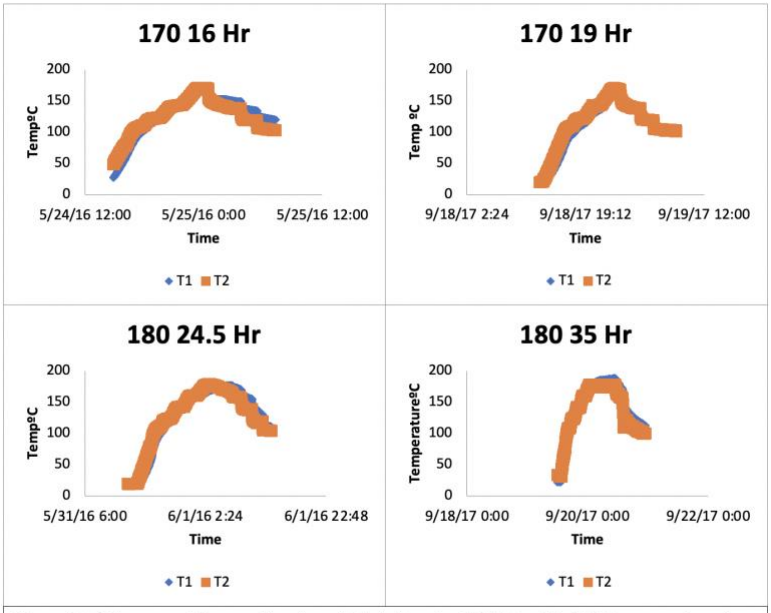


Figure 4.7.1 Four oven kiln wood treatment trials done by NRRI. Top left 170°C at approximately 16 hours. Top right 170°C at approximately 19 hours. Bottom left 180°C at approximately 24.5 hours. Bottom right 180°C at approximately 35 hours. Each showing two temperature probes inside the oven in respect to time.

In Figure 4.7.1, a few observations can be made in regard to the oven data. The first observation is that with each trial the temperature reported for treatment only barely reached, or shortly reached, the reported temperature.

Also, the total run time for each isn't the same, with the timings being 16, 19, 24.5, and 35 hr. Finally, the ramp of temperature and decrease of temperature is dissimilar. With so many variables, it becomes obvious why it was difficult to compare the samples and their radical content. An attempt to correct a few of these variables with an in-house kiln was made. The components and set-up of this kiln was described in Chapter 2.4 in the Materials and Methods section. A wood thermal treatment run was performed and is shown in Figure 4.7.2 below for comparison to the industrial pilot scale kiln.

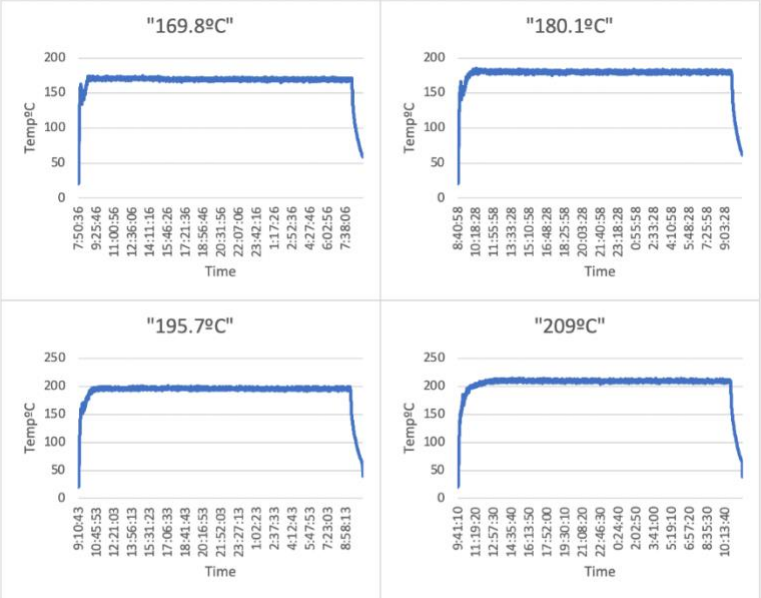


Figure 4.7.2 Four oven kiln wood treatment trials done in house. Top left 169.8°C at 24 hours. Top right 180.1°C at 24 hours. Bottom left 195.7°C at 24 hours. Bottom right 209°C at 24 hours. Each showing the temperature in respect to time.

The data shown in Figure 4.7.2 shows the four in-house oven kiln trials. Each of these used a smaller size oven and used a data logger probe to record the temperature. For each of these treatments, the oven was allowed 1 hr to

warm up with adjustments in temperature until it was as close to the goal temperature as possible (170 ℃, 180 ℃, 195 ℃, 210 ℃). After the oven was held "at temperature" for 24 hr it was then switched off for a cool down period of 1 hr. A comparison between Figure 4.7.2 and 4.7.1, shows the time, the temperature, and the overall method was consistent and much more reproducible for the in-house kiln and the industrial pilot-scale kiln.

Conclusion:

To conclude, testing with an in-house pilot scale of the kiln works to great efficiency. When examining the NRRI data, inconsistencies were found in time and temperature within the trials. With the in-house kiln, those inconsistencies were controlled and resolved. The hypothesis of controlling temperature at a higher degree with the in-house kiln was confirmed. With the added ease of using the kiln in house, no restrictions to access, and the confirmation of the added control of variables, it was concluded that the in-house oven kiln should be used for all future kiln experiments.

4.8 Conclusion

Addressing the areas of concern was crucial to the forward advancement of the overall experiments and bigger picture questions. Some of these areas included questioning why there was such a high EPR radical signal area for the untreated wood, how does sample size and weight play a role in EPR radical signal, how to effectively minimize signal to noise, how to account for moisture

and the most efficient way for all samples to contain the same moisture level, and addressing why there wasn't a trend in the wood from NRRI and if something could be done about it. The issue of a high untreated signal was resolved by acquiring fresh wood that was not previously oven-dried. Better overall data and better sample comparison was accomplished through cutting each sample of wood to a uniform size, using wood in a similar starting weight range, and correcting the signal to weight. The issue of signal to noise ratio and achieving a more accurate representation of the sample was solved by taking a blank scan and subtracting that from the sample. The utilization of the desiccation method ensured each sample was at the same starting moisture content. The final problem that was faced was to address the inaccuracy of the wood samples from NRRI. This was solved through the creation of an in-house oven kiln and the implementation of a data logger to keep record of temperature with respect to time, under much more reproducible kiln runs.

When combining all of these adjustments, an excellent data set may be provided. Using the oven kiln, cutting the wood more precisely, and desiccating will ultimately lead to a much more precise method of comparing the samples to each other. Using fresh wood and cutting the same size wood will provide for much better sample prep and results, while practicing a blank delete and adjusting for weight will allow for a better representation of each sample. Once all of these small changes are put into effect, the minimization of variables will occur and in turn allow for more freedom within future tests.

Chapter 5

Industry Questions

5.1 Rationale

As the preliminary control experiments were completed and the experimental parameters were tuned, it was time to revisit to the original question as well as explore some industry questions related to this project. Many of the questions within the industry, as well as my project, revolve around the study of quantifying thermal treatment by EPR spectroscopy. Being able to tackle experiments without the many issues that ensued previously would allow a smooth transition to our end goal.

5.2 Moisture study

Rationale:

In Chapter 4.6, a new way to equilibrate all samples before testing in the EPR was created. The effects of moisture on EPR signal needed a closer look. As an EPR sweeps the magnetic field, it directs microwaves into the resonating cavity and records the change at the detector. Many individuals warm food in the microwave every day, yet many do not know that what warms the food is the rotation of the food's water molecules stimulated by the microwaves.[29] So, if there is any water (moisture) in the EPR samples it may absorb some of the microwaves resulting in a weaker microwave energy exciting the radicals, thus attenuating the EPR signal. Due to the common property of moisture content

amongst all types of wood, it is an important parameter to control or measure when doing quality measurements of wood.[33]

The scope of this experiment is to hydrate and desiccate samples of heat-treated wood in different ways and record the effect. The wood samples were treated in the TGA using the methods in Chapter 2.2 under a nitrogen atmosphere. The samples were treated at 180 °C, 195 °C, and 210 °C as well as an untreated sample. The Varian EPR spectrometer and standard settings were used (vide supra Chapter 2.5), with 2 scans per spectra, and 15 spectra per experiment. All data was processed per the EPR data processing description given in Chapter 2.6 Materials and Methods. A range of moistures needed to be obtained. There were four different ways each group was treated and measured, and moving forward, this is referred to as batches. Each Batch consisted of four samples of wood treated at 180 °C, 195 °C,210 °C and one untreated sample. The first batch was desiccated for 24 hr and measured as normal. The second batch was hydrated with 300 microliters of milli-Q water for 24 hr and then desiccated for only 1 hr before EPR measurement. The third batch was hydrated with 300 microliters of milli-q water for 24 hr and desiccated for 24 hr before EPR measurement. The fourth batch was hydrated with 300 microliters of milli-q water for 24 hr and desiccated for a week before EPR measurement. It was hypothesized that in comparison to the first batch the second batch would have the biggest attenuation in signal resulting in the smallest EPR radicals signal area, the third batch would also have an attenuated EPR radical signal area and

would be smaller than batch one but larger than batch two, and finally batch four is hypothesized to have the same/similar EPR radical signal area to batch one.

Results and discussion:

All of the wood was treated as according to the experiment above and each batch was treated and measured with EPR. Batch one had a good trend with a correlation of heat treatment to EPR radical signal with untreated being the lowest signal with an incremental increase of signal in order of 180 °C, 195 °C, and 210 °C. Batch two had the lowest EPR radical signal area. A trend was also observed. The third batch had a slightly lower signal than batch one and had the same trend. Batch four had almost the same EPR radical signal area as batch one. The results can be seen in Figure 5.2.1 below and Table 5.2.1.

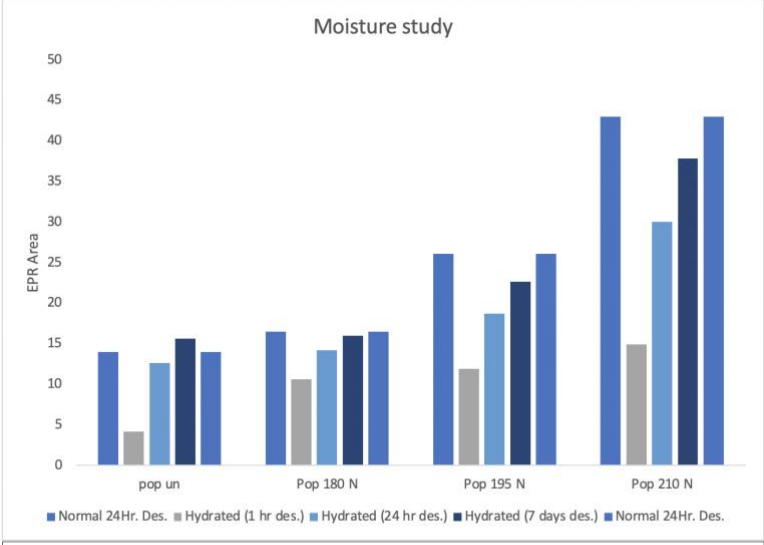


Figure 5.2.1 Moisture study of wood untreated and at 180°C, 195°C, and 210°C; Showing from left to right batch one (normal 24Hr. Desiccation), batch two (hydrated for 24Hr., 1Hr. desiccation), batch three (hydrated 24Hr., 24Hr. desiccation), batch four (hydrated 24Hr., 7 days desiccation), batch one (normal 24Hr. Desiccation).

Table 5.2.1 Numerical EPR signal area data from Figure 5.2.1					
Sample	Normal 24Hr. Des.	Hydrated (1 hr des.)	Hydrated (24 hr des.)	Hydrated (7 days des.)	Normal 24Hr. Des.
pop un	14.0	4.13	12.6	15.6	14.0
Pop 180 N	16.5	10.6	14.2	16.0	16.5
Pop 195 N	26.1	11.9	18.7	22.6	26.1
Pop 210 N	43.0	14.9	30.0	37.8	43.0

In Figure 5.2.1, you can see the results of each batch with batch one plotted on the left and right of each temperature for better data comparison. Thinking of the different batches in relation to how wet each batch would be or how high their moisture content would be, batch two would have the highest moisture content, followed by batch three as the next highest and then either batch four or one with the smallest moisture content. It makes sense why the data followed this pattern of attenuated EPR radical signal due to the hydrated samples with the moisture content being batch 2 $>$ batch 3 $>$ batch 4 $\geqq$ batch 1.

Conclusion:

It was concluded that excess water or moisture in an EPR sample would attenuate the signal in a correlation to moisture content. The hypothesis of having EPR radical signal area attenuation be in the order of being batch 2 $>$ batch 3 $>$ batch 4 $\geqq$ batch 1 due to moisture was confirmed by this study. Due to these results, it was confirmed that taking recently heat-treated samples (that are low in moisture by default) and desiccating them for 24 hr before running EPR is the best process for minimizing signal attenuation and for equilibrating the samples for EPR.

5.3 Relation between heat treatment and EPR signal utilizing TGA

Rationale:

With the standard methods for the preparation of samples finalized to mitigate any unwanted variables and to improve measurements, a closer look was made into the correlation between EPR radical content and the extent of thermal treatment. The thermogravimetric analyzer (TGA) was utilized for this experiment to treat the wood to an accurate and precise level. This allowed a closer focus on the relationship of heat treatment to EPR radical signal. There were 8 different samples that were run in the TGA. Four temperatures were selected to reflect a range of industry standard treatments 170 °C, 180 °C, 195 °C, and 210 °C.[34,35] Two samples would be treated at each temperature, one under a nitrogen atmosphere and the other under an oxygen atmosphere (again for industry standards) for a total of eight samples. All samples were prepared using standard methods (vide supra Chapter 2.1).

After all samples were treated with the TGA, they were desiccated for 24 hr before measurement by EPR. EPR was run on the Magnettech using EPR data collection method (vide supra Chapter 2.5), with two scans per spectra and 15 spectra per experiment. The data was then processed per the EPR data processing method (vide supra Chapter 2.6). The data will also be shown as EPR radical signal area per mg of wood for a better representation of radical content inside the full sample of wood (vide supra Chapter 4.4). It was hypothesized that a trend in the correlation of EPR radical signal area per mg of

wood to heat treatment temperature would be found. More specifically, the data would show a higher signal for higher treatment temperatures and a lower signal for lower treatment temperatures.

Results/discussion:

All samples were prepared, treated, and measured using the EPR to observe and to calculate the EPR radical signal per mg of wood. The samples treated under a nitrogen atmosphere can be seen in Figure 5.3.1 vide infra, whereas the samples treated in an oxygen atmosphere can be seen in Figure 5.3.2 vide infra. All numerical data is shown in Table 5.3.1.

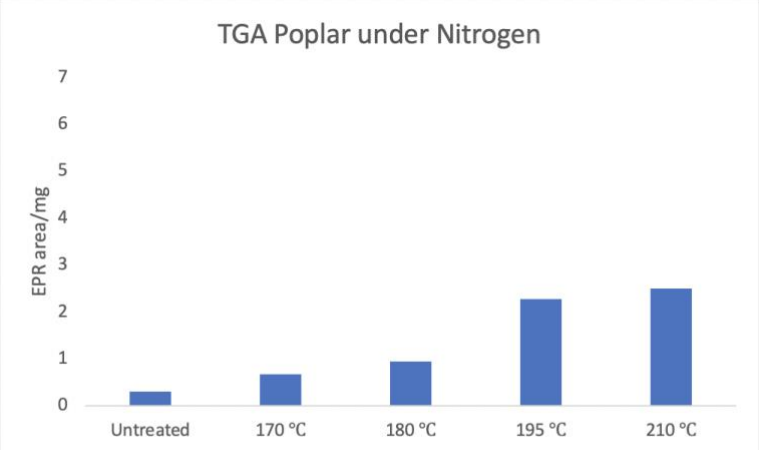


Figure 5.3.1 Balsam Poplar untreated and treated with TGA under nitrogen at 170 °C, 180 °C, 195 °C, and 210 °C showing correlated EPR area/mg of wood.

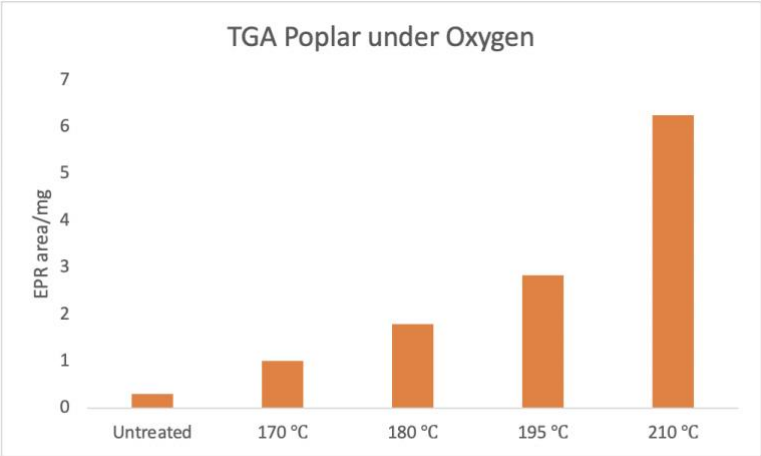


Figure 5.3.2 Balsam Poplar untreated and treated with TGA under oxygen at 170 °C, 180 °C, 195 °C, and 210 °C showing correlated EPR area/mg of wood.

Table 5.3.1 Numerical EPR signal area per mg of wood data from Figures 5.3.1 and 5.3.2		
sample	nitrogen	oxygen
Untreated	0.305	0.305
170 °C	0.677	1.01
180 °C	0.936	1.79
195 °C	2.27	2.84
210 °C	2.49	6.24

A trend can be seen in Figure 5.3.1 with EPR radical area per mg of wood to thermal treatment temperature under a nitrogen atmosphere. As temperature increases, EPR radical area per mg of wood also increases. The same trend can be seen in Figure 5.3.2 with an oxygen atmosphere. Overall, the signal in the oxygen samples were much higher than the nitrogen samples. Also, the untreated sample of wood had a far smaller signal in comparison to the heat-treated wood.

Conclusion:

Both studies (oxygen and nitrogen) have a direct increase in EPR signal with an increase in thermal treatment. This was a big deal because this

supported a correlation of EPR radical signal area per mg of wood to the extent of heat treatment temperature, thus supporting the hypothesis. With this, the hypothesis was further explored by repeating this same experiment using an in-house oven kiln to replicate industry standards. The same experiment was also repeated with more replicates for statistics to further support our hypothesis.

5.4 Relation between heat treatment and EPR signal utilizing an in house kiln

Rationale:

The TGA presented two major restrictions with treating wood. The first restriction is the limitation of treating one sample at a time. This makes for numerous hours of sample treatments (at about one sample per 48 hr) with low turnover for total number of samples. The second restriction is that in the manufacturing process, industrial wood is treated in large quantities, in the same kiln, at the same time.[36] Due to the inability to use an industry size kiln, an expedient kiln was built in-house for this next study to allow more wood to be treated at once and to be closer to an industrial process.

The kiln was built to the specification in the oven kiln method (vide supra Chapter 2.4 and Chapter 4.7). Four different treatment experiments were executed at goal temperatures of 170 °C, 180 °C, 195 °C, and 210 °C. Five pieces of wood were treated at each temperature for a total of 20 total samples for this experiment and all samples were treated for 24 hr. The wood samples were prepared, treated in the kiln, and tested in the EPR according to the method

section (vide supra Chapter 2.5), with two EPR scans per spectra and fifteen spectra per experiment were taken for a total of 30 spectra. It was hypothesized that a similar relationship seen in the TGA experiment would be seen with a correlation between EPR radical signal to heat treatment temperature with a rise in signal as the temperature increased.

Results/discussion:

The four heat treatment trials in the oven kiln were completed per the design of the experiment. For the goal temperature of 170 °C the average temperature was 169.8 °C, for the goal temperature of 180 °C the temperature was 180.1 °C, for the goal temperature of 195 °C the temperature was 195.7 °C, and for the goal temperature of 210 °C the temperature was 209 °C. Each of the treatment experiment results can be seen in Figure 5.4.1 and table 5.4.1.

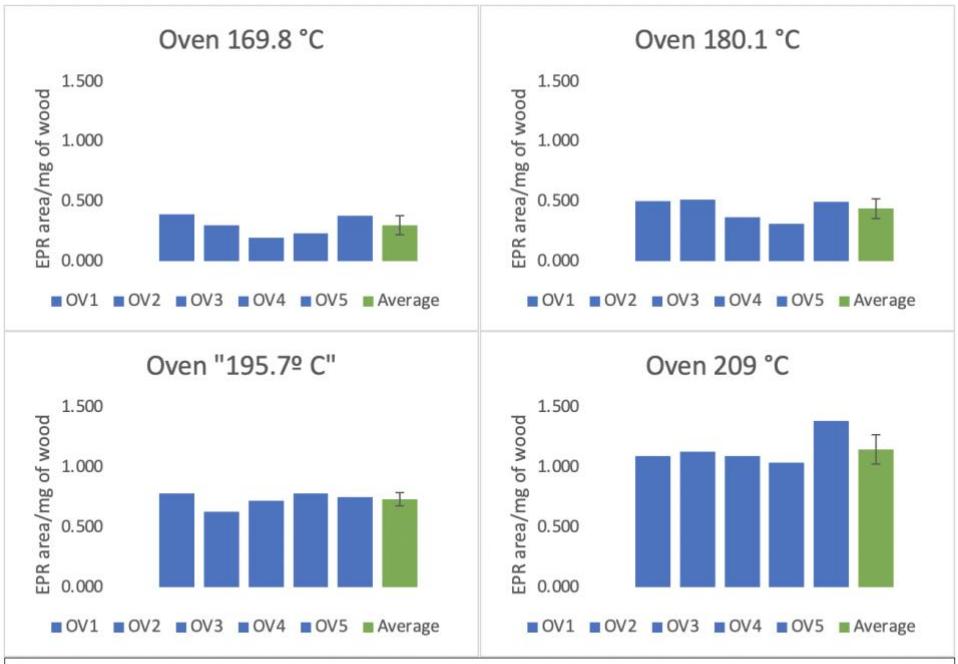


Figure 5.4.1 Heat treatment experiments showing EPR area per mg of wood at temperatures of 169.8 °C, 180.1 °C, 195.7 °C, and 209 °C top left, top right, bottom left, and bottom right consecutively. Each graph showing the five treated samples with an average of each group on the far right.

Table 5.4.1 Numerical EPR area per mg of wood data from Figure 5.4.1

sample	169.8 °C	180.1 °C	195.7 °C	209 °C
OV1	0.395	0.504	0.785	1.097
OV2	0.304	0.516	0.633	1.130
OV3	0.199	0.370	0.723	1.094
OV4	0.233	0.317	0.782	1.042
OV5	0.380	0.495	0.752	1.387
average	0.302	0.440	0.735	1.150

For each heat treatment experiment, the five wood samples are shown with their EPR radical signal per mg of wood as well as the average signal of all five. All groupings stayed in a close range of each other. In order to clearly see if a trend emerged, the average of each group was combined to create a new graph seen in Figure 5.4.2. Standard deviation bars are shown on the graphs.

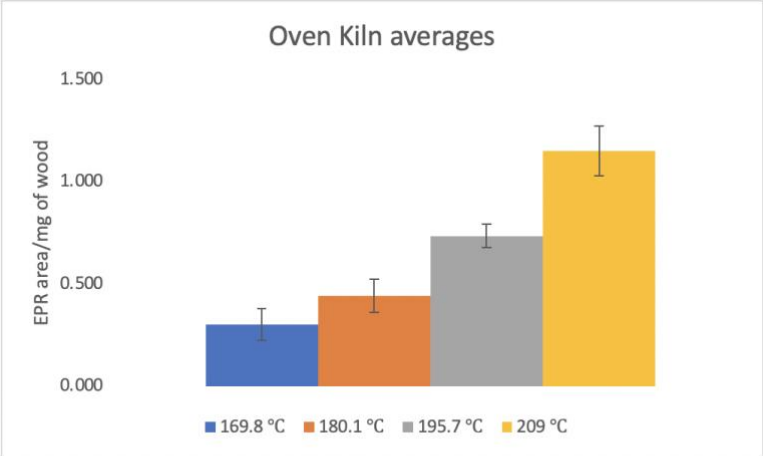


Figure 5.4.2 Average EPR area per mg of wood of each temperature groups five samples are shown left to right 169.8 °C, 180.1 °C, 195.7 °C, and 209 °C consecutively.

Table 5.4.2 Numerical EPR area per mg of wood data from Figure 5.4.2

sample	EPR area/ mg of wood
169.8 °C	0.302
180.1 °C	0.440
195.7 °C	0.735
209 °C	1.15

With the average data from each temperature plotted on one graph, as seen in Figure 5.4.2, it becomes easier to compare the data between each heat treatment oven kiln experiment. A trend can be observed. As heat treatment temperature rises, the EPR radical signal area per mg of wood increases.

Conclusion:

It was concluded that as the heat treatment temperature increased, the EPR radical signal area per mg of wood also increased, supporting the hypothesis. This was huge for a few reasons. The first reason was that just like in Chapter 5.3 the original goal to correlate this relationship was achieved, but this time in conditions similar to industry. Secondly, a higher sample turn around

was accomplished. Heat-treating 5+ samples (upwards to 30+) per 48 hr verses 1 sample max per 48 hr was a large advancement. And of course, this could be scaled up to treat hundreds of samples in 48 hr if desired. Lastly, this industrial expedient kiln provided the same results and conclusions for the correlation of EPR signal and heat treatment like the TGA experiment. With this a push toward collecting statistical data for the oven kiln and TGA relationship could be studied.

5.5 Statistics studies

Rationale:

With the success in both tests for correlation of EPR radical signal with extent of thermal treatment using TGA (vide supra Chapter 5.3) and by using an in-house kiln (vide supra Chapter 5.4), there was a need for statistical backing. To do this, both tests would need to be redone but done with multiple samples or with duplicate treatments to show reproducibility.[37] A higher insight on how effective the treatment types are, and how effective the method of using EPR to quantify the extent of heat treatment can be gained through repeating the experiments to gain statistics.

TGA statistic study overview:

The goal of this study was to collect statistical results for the study done in Chapter 5.3. The method of thermal treatment of wood will be the TGA analyzer with EPR spectroscopy to measure the radical output. A triplicate statistical test will be done with three samples of wood for each temperature of 170 °C, 180 °C,

195 °C, and 210 °C for a total of twelve samples that will be heat treated. They were thermally treated at their temps using the standard TGA method under nitrogen (vide supra Chapter 2.3). The wood will be prepared by the wood sample preparation method (vide supra Chapter 2.1).

The Magnettech Miniscope 5000x spectrometer and standard settings were used (vide supra Chapter 2.5), with 2 scans per spectra, and 15 spectra per experiment. All data was processed per the EPR data processing description given in Chapter 2.6 Materials and Methods.

Results discussion:

Each group of samples were treated at their respective temperatures, measured with the EPR, and processed. The EPR area per mg of wood for each wood sample in the triplicate set, along with the average is plotted in Figure 5.5.1.

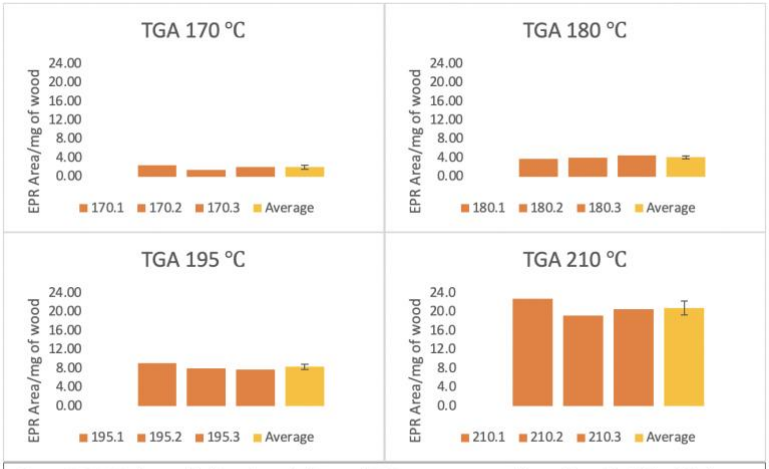


Figure 5.5.1 Each graph showing triplicate of EPR area per mg of wood on the left with the average of each set on the right. 170 °C, 180 °C, 195 °C, and 210 °C shown top left, top right, bottom left, and bottom right consecutively.

Each group of temperatures had a slight variation of EPR signal. Each triplicate group had signal responses that were close to each other. In order to be able to say they were close, and to give a statistical significance, the averages were plotted with each other with error bars showing the standard deviation of each set. This can be seen in Figure 5.5.2 and table 5.51.

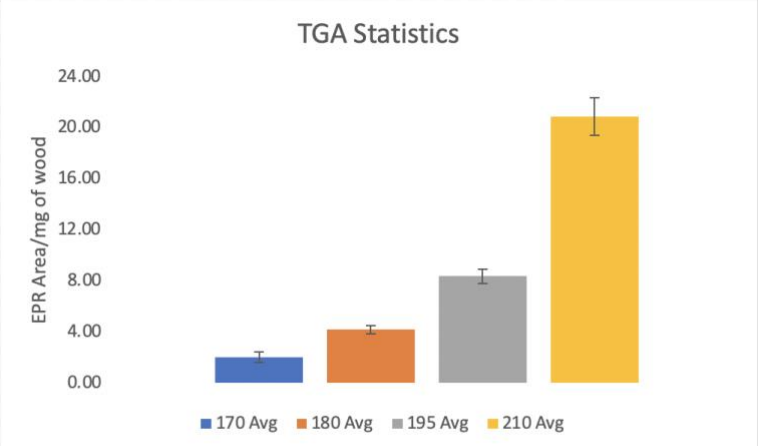


Figure 5.5.2 Averages from each temperature triplicate set of 170 °C, 180 °C, 195 °C, and 210 °C from left to right. The standard deviation is plotted as error bars.

Table 5.5.1 Numerical EPR area per mg of wood data from Figures 5.5.1 and 5.5.2

sample	170 °C	180 °C	195 °C	210 °C
Rep 1	2.48	3.83	9.15	22.8
Rep 2	1.47	4.04	8.07	19.3
Rep 3	2.13	4.59	7.83	20.6
Average	2.03	4.15	8.35	20.9

Looking at Figure 5.5.2, it is supported that each of the triplicates fell within a good range of EPR radical signal with the averages displayed in the bar graph. The error bars show the statistical significance between each set of samples. Each average temperature set falls outside the error bars. The p-

values are displayed in table 5.5.2. This shows that each signal output from each range is significantly separate from the next, thus further supporting the correlation of signal to thermal treatment.

Table 5.5.2 p-value for statistical comparison of each temperature group.

Comparison temp in °C	p-value
170-180	0.0047
170-195	0.0002
170-210	0.0001
180-195	0.0008
180-210	0.0001
195-210	0.0004

Kiln statistics overview:

The goal of this study was to collect statistical results for the study done in Chapter 5.4. The method of thermal treatment of wood will be the in-house oven kiln with EPR spectroscopy to measure the radical output. A statistical test will be done with six samples of wood for each goal temperature of 170 °C, 180 °C, 195 °C, and 210 °C for a total of twenty-four samples will be heat treated. They were thermally treated at their temps using the oven kiln method (vide supra Chapter 2.4). The wood will be prepared by the wood sample preparation method (vide supra Chapter 2.1).

The Magnettech Miniscope 5000x spectrometer and standard setting were used (vide supra Chapter 2.5), with 2 scans per spectra, and 15 spectra per experiment. All data was processed per the EPR data processing description given in Chapter 2.6 Materials and Methods.

Results/discussion:

Each set of oven kiln runs were accomplished successfully with measured average temperatures of 169.7 °C, 179 °C, 194.4 °C, and 209.2 °C. The EPR data was reported as EPR radical signal area per mg of wood seen in Figure 5.4.3 with the average taken of each set of six samples.

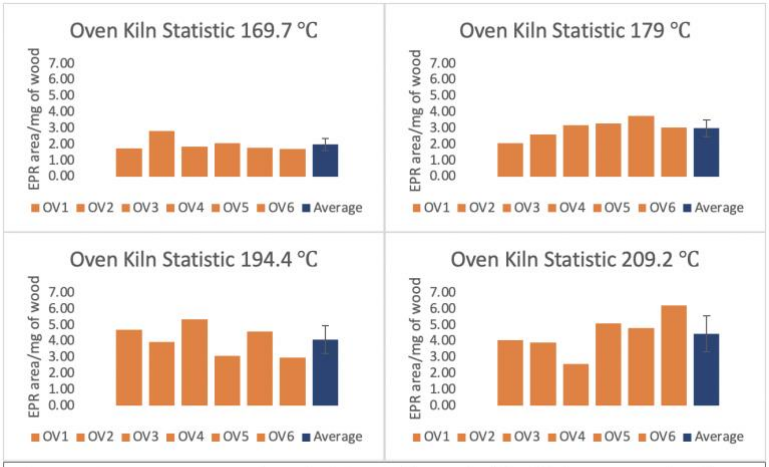


Figure 5.5.3 EPR area per mg of wood of six samples on the left with the average of each set on the right. 169.7 °C, 179 °C, 194.4 °C, and 209.2 °C shown top left, top right, bottom left, and bottom right consecutively.

Each set of oven kiln samples stayed within a close range of each other. To give a better representation of how each set related to each other a graph displaying the averages of each set was made with error bars showing the standard deviation of each set. This can be seen in figure 5.5.4 and table 5.5.3 below.

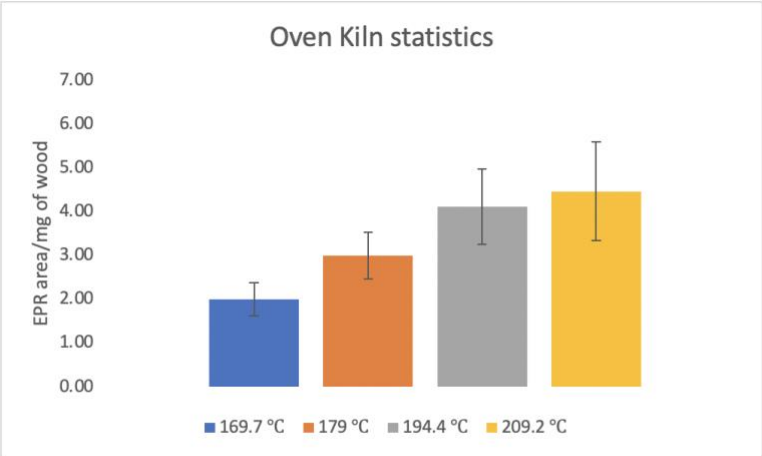


Figure 5.5.4 Averages of each oven Kiln set of 169.7 °C, 179 °C, 194.4 °C, and 209.2 °C from left to right. Standard deviation shown as error bars.

Table 5.5.3 Numerical EPR area per mg of wood data from Figures 5.5.3 and 5.5.4

sample	169.7 °C	179 °C	194.4 °C	209.2 °C
Rep 1	1.74	2.07	4.72	4.08
Rep 2	2.82	2.60	3.96	3.93
Rep 3	1.85	3.18	5.35	2.58
Rep 4	2.06	3.31	3.11	5.11
Rep 5	1.79	3.75	4.60	4.84
Rep 6	1.72	3.05	2.97	6.21
Average	2.00	2.99	4.12	4.46

A linear relationship can be seen in Figure 5.5.4 of EPR radical signal area per mg of wood. The error bars only overlap the average area on the 194.4 °C, and 209.2 °C sets. The p-values can be seen in table 5.5.4, which shows statistical significance in all comparisons besides 194.4 °C and 209.2 °C. One reason for no statistical difference could be from the actual set up of the in-house kiln. The kiln was made to replicate an industrial kiln chamber as much as possible, but there are drawbacks and limitations. One of which is the open space of the model and amount of wood, industrial kilns have a higher wood to air ratio inside of the kiln.

Table 5.5.4 p-value for statistical comparison of each temperature group.	
Comparison temp in °C	p-value
169.7-179	0.0071
169.7-194.4	0.0005
169.7-209.2	0.0009
179-194.4	0.0318
179-209.2	0.0246
194.4-209.2	0.6032

Conclusion:

In conclusion, there was a support for the hypothesis that heat treatment and EPR signal area could be correlated, by both the TGA statistic study and oven kiln statistic study. The study in Chapter 5.3 was repeated with more samples utilizing the TGA analyzer. The EPR radical signal per mg of wood increased as thermal treatment temperature increased. The added samples allowed for statistical analysis, and in result confirmed a statistical significance. In addition, the same study as explained in Chapter 5.4 was conducted containing more samples utilizing the in-house oven kiln. The EPR radical signal per mg of wood increased as thermal treatment temperature increased. The added samples allowed for statistical analysis, and although more radicals were observed with higher treatment temperatures, all testes showed statistical significance besides 194.4 °C and 209.2 °C for the kiln study. More samples would need to be run and tested here to see if a statistical difference arises. The reason behind the lack in statistical difference is unknown. The oven kiln was designed to be a scale model of what is found in industry, that model made was still not perfect. The statistical difference found in the TGA study was supportive evidence that the same controlled environment that was achieved with TGA is similar to the controlled environments in industry, so adjusting the oven kiln to be closer to industry should help the statistical difference. It was already confirmed

in previous Chapters (vide supra Chapter 5.3 and 5.4) that there is an EPR radical signal response to thermal treatment temperature. The results of these two tests further supports the results of those studies and the overall goal of this project.

5.6 Radical formation rate study

Rational/ overview:

Different lengths of thermal treatment were to be tested next. Industry treatment times can vary depending on the company and can range from 16-36 hr in total time under heat.[9, 34] Heat could trigger the depolymerization of hemicellulose or lignin, the two radical creating suspects.[38] To acquire another dimension in the measurement of EPR radical signal and how it relates to heat treated wood, a test was performed to see if there is a rate of formation of radicals with respect to time.

To test for the rate of formation of radicals, the TGA analyzer will be utilized for the thermal treatment of wood. Six pieces of wood were treated at each temperature of 170 °C, 180 °C, and 195 °C. Instead of treating each sample for 24 hr, the samples will be treated for 2, 8, 16, 24, 36, and 48 hr long all under nitrogen atmosphere. There were six samples at each temperature and one per treatment length, for a total of 18 samples, with all being prepared by the standard wood preparation method (vide supra Chapter 2.1).

The Magnettech EPR Spectrometer and standard settings were used (vide supra Chapter 2.5), with 2 scans per spectra, and 15 spectra per

experiment. All data was processed per the EPR data processing description given in Chapter 2.6 Materials and Methods.

Results/discussion:

All samples were treated, tested, and analyzed per the experimental set up. The data was grouped together by temperature and displayed as EPR area per milligram of wood verses treatment time (2, 8, 16, 24, 36, and 48 hr) (Figure 5.6.1). The calculated rate slope of each temperature was also plotted (Figure 5.6.1, Table 5.6.1).

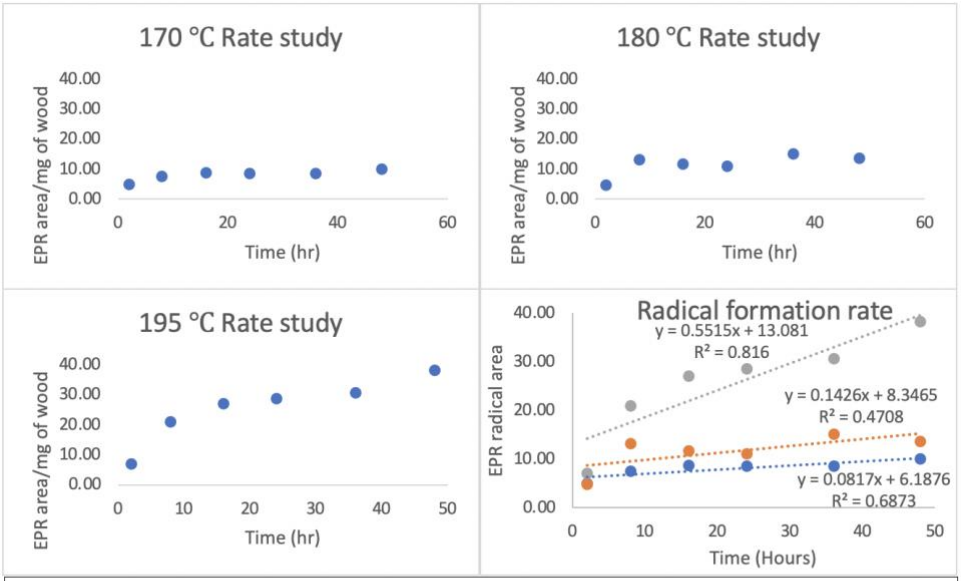


Figure 5.6.1 EPR area per milligram of wood in respect to thermal treatment times of 2, 8, 16, 24, 36, and 48 hours left to right in each graph. 170 °C, 180 °C, and 190 °C groups shown top left, top right, and bottom left consecutively. Bottom right graph showing radical formation rate trend lines with 195 °C, 180 °C, and 170 °C top to bottom.

Table 5.6.1 EPR area per mg of wood data from Figure 5.6.1			
time (hr)	195 °C	180 °C	170 °C
2	4.91253859	4.7673152	6.98727103
8	7.50570813	13.1038962	20.9678999
16	8.72681395	11.6022882	27.0811899
24	8.48019074	11.0647234	28.6002162
36	8.48057719	15.0476801	30.570776
48	9.9687945	13.6003683	38.1786665

Each temperature group had an overall trend with treatment time and EPR radical area per milligram of wood. Each treatment time had a respective EPR radical signal for its respective temperature (170 the smallest, followed by 180, and 195). For the samples treated at 170 °C, the trend had a radical growth rate of $y = 0.0817x + 6.1876$ with respect to time in hr. For the samples treated at 180 °C, the trend had a radical growth rate $y = 0.1426x + 8.3465$ with respect to time. For the samples treated at 195 °C, the trend had a radical growth rate of $y = 0.5515x + 13.081$ with respect to time. With all of the trend lines plotted together it is seen that there is an increase in slope as treatment temperatures rise.

Conclusion:

A few observations ultimately confirmed a radical formation rate. Each treatment temperature group showed an overall upward trend in EPR radical signal area with respect to time. For each treatment time, there was a higher EPR radical signal for a higher temperature respectively. When comparing each trend line slope, it was observed that as the treatment temperature rose the slope became steeper. In applying these observations, it was confirmed that there is a rate at which radicals form through thermal treatment. This could be useful

industrially, where higher temperatures could be used to achieve the same results in a shorter amount of time. However, the bulk wood properties would need be measured to confirm that radical content in the wood still correlated with the desirable wood properties. In future studies, higher treatment temperatures will be tested to obtain similar rate plots.

5.7 Polyacrylamide Study

Rationale:

When the wood samples are heat treated, a loss in mass is observed. It is assumed that a reduction in mass is due to the evaporation of water within the specimen initially, as well as the ultimate chemical breakdown of hemicellulose and lignin. The question arose of how much reduction in mass was due to each factor. When looking at TGA data of mass loss and temperature, there is a significant but consistent drop of mass in the beginning of the temperature ramp and up to the final hold temp. This was followed by a very slow decrease in mass after the initial drop. It was assumed that the first mass loss was due to moisture (water content) but it was best to try and get a concrete answer.

To answer this question, it was decided polyacrylamide would be examined. Due to its similar properties as wood, polyacrylamide was a good choice to use for comparison because of its structure and water storing capabilities. Wood is composed of an interwoven network of a variety of polymers and naturally retains water; polyacrylamide has the same water storing capabilities and is a woven polymer itself.

The polyacrylamide samples were hydrated for 1 hr and thermally treated in the TGA using the same parameters of the wood samples- 10 °C per min up to the temperatures of 180 °C, 195 °C, and 210 °C, followed by an isothermal period of 45 min. It was hypothesized that this first drop was water and the second consistent drop in mass was a chemical breakdown inside the wood leaving a radical.

Results/ discussion:

All samples were hydrated and treated in the TGA at the 3 selected temperatures. To compare the mass loss, each sample of polyacrylamide is compared to a corresponding wood sample treated at the same temperature.

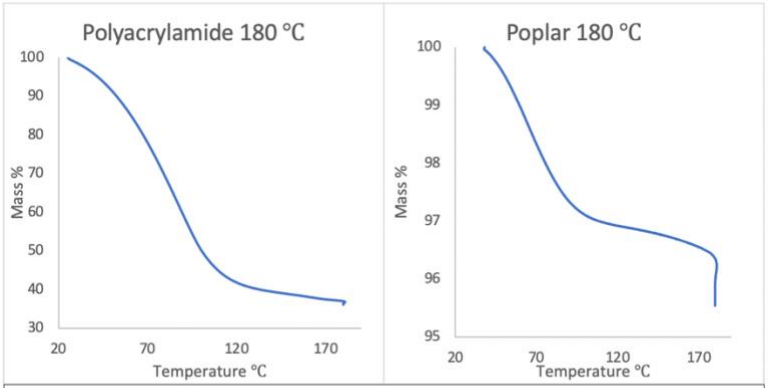


Figure 5.7.1 TGA data of hydrated polyacrylamide and Poplar at 180 °C showing Mass % and Temperature °C.

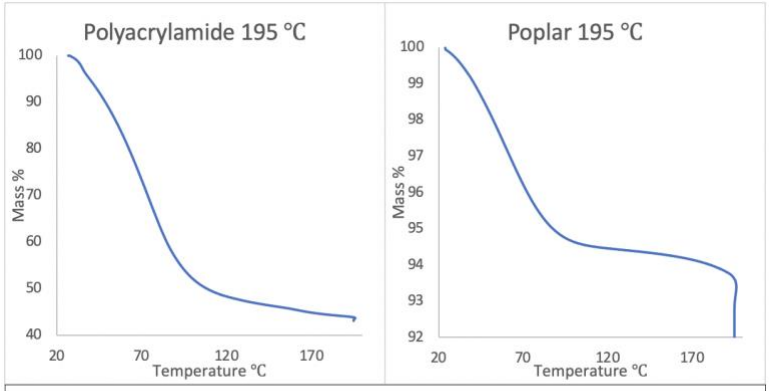


Figure 5.7.2 TGA data of hydrated polyacrylamide and Poplar at 195 °C showing Mass % and Temperature °C.

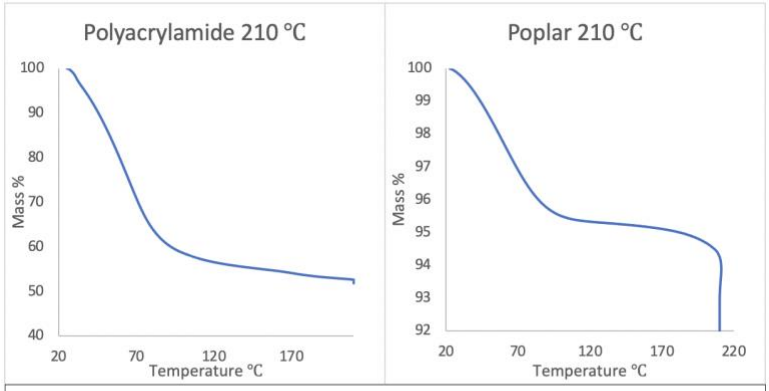


Figure 5.7.3 TGA data of hydrated polyacrylamide and Poplar at 210 °C showing Mass % and Temperature °C.

Seen above in Figures 5.7.1, 5.7.2, and 5.7.3 the correlation and similarity in the initial mass drop from start to final temperature can be seen between the polyacrylamide and Poplar wood samples for each corresponding temperature profile. In 2017, Shaikh conducted a study to examine the thermal degradation of polyacrylamide up to 900 °C. Shaikh attributed the first mass loss to moisture or in this case water.[39] The data from Shaikh's paper can be seen in in Figure 5.7.4.[39]

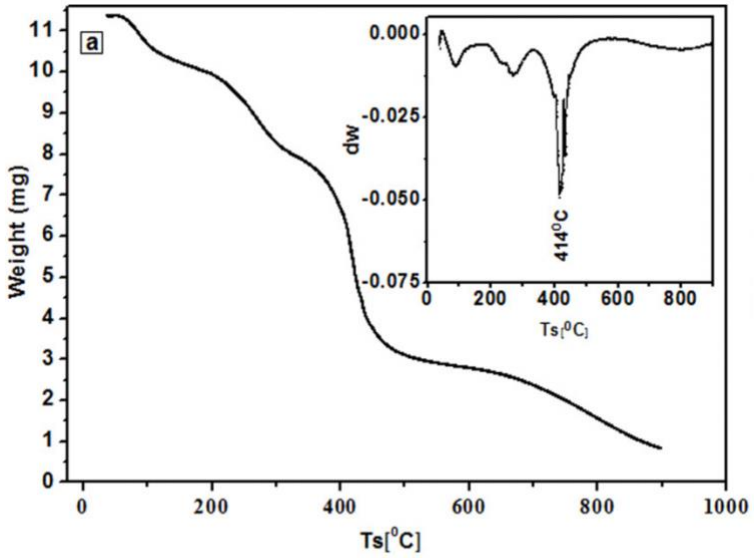


Figure 5.7.4 TGA data of Polyacrylamide treated by Shaikh with weight (mg) verses Temperature °C.[37]

As an addition to Shaikh's supporting information, the moisture content was also calculated from my TGA data. For the polyacrylamide study at 180 °C, the water content was around 64% leaving the other 36% to be polyacrylamide. For the polyacrylamide study at 195 °C, the water content was around 57% leaving the other 43% to be polyacrylamide. For the polyacrylamide study at 210 °C, the water content was around 48% leaving the other 52% to be polyacrylamide. The ending masses in Figures 5.7.1-3 are close to the calculated value of what dehydrated polyacrylamide would be, giving a second confirmation on the first drop in mass to be water.

Conclusion:

It was concluded that the initial drop in mass during thermal treatment is a loss in water. With similar TGA degradation profiles, Shaikh's paper, and manual calculation as supporting evidence, this allowed me to confirm this assumption of the first mass loss being water, therefore proving my hypothesis.

5.8 Conclusion

Using knowledge from previous Chapters, many tests helped answer the main question at hand: Can you quantify heat treatment? The effects on EPR signal due to moisture was studied. A confirmation of signal attenuation leads to a method to equilibrate samples using a desiccator before EPR measurement to mitigate such signal attenuation. Thermally treated wood by use of a TGA analyzer was utilized to see the corresponding EPR radical signal area per milligram of wood. Using this instrument allowed for accurate control of time, temperature, and weight loss measurement. A direct correlation of EPR radical signal per milligram of wood to thermal treatment temperature was observed. Thermally treated wood by use of an in-house kiln was utilized to see the corresponding EPR radical signal area per milligram of wood. Using this kiln allowed to be closer to industry standards and allowed for a higher sample yield (with respect to time). A direct correlation of EPR radical signal per milligram of wood to thermal treatment temperature was observed. Thermally treating wood for different lengths and measuring their EPR radical signal area per milligram of wood response was also done. It was found that there was an overall rate of radical formation with respect to treatment temperature. Lastly, both the TGA experiment and oven kiln experiment were done again but with multiple samples to obtain statistics. It was found that the correlation of EPR radical signal per milligram of wood to thermal treatment temperature was statistically significant with the TGA, however, more data will need to be collected with the in-house kiln

to make the expected trend statistically significant. With these experiments performed and their positive results, it can be confirmed that the extent of wood thermal treatment can be measured by EPR spectroscopy.

Chapter 6

Conclusion and future directions

The main goal of this project was to find a reliable, quantifiable and efficient way to determine the extent of heat treatment of wood. This would provide benefits to the industrial heat treatment of wood in the ability to provide a more consistent product. One idea to determine the extent of heat treatment in wood was to examine the free radicals that form as the wood decomposes under the heating process.

To begin the studies, EPR was utilized to measure DPPH and TEMPO, compounds with known radical presence, to quantify radicals of different concentrations (vide supra Chapter 3.2). A direct relationship between EPR radical signal and concentration of radicals was confirmed. With this relationship found, an initial test was done to confirm radicals in thermally treated wood (vide supra Chapter 3.3). This allowed the direction to see if there was a correlation of wood thermal treatment temperature and EPR radical signal.

To study this, more in-depth tests were done to get to that final goal. Utilizing a TGA analyzer allowed accurate control of the temperature and atmosphere of thermally treating wood. By using TGA and measuring EPR radical content of the thermally treated wood samples, it helped find and confirm that fresh wood not store-bought wood needed to be used for tests because of the kiln drying process of commercially bought wood (vide supra Chapter 4.2). In utilizing both the TGA analyzer and an in-house kiln to thermally treat wood and

analyzing their EPR radical signals area, a few key discoveries were made. These discoveries include the importance of sample size (vide supra Chapter 4.3, 4.4), proper data calculations (vide supra Chapter 4.5), desiccating to equilibrate samples (vide supra Chapter 4.6), and accounting for unwanted background signal (vide supra Chapter 4.5). In additional studies, It was confirmed that moisture attenuates EPR radical signal. It was also found that it attenuates signal with a correlation to how high the moisture content is (vide supra Chapter 5.2).

The main goal of this project was to be able to measure heat treatment of wood by the use of EPR. The thermal treatment of wood was performed utilizing two methods for different advantages; first the TGA analyzer for the advantage of temperature, atmosphere, and weight measurement accuracy and control (vide supra Chapter 5.3), and second the in-house oven kiln for the advantage of a higher sample yield, and a closer representation of industry (vide supra Chapter 5.4). A positive correlation to thermal treatment temperature and EPR radical signal area was found in both treatment methods. With that confirmation, repeats of both methods where done to get statistics on the reproducibility of the experiments (vide supra Chapter 5.5). The experiments were proven to be reproducible. With the statistical reproducibility, the positive correlation between thermal treatment temperature and EPR radical signal area was supported.

Future studies focus around additional places to explore or questions that arose during this project. From the beginning, the want was to find a radical standard that resembles the radical found in wood with one EPR peak. It was

not found in DPPH and TEMPO, but it was speculated that a manganese radical standard could provide a signal that is able to be used for quantification and comparison. Finding the manganese radical standard having a similar single EPR peak will allow for direct radical comparison and radical quantification of thermally treated wood radicals. Further studies would also be done to narrow down exactly where the radical is forming. Cellulose and lignin should be studied using TGA, EPR, and pyrolysis GC-MS to study the decomposition and possible radical formation during thermal treatment. Regarding precision of EPR measurements, the exploration of EPR cavity temperature (at time of scan) and how it effects the EPR data is a future goal. A collaboration with Vim Williams of Firmolin that started looking to analytically account for moisture for an EPR measurement in any sample will be continued. Lastly, a statistical test will be done on the EPR rate formation study for reproducibility.

Bibliography:

1. Woodford, C. Wood. Explain That Stuff [Online], 2010. https://www.explainthatstuff.com/wood.html#:~:text=Hardwoods%20have%20lovely%2C%20attractive%20grains,poles%2C%20and%20so%20on). (accessed Dec 7, 2020).
2. Wood/Timber/Lumber as a construction material. Understand construction[Online]. http://www.understandconstruction.com/wood.html#:~:text=types%20of%20WOOD&text=Hardwoods%20are%20commonly%20used%20in,cherry%2C%20walnut%2C%20and%20teak. (accessed Dec 7, 2020).
3. Kohler, M.; Lecomte, C. Dec 31, 2013. Lumber choices for wood framed construction - Choosing Timber For Framing and Building homes. Ecohome [Online], Oct 5, 2020. Walls and Roofs. https://www.ecohome.net/guides/2283/best-material-choices-for-wood-frame-construction/ (accessed Dec 7, 2020).
4. Toxic Substances Portal – Creosote; Public Health statement for Creosote, 2002. Agency for Toxic Substances and Disease Registry (ATSDR). https://www.atsdr.cdc.gov/phs/phs.asp?id=64&tid=18 (accessed Dec 7, 2020).
5. Kazmi, M.Z.H; Karmakar, A.; Michaelis, V.K.; Williams, F.J. Separation of cellulose/hemicellulose from lignin in white pine sawdust using boron trihalide reagents. Tetrahedron 2019, Elsevier Volume 75, Issue 11, 1465-1470.
6. Gamache, S.; Espinoza, O. Marketing Strategy Recommendations for the U.S. Thermally Modified Wood Industry; The Forest Products Management Development Institute (FPMDI): Saint Paul, Minnesota, Sep 12, 2017; 1-53.
7. Horvat, A. A study of the uncertainty associated with tar measurement and an investigation of tar evolution and composition during the air-blown fluidised

bed gasification of torrefied and non-torrefied grassy biomass, 2016. ResearchGate. https://www.researchgate.net/figure/3-Structure-of-lignocellulosic-biomass-with-cellulose-hemicellulose-and-lignin_fig3_321075806 (accessed Dec 7, 2020).

8. Donahue, P.; Aro, M. Progress Report: Using Thermal Modification Technology to Add Value to Small-Diameter Logs; NRRI/TR-2018/07; USDA Wood Education and Resource Center: Duluth, Minnesota, March, 2018; 1-159.
9. ThermoWood, 2003. Kansilehti Kuvilla. https://asiakas.kotisivukone.com/files/en.thermowood.palvelee.fi/downloads/tw_handbook_080813.pdf (accessed Dec 7, 2020).
10. Beall, FC.;, Eickner, HW. Thermal Degradation of Wood components: a review of the literature. USDA 1970, FPL 130, 1-27.
11. Gamache, SL.; Espinoza, O.; Laguarda-Mallo, MF. Professional Consumer Perceptions of Thermally-Modified Wood; Forest Products Management Development Institute; University of Minnesota: Saint Paul, Minnesota, Spring 2017; 1-3.
12. Wilson, D.R.; Villines, Z. How do free radicals affect the body? MNT [Online] 2017, https://www.medicalnewstoday.com/articles/318652 (accessed Dec 7, 2020).
13. Lobo, V.; Patil, V.; Phatak, A.; Chandra, N. Free radicals, antioxidants and functional foods: impact on human health. Pharmacognosy reviews 2010, 4(8), 118-126.
14. Eaton. GR.; Eaton, SS.; Barr, DP.; Weber, RT. Quantitative EPR; SpringerWienNewYork: New York, 2010.
15. Thermogravimetric Analysis (TGA): A Beginner's Guide, 2010. PerkinElmer. https://www.perkinelmer.com/lab-solutions/resources/docs/faq_beginners-guide-to-thermogravimetric-analysis_009380c_01.pdf (accessed Dec 7, 2020).

16. Rietz, RC.; Robertson, EA. The Kiln Drying of Wood. Moisture in Materials in Relation to Fire Tests. ASTM international 1965, STP 385, 38-51.
17. Zasada, JC.; Phipps, HM. Populus balsamifera L. Balsam Poplar. USDA [Oniline],Volume 2. https://srs.fs.usda.gov/pubs/misc/ag_654/volume_2/populus/balsamifera.htm (accessed Dec 7, 2020).
18. Apiezon H Grease, M & I Materials. Apiezon. https://apiezon.com/products/vacuum-greases/apiezon-h-grease/ (accessed Dec 7, 2020).
19. 1,1-Diphenyl-2-picrylhyrdazy Free Radical, 2020. TCI Chemicals. https://www.tcichemicals.com/AU/en/p/D4313 (accessed Dec 23, 2020).
20. 4-Hydroxy-TEMPO, 2020. Sigma Aldrich. https://www.sigmaaldrich.com/catalog/substance/4hydroxytempo17224222696211?lang=en&region=US (accessed Dec 23,2020).
21. Barriga, S. 2,2,6,6- Tetramethylpiperidin-1-oxyl (TEMPO). Synlett [Online] 2001, Spotlight 28, No.4, 563. https://www.thieme-connect.de/products/ejournals/pdf/10.1055/s-2001-12332.pdf (accessed Dec 7, 2020).
22. D4442-20 Standard Test Methods for Direct Moisture Content Measurement of Wood and Wood-based Materials, 2020. ASTM International. https://compass.astm.org/EDIT/html_annot.cgi?D4442+20#s00014 (accessed Dec 7, 2020).
23. Bergman, R. Drying and Control of Moisture content and Dimensional Changes. General Technical Report FPL-GTR-190, Ch13; 1-20.
24. Dietenberger, M.A.; Hasburgh, L.E. Wood Products: Thermal Degradation and Fire. Reference Module in Materials Science and Materials Engineering. Elsevier 2016.
25. Hyde, J.S.; Sidabras, J.W.; Mett, R.R. Uniform Field Resonators for EPR Spectroscopy: A review. Cell Biochem Biophys 2019, 77, 3-14.

26. EPR User Service Training Course, Bruker Biospin. iastate. https://www.cif.iastate.edu/sites/default/files/uploads/EPR/Resonators.pdf (accessed Dec 7, 2020).
27. Coleman, D.; Vanatta, L. Statistics in Analytical Chemistry: part 40-Blanks. CNI [Online] 2010. https://www.americanlaboratory.com/914-Application-Notes/1114-Part-40-Blanks/ (accessed Dec 7, 2020).
28. Burns, D.T.; Flockhart, B.D.; Application of Quantitative EPR [and Discussion]. The Royal Society, Philosophical Transactions: Physical Sciences and Engineering (1990), 333(1628), 37-48.
29. Microwave Oven Radiation, Dec 12, 2017. Food and drug Association (FDA), The division of Industry and Consumer Education (DICE). https://www.fda.gov/radiation-emitting-products/resources-you-radiation-emitting-products/microwave-oven-radiation (accessed Dec 7, 2020).
30. Laurenzi, T. How to Measure the Moisture Content of Wood for DIY Projects, May 15, 2018. Delmhorst instrument CO. https://www.delmhorst.com/blog/measure-the-moisture-diy-projects#:~:text=To%20use%20a%20pin%2Dtype,the%20resistance%20to%20the%20current. (accessed Dec 7, 2020).
31. Desiccant Chart Comparisons, 2006. Sorbent Systems. https://www.sorbentsystems.com/desiccants_charts.html (accessed Dec 7, 2020).
32. Hammond, W.A. Drierite Desiccants. https://secure.drierite.com/catalog3/page3.cfm?activeMenu=0 (accessed Dec 7, 2020).
33. Militz, H.; Altgen, M. Processes and Properties of Thermally Modified Wood Manufactured in Europe. Deterioration and Protection of Sustainable Biomaterials ACS symposium Series; American Chemical Society 2014, Ch.16, pg 269-285.
34. Militz H. 2014. Processes and Properties of Thermally Modified Wood Manufactured in Europe. Development of Commercial Wood

Preservatives ACS symposium Series; American Chemical Society, Ch.22, pg 372-388.

35. Brischke, C. 5 - Timber. Long-term Performance and Durability of Masonry Structures, Woodhead publishing 2019; 129-168.
36. Altgen, M.; Willems, W.; Militz, H. Wood degradation affected by process conditions during thermal modification of European beech in a high-pressure reactor system. Eur J. Wood Springer Nature 2016, Prod. 74, 653-662.
37. Ali, Z.; Bhaskar, S.B. Basic Statistical tools in research and data analysis. Indian journal of anaesthesia 2016, 60(9), 662-669.
38. Levine, I.N. Physical chemistry. 4th ed; McGraw-Hill: New York, 1995. Ch9, 1-9.3.
39. Shaikh, S.H.; Kumar, S.A. Polyhydroxamic acid functionalized sorbent for effective removal of chromium from ground water and chromic acid cleaning bath. Chemical Engineering Journal 2017, 326, 318-328.