Novel Relative Spontaneous Ignition Temperature Determination Using Carbon Dioxide Onset with STA/IR

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NOVEL RELATIVE SPONTANEOUS IGNITION TEMPERATURE DETERMINATION USING CARBON DIOXIDE ONSET WITH STA/IR

By

ANTONIO D. TREVINO, Bachelor of Science in Chemistry

Presented to the Faculty of the Graduate School of Stephen F. Austin State University
In Partial Fulfillment
Of the Requirements

For the Degree of Master of Science in Natural Science

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NOVEL RELATIVE SPONTANEOUS IGNITION TEMPERATURE DETERMINATION USING CARBON DIOXIDE ONSET WITH STA/IR

By

ANTONIO DAVID TREVINO, Bachelor of Science in Chemistry

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Abstract

Simultaneous thermal analysis, coupled with infrared spectroscopy (STA/IR), was utilized to monitor the evolution of gaseous products during the thermal degradation of samples from *Triadica sebifera* (Chinese tallow), *Ligustrum sinense* (Chinese privet), and *Ilex vomitoria* (yaupon) plants. Identification of carbon dioxide was successful with a spectral match of 90.2 percent and further used in the determination of relative spontaneous ignition temperature, or RSIT. The RSIT value during the growing season for Chinese tallow, Chinese tallow stem, Chinese privet, and Yaupon were 208.4°C, 250.3°C, 210.1°C, and 232.3°C respectively. During the dormant seasons, the values for Chinese tallow stem, Chinese privet, and yaupon were 227.4°C, 211.8°C, and 237.8°C respectively. The most ignitable plant samples were determined to be Chinese tallow stem, yaupon leaves, Chinese privet leaves, and the least ignitable was Chinese tallow leaves during the growing season. The dormant season samples ignitability rankings were as follows; yaupon, Chinese tallow stem, and Chinese privet leaves. Although other peaks were present in the IR spectra obtained from the samples, the identification of peaks other than carbon dioxide was unsuccessful due to low signal to noise ratios.
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I would like to thank my friends and family for understanding my limitations and forgiving me for not being able to be with them and socialize during times that I needed to work.

Last, but certainly not least, I want to give my most sincere gratitude and appreciation to my wife, Kelsey, for her endless love, support, and patience. Without you, I would be lost. I love you.
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<tr>
<td>STA/IR</td>
<td>Simultaneous Thermal Analysis/Infrared Spectroscopy</td>
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<tr>
<td>RSIT</td>
<td>Relative Spontaneous Ignition Temperature</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compounds</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas Chromatography/Mass Spectroscopy</td>
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<tr>
<td>min</td>
<td>minute</td>
</tr>
<tr>
<td>NFE</td>
<td>Nitrogen Free Extracts</td>
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<tr>
<td>mg</td>
<td>milligram</td>
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<tr>
<td>g</td>
<td>gram</td>
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<td>w/w</td>
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<td>TG-MS</td>
<td>Thermogravimetry/Mass Spectroscopy</td>
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<td>Quadrupole Mass Spectrometer</td>
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<td>Differential Thermal Analysis</td>
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<tr>
<td>m/z</td>
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<tr>
<td>IDT</td>
<td>Initial Degradation Temperature</td>
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<tr>
<td>FDT</td>
<td>Final Degradation Temperature</td>
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<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
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<td>Abbreviation</td>
<td>Description</td>
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<td>-------------</td>
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<td>K</td>
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<tr>
<td>ASTM</td>
<td>American Society for Testing Materials</td>
</tr>
<tr>
<td>IT</td>
<td>relative self-Ignition Temperature</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier Transform</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic Aromatic Hydrocarbons</td>
</tr>
<tr>
<td>WUI</td>
<td>Wildlife Urban Interface</td>
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<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>NIH</td>
<td>National Institutes of Health</td>
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<tr>
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<td>Stephen F. Austin State University</td>
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<tr>
<td>STD DEV</td>
<td>Standard Deviation</td>
</tr>
<tr>
<td>RSD</td>
<td>Relative Standard Deviation</td>
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<tr>
<td>MCT</td>
<td>Mercuric Cadmium Telluride</td>
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CHAPTER 1: Introduction and Objectives

Introduction

The initial step in wildland fires is the heating of forest fuels called preignition. Dehydration and volatilization constitute the series of endothermic reactions during preignition. Volatile organic compounds (VOCs), such as terpenoid hydrocarbons and phenol derivatives, volatilize at low temperatures. The evolution of these compounds from organic plant matter can increase the flammability of forest fuels during wildland fires. Terpenes, fats, oils, and waxes present in the forest fuel constitute other VOCs that can increase forest fuel flammability.\(^1\)\(^-\)\(^3\) Individual components of plant matter, such as cellulose, hemicellulose, and lignin, have been separately analyzed using simultaneous thermal analysis coupled with infrared spectroscopy (STA-IR) to determine their thermal degradation patterns and monitor volatilization products with heating.\(^4\)\(^-\)\(^6\) However, monitoring the volatilization of VOCs in whole plant matter samples with STA-IR has not been accomplished with *Ilex vomitoria*, *Ligustrum sinense*, and *Triadica sebifera*, known as yaupon, Chinese privet, and Chinese tallow respectively. Yaupon has been determined as a highly flammable invasive native plant in the southern United States.\(^7\) Furthermore, the ability to predict the impact and scope of a wildfire is limited due to the great variability of fire behavior in different plant communities due to the variance in biodiversity and biomass.\(^8\)
During the 2011 Texas wildfire season, nearly four million acres of land burned. The fires in Texas accounted for 47% of all land burned in the U.S. in 2011. The extent and intensity of the 2011 Texas wildfires were driven by record-setting drought conditions, unusually dry and strong winds from La Niña, and Northwest Pacific troughs that swept across the southern portion of the United States. The rainfall between October 2010 and November of 2011 was 11.18 inches, the lowest twelve-month rainfall period in state history. The previous twelve-month rainfall period record of 14.8 inches was set in 1956. Additionally, 2010 had good rainfall that resulted in lush growth. The lush growth year, followed by the state’s worst drought, made conditions that favored extreme wildfires (Figure 1).

**Figure 1.** Rainfall during Summer 2010 with respect to each states’ annual rainfall, in which Texas received above normal rainfall.
The composition of the growth has changed dramatically in the past 30 years when fuel load parameters were originally determined for East Texas.\textsuperscript{13} Chinese privet and Chinese tallow have been declared invasive exotic species of East Texas. Yaupon has replaced much of the open savannah rangeland of Texas, and is considered a native invasive plant species due to its proliferation in the Post Oak Savannah ecoregion.\textsuperscript{14} These plants often out-compete native non-invasive plants and decrease the biodiversity of plant species in East Texas forest and rangeland ecosystems.\textsuperscript{15}

Due to high spatial and temporal variability of fuel conditions in the southeastern United States, course-scale assessment tools may not be sufficient to mitigate fire hazard assessment.\textsuperscript{16} This necessitates the need for updating specific fuel load parameters for East Texas, Blackland Prairie, and the Post Oak Savannah ecoregions, with particular concern for the proliferation of native and exotic plant species that have resulted from altered management techniques.\textsuperscript{17, 18}

To make accurate wildfire predictions, many topographical and forestry/rangeland ecological parameters need to be taken into consideration. Factors such as slope, biodiversity, fuel loading, canopy and understory fuel loads, and fuel moisture can all play roles in the spread and intensity of a wildfire.\textsuperscript{19} Fuel load parameters and forest fuel mapping are some of the biggest contributors when trying to predict wildfires. In-field determination of understory fuel loading parameters is one of the most effective methods for determining the potential for understory fires to gain a vertical component sufficient to create crown fires, or canopy fires. The original 13 fuel models are sufficient for
predicting fire intensity and spread rate at the peak of the fire season, but there is a need for improving the accuracy of fire behavior predictions outside of the severe period of the fire season, increasing the number of fuel models for forest litter and litter with grass or shrub understory, and increasing the number of fuel models for high-humidity areas. These are components that can be better determined by observations made at the site of study under field work conditions. The necessity of determining fuel loading parameters brings about the need to understand plant biodiversity and plant biomass in an ecoregion being studied.

The plants described above have drastically changed the landscape of understory growth in the southeastern region of the United States, and consequently, the understory fuel loads and biomass that are available for wildfires. Along with this, the urbanization of these regions has resulted in growth of the Wildland Urban Interface, WUI, an area in which urban development encroaches on forest ecosystems, that increases the risk of property damage, property loss, and potentially risks human and animal life. For these reasons, a study that determines the temporal variability in chemical composition of the Chinese privet, Chinese tallow, and yaupon species would be beneficial for utilization in wildfire predictive software, especially considering that these plants have become increasingly abundant and shifted the biodiversity typically found in East Texas, Blackland Prairie, and Post Oak Savannah ecoregions.
Objectives

The over-arching goal for this research was to obtain quantitative analyses of yaupon, Chinese privet, and Chinese tallow by observing their seasonal fluctuations in relative spontaneous ignition temperatures. The specific objectives were to:

(1) Determine if Simultaneous Thermal Analysis/Infrared Spectroscopy (STA/IR) is a valid technique for monitoring evolved gaseous products during combustion conditions (air) of the target species.
   a. Identify compounds produced under combustion conditions with STA/IR and compare plant analysis for the growing and dormant seasons to determine temporal variations.

(2) Determine Relative Spontaneous Ignition Temperature, RSIT, for the target species during both the dormant and growing seasons using a new CO$_2$(g) onset peak from the IR coupled with the heating time frame and mass loss of the STA.
CHAPTER 2: Literature Review

Extractions from plant material, such as the Chinese privet seeds, have been analyzed with gas chromatography/mass spectroscopy (GC-MS) to isolate and identify volatile compounds present in the plant species. In this study, it was concluded that mature seeds for the Chinese privet produced higher proportions of oxygenated cyclic alkenes, such as cyclopentenones, and alkyl pyridines, when compared to the immature seeds (Figure 2). It was determined that the seasonal, or temporal, variation in chemical composition impacts the yield of their hydrothermal treated products. From the analysis, they concluded that the timing, seasonally, in which the feedstock was collected to be used would need to be considered to maximize the usefulness of the hydrothermal products. Some of the hydrothermal products are processed into a solid fuel for energy use. Other fractions of the hydrothermal products are used as liquid fertilizer, or livestock feed.

![Chemical structures](image)

**Figure 2.** Common volatile products found in mature Chinese privet seed extractions using GC-MS (cyclopentenone left, pyridine right). Drawn using ChemDraw®
A study by Eberhardt et al. confirmed the seasonal/temporal variations in chemical composition of Chinese privet seeds. Additional research to determine if other chemical compound variations occur in the leaves of this species temporally is therefore justified. Studies of the Chinese privet and its temporal variation of thermochemical properties have recently been studied in respect to its leaves and stems.\textsuperscript{17}

In Tillers’ study, a comparison between yaupon, Chinese tallow, and Chinese privet was completed to compare the dormant and growing season of each plant species against the other species. It was concluded that yaupon, out of the target species, was the highest ranking in growing season ignitability, and second in overall combustibility with a gas phase combustion rate of 4.42 % mass/min, compared to only 3.58 % mass/min for Chinese privet, and only 3.32 % mass/min for Chinese tallow. Ignitability can be determined using a characteristic called Relative Spontaneous Ignition Temperature, RSIT, which is the lowest temperature required for a material to ignite without a flame source. It was determined that yaupon had a significant drop in ignitability in the dormant season with a change of RSIT of 178.33°C during the growing season and only 162.52°C during the dormant season. Chinese privet and Chinese tallow had much less significant variations in RSIT during the growing and dormant seasons; Chinese privet RSIT values were 155.35°C during the growing season, and 150.15°C during the dormant season. Chinese tallow’s RSIT values were 144.25°C during the growing season, and no dormant season data is available because this plant does not retain its leaves during the dormant season. This suggests that yaupon undergoes a significant chemical composition variation
during the growing and dormant seasons that impact its’ ignitability. Other results were that Chinese privet was low in overall ignitability and that Chinese Tallow was the lowest in overall ignitability and combustibility in the study.\textsuperscript{17}

Temporal chemical composition variation is not an uncommon characteristic of plants as they develop and grow. As plants shift from the growing season to the dormant season, many plants undergo a vegetative development change. During this dormant/vegetative state, the plants biochemistry shift to better suit the changing conditions.\textsuperscript{17, 23, 24} Nutrition-focused research on temporal chemical composition variations have been analyzed in species such as the Saltbrush, \textit{Atriplex halimus}. In Saltbrush, it was determined that Nitrogen Free Extracts (NFE) as well as crude protein and phosphorus levels showed a strong correlation of variation between the growing and dormant seasons.\textsuperscript{24} In the growing season, levels of NFE, crude protein, phosphorus, and calcium had higher concentrations than when compared to the samples analyzed in the dry season. Crude protein was determined to be 22.7\% higher during the growing season, compared to 15\% during the dry season. NFE followed the same trend, with 44\% at the peak of the growing season and 35\% during the dry season. The results suggested Saltbrush as an alternative feedstock for sheep in the rangelands of Jordan during the dry season, even though nutritive content was temporally affected. The nutritive content of Saltbrush did reduce during the dry season, but much less than the 75\% crude protein and 52\% phosphorus loss that was typical of previous feedstocks of wheat and barley.
residues. It was proven that the chemical composition of even more plant species can vary greatly during the growing and dormant seasons relative to the plant.

During wildfires, endothermic reactions occur in a process called preignition, in which the fuel is heated, dehydration occurs, and organic compounds are volatilized, sometimes called volatile organic compounds, or VOCs. Compounds, such as terpenoid hydrocarbons volatilize at low temperatures. Pyrolysis of forest fuels happens at higher temperatures, where the substance breaks down into low molecular weight gases, hydrocarbons, and mineral ash.¹ Temporal variations in chemical composition can result in alternative values for the heat of combustion of invasive plant species, which can drastically affect the predicted path, intensity, and duration of wildfires.²⁵ A 1998 study of Juniperus ashei focused on seasonal variations between the gross heat content with bomb calorimetry and the monoterpenoid content, or volatile oil content with GC comparison of retention time with known external standards. Analysis concluded that monoterpenoid content, specifically limonene, could increase plant flammability by up to 30 %, with monoterpenoid and volatile oil content being highest in the winter and spring, 17.3 mg/g (volatile oil/sample mass), and lowest in the summer and fall 7.9 mg/g.²⁶ The presence of bornyl acetate had a negative correlation to overall plant flammability by decreasing the flammability of the plant by up to 10%. The relationship between plant flammability and bornyl acetate concentration was determined to be a 2% reduction in plant flammability per 1mg/g (bornyl acetate/sample mass).
Non-nutrition based studies, in which terpene and essential oil chemical composition variation was analyzed, showed a correlation in amount produced versus the growing or dormant/vegetative cycles in *Pelargonium species*.\(^{27}\) Samples at the peak of the growing season, had 1.2\% higher essential oil and terpene content than their counterparts during the dormant/vegetative season. The essential oil/terpene content is a significant difference considering the average essential oil/terpene content of the species is only 1.8\% by mass. Essential oil/terpene extraction chemical composition was also determined using GC-MS to determine that over 65 compounds were present, with the major constituents being menthol, menthene, and α-pinene. All were present in higher amounts during the growing season than in the dormant season. Menthols’ peak area percentage was determined to be 23.43 during the growing season, compared to only 15.80 during the dormant season. A similar study can be extended to Chinese privet, Chinese tallow, and yaupon to experimentally determine chemical composition variations that occur in the dormant versus growing season with GC-MS.

Chinese tallow seeds’ oil content has been studied using GC-MS, but the Yang et al. study focused on the volatile oil quantification for use as a bio-material to produce an alternative fuel source, in the form of biodiesel, using only the seeds. The study did not include temporal variations in the volatile oil quantification of Chinese tallow seeds. Chinese tallow seeds were analyzed because this plants’ seeds are a non-edible, but high fatty acid containing seed, so biodiesel production would not impact food sectors.\(^{28,29}\) A comparison between two different extraction methods in extracting oil from Chinese
tallow seeds were compared. Conventional Soxhlet extraction was the more effective oil extraction method when compared to solventless super-critical CO\textsubscript{2} extraction. Soxhlet extraction had a yield of about 81\% w/w compared to only 46\% w/w with the super-critical CO\textsubscript{2} extraction method.

Chinese tallow GC-MS analysis resulted in the confirmation of flavonoids such as kaempferol, hyperin, and rutin. Also, triterpenoids of Chinese tallow were confirmed as lupeol, moretenol, and sebiferone. Phenolics found in Chinese tallow were ethyl and methyl gallate, xanthoxylin, and cinnamic acid. The presence of triterpenoids such as amyrin and lupeol and other compounds such as kaempferol, phenol, limonene, pinene, ocimene, linalool, and squalene have been confirmed in both yaupon and Chinese privet\textsuperscript{30-33} However, there was no comparison between the dormant and growing season chemical composition of these plants in any of the studies.

Thermogravimetry coupled with mass spectroscopy analysis, TG-MS, on the effects of flame retardants on thermal decomposition of wood resulted in successful differentiation of volatile products from the thermal degradation of wood treated with three different flame retardants\textsuperscript{34} K\textsubscript{2}CO\textsubscript{3}, Na\textsubscript{2}SiO\textsubscript{3}·9 H\textsubscript{2}O, and Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7}·10H\textsubscript{2}O flame retardants were treated onto samples of Chinese poplar, \textit{Populus adenopoda}, a common building lumber in Eastern China. The application of the flame retardants was accomplished by soaking the wood samples in aqueous solutions of various concentrations of 1, 5, 10, and 20\% by mass.
Qu, et al. used a Netzsch Co. STA 449 C-QMS 403C to perform analysis on the variously treated wood samples. In a pure argon environment, samples were heated from ambient room temperature to 800°C at 10 °C/min with a gas flow rate of 10 mL/min. The connection between the thermobalance and the mass spectrometer was a quartzose capillary maintained at 200°C. TG, DTG, and DTA analyses were run under the same temperature range with a heating rate of 20 °C/min in air with a gas flow rate of 60 mL/min. TG-MS analysis led to the confirmation that typical cellulose degradation can take place through two competing pathways, which typically occur in the temperature range of 250-400°C. The first pathway is that of dehydration of cellulose that typically leads to char and gaseous products such as CO, CO₂, and H₂O (m/z = 28, 44, and 18 respectively). The second competing pathway is through a depolymerization process in which tar, various volatiles, and levoglucosan/levoglucosenone formation occurs. Common MS signal peaks attributed to this depolymerization process are m/z = 60 and 68. During this research, products of both competing pathways were successfully identified in TG-MS analysis.35-37

Results suggested that the boron containing flame retardant was an extremely effective flame retardant to use for wood due to the formation of a glassy protective B₂O₃ layer on the surface of the wood samples. This protective glassy layer accounted for the majority of the increase in the initial degradation temperature, IDT, when compared to untreated wood samples as seen in TG analyses.38 The other two flame retardants decreased this IDT value significantly. The Na₂SiO₃·9 H₂O reduced the IDT from the
untreated wood IDT value of 245°C to 225°C. The K₂CO₃ IDT value was shifted even more drastically to 202°C. The most useful information from this research involves the parameters at which the STA and the MS are set at. These are useful parameters that can be tested and applied to this thesis. Other useful information involves the breakdown of the thermograms into four distinct sections. In Qu, W. et al., the first mass loss is attributed to water and falls within the range of ambient room temperature and 100°C. The second stage, ranging from 200°C to 350°C, corresponds to the decomposition of hemicellulose and cellulose. The decomposition products produced are typically char residues, CO, CO₂, CH₄, CH₃OH, and CH₃COOH. It has been reported that during this second stage, as temperature increases, the TG curve accelerates, and this is a key attribute in the combustibility of the target sample.¹ It is suggested that the third stage, 353°C to 428°C, is the home of less stable aliphatic groups that are thermally decomposed via homolytic cleavages of C—C and C—H bonds. This stage tends to be much slower in mass loss rates and produces a highly condensed cross-linked carbonaceous material. Finally, the fourth stage, 428°C to 679°C, is mostly attributed to the oxidation of char residue.⁴ Stability of the char residue improved, as shown by the increased final degradation temperature, FDT, and the decrease in the peak mass loss. Results are indicative of improved flame retardancy of treated wood samples, but this may also relate to flammability characteristics of plant materials when comparing different species.³⁴
Other articles breakdown the thermograms of thermal degradation for plant material differently. For example, Leroy et al. reports that the temperature range between 100°C and 200°C is related to non-combustible products such as carbon dioxide, water vapor, and traces of organic compounds being evolved from the thermal degradation of forest fuels. This temperature range is not discussed in the work by Qu et al. but is discussed in detail by many others.41-45 They also report that at temperatures above 500°C, all of the volatiles are gone and that what remains is oxidized char that is left as glowing combustion.40,46 Leroy et al. also reported the general composition of wood as being a complex organic material with 38-50% cellulose in leafy trees, 23-30% lignin, 19-26% hemicellulose, less than 15% extractives, and less than 1% ashes, water, and mineral matter.40,47,48 Furthermore, they explain that chemical composition variation can be a factor of not only species, but also within individual plants due to the differences in botanical origin, age, and location within the plants itself, that chemical composition varies within the same plant between the trunk, roots, branches, and crown segments. Their research made a critical assumption, in which the overall heat content and thermal behavior of the whole fuel can be represented accurately by the principal components that make up the fuel, i.e., lignin, cellulose, and hemicellulose.40,49-51 The overall purpose of their research was to create a thermal model in which the fuel and its components’ reaction enthalpy of thermal degradation can be accurately represented using DSC, Differential Scanning Calorimetry. This may give insight for future work in which extractions of the principal components of the plant material, mainly cellulose, lignin,
and hemicellulose, can be studied independently with STA-IR analysis. Separation of the components may simplify the IR spectra that results from the evolution of gaseous products during thermal degradation of plant material. Leroy et al. used a Soxhlet extraction method with dichloromethane over the course of six hours followed by washing with distilled water and oven-dried.\textsuperscript{52} The lignin is obtained through a sulphuric acid attack, called a “Klason” content, in which the lignin is acid insoluble and can easily be separated from the other two principal components.\textsuperscript{53} The left over cellulose and hemicellulose, called holocellulose as a mixture, can then by separated by workup with sodium chlorite in acetate buffer, a process called delignification and subsequent treatment with sodium hydroxide.\textsuperscript{54, 55} Due to the similar structure of hemicellulose and cellulose, their separation is not feasible. Instead, the proportions and the thermograms are deducted from the difference between the holocellulose and cellulose to determine their overall contributions and individual proportions.

The operating conditions were a temperature range of 400-900K in air, gas flow of 30 mL/min and a heating rate of 20°C/min in an aluminum crucible. The choice in operating parameters were influenced by the reproducibility of results and were chosen after optimization of deviations to make them as small as possible. The importance of noting their operating conditions lies in comparing the Leroy et al. study to the study by Qu et al. Even with similar overarching goals, their operating conditions varied greatly. This suggests that there is not a set of operating parameters that is sufficient for any and
all types of STA/TG analysis, but that they can differ based on a combination of external factors that must be optimized for targeted results.\textsuperscript{34,40}

Leroy et al. had an accepted error of 2-3\% on the experimental values of enthalpy. It was determined that lignin was the most energetic constituent of the three principal constituents studied, followed by hemicellulose, and finally cellulose. Their enthalpy values were: lignin- 16,278 J/g, holocellulose- 10,565 J/g, and cellulose- 6,935 J/g. The lignin enthalpy value was even higher than that of the whole fuel itself, which was only 11,410 J/g of sample. They ultimately concluded that the sum of the principal constituents was sufficient in modeling the whole fuel itself given two stipulations: 1) the enthalpies of each constituent were constant; and 2) a complex mixture of extractives, containing waxes, tannins, essential oils, and coloring agents would also need to be considered. The extractives were determined to be in low proportions compared to the other principal constituents, but were shown to have high enthalpy values, although these values are never stated within the article.

Relative spontaneous ignition temperature, or RSIT, in relation to thermal characteristics of plants is one that has been reported infrequently across most literature, except by Liodakis et al.\textsuperscript{56} They define relative spontaneous ignition temperature as the minimum temperature required for flaming to develop spontaneously within the flammable vapor-air mixture without an ignition source.\textsuperscript{57} They also refer to articles that have proposed ignition temperature determination in laboratory-scale called pulse ignition test.\textsuperscript{58} The most common determination test is known as the Setchkin ignition
test which is based on the lowest initial temperature of air passing around the specimen at which sufficient amount of combustible gas is evolved to be ignited in the presence or absence of an external pilot flame. This protocol is specific to plastic materials and involves a sort of trial and error approach to determining the spontaneous ignition temperature. The protocol sets the air velocity to 25 mm/s in a hot-air ignition furnace with specific locations for thermocouples, sample pan, and air influx hoses/pipes (Figure 3). The set protocol for determining the spontaneous ignition temperature is to start at 400°C and hold for 10 minutes and determine if any ignition has occurred. If no ignition has occurred, the temperature is to be increased by 50°C until an ignition is observed. Once this is seen, the temperature is lowered by 10°C increments and repeated until no observable ignition has occurred on fresh samples each time. The lowest temperature in which ignition is observed is the spontaneous ignition temperature.

Liodakis et al. had an objective of developing a simple method for evaluation of the relative flammability and heat content properties of forest species. Furthermore, the main purpose of the study was to find the relative fire hazard properties of common forest species in the target area and to rank them into categories. Samples were collected and dried in a vacuum oven for 24 hours at a pressure of 10 torr and a temperature of 60 °C. They ran samples in a custom-built apparatus that was designed according to 79/831 European Commission Directive, which also resembles the apparatus used described in ASTM method D 1929-96.
Figure 3. Hot-air furnace used in ASTM method D 1929-96 for plastic relative spontaneous ignition temperature determination, specifically called the Setchkin ignition test.59

Liodakis et al. (2005) set parameters of 0.5 °C/min from ambient room temperature to 500 °C. The apparatus operated in atmospheric air and did not require an external supply of air, therefore there was no gas flow parameters that were required
during the study. The relative self-ignition temperature was defined as the oven temperature at which the sample temperature reaches 400°C (Figure 4). This value is not referenced to any particular literature and its choice appears to be ambiguous until the ASTM standard test method is considered. The ASTM standard test method for determining ignition temperature only used 400°C as a starting point and altered this temperature until the correct spontaneous ignition temperature was pinpointed in a trial-and-error type methodology.

![Figure 4. Liodakis RSIT value determination from a temperature profile using the temperature of the oven when the sample reaches 400°C.](image)

The 400°C temperature point is used to determine the relative self-ignition temperature of all six target plant species as it is defined, though only two are shown (Figure 5). Regardless of the point at which the sample temperature slope is seen to
quickly increase due to self-ignition and subsequent runaway exothermic reactions of combustion, the relative self-ignition temperature, has no relation to this sudden increase in sample temperature which instinctively seems to be the starting point of combustion.

![Figure 5. RSIT determination by Liodakis using oven temperature, sample temperature, and 400°C temperature line for Pinus brutia and Pinus halepensis. As sample temperature reaches 400°C, the recorded oven temperature is determined as the RSIT.](image)

Looking closely at the sample temperature curve, it is observed that the IT value, which represents the relative self-ignition temperature, is solely determined by the 400°C temperature line. The sudden increase in the slope of the sample temperature line is indicative of an exothermic reaction occurring from the plant material spontaneously
igniting. However, the point at which the IT is determined does not correlate at the same point in which this sudden slope increase occurs between the two different species seen in Figure 5. For *Pinus brutia*, it appears that the IT point is just below the point at which the sample temperature suddenly increases in slope. In contrast, the sample for *Pinus halepensis* has the IT point very clearly just past the sudden increase in slope, with the only obvious conclusion being that IT is determined from the 400°C mark. This number seems arbitrary without any literature reference or any explanation as to why this temperature point was chosen, but the ramifications of this choice appear to be very influential on the results obtained from the experiment. It was determined, through the aforementioned method, that the highest RSIT value determined was that of *Pinus brutia* at a temperature of 242°C and the lowest being *Pistacia lentiscus* at a temperature of 222°C. This experiment does provide insight to RSIT values that may be reasonable, however, the determination method used is not one that will be considered or used in this research.

When Simultaneous Thermal Analysis (STA) is coupled with Fourier Transform Infrared Spectroscopy (FT-IR), the products that are generated from volatilization and thermal decomposition in the STA can be identified. The identification of VOCs is useful to determine what compounds may be increasing plant material flammability. Volatile compounds can contain secondary chemicals with even higher heats of combustion and increased volatility that can increase the fuel flammability of certain species of plants.³ Fuel moisture content can also be determined from STA and when coupled with FT-IR,
the products of combustion, under oxidative (air) and pyrolysis (N₂) conditions, can be identified. Not only can these byproducts increase fuel flammability, but they can also be harmful to forest management personnel and firefighters. Possible byproduct formation includes compounds such as Polycyclic Aromatic Hydrocarbons (PAHs), sulfur oxides, nitrogen oxides, aldehydes, and other irritating, harmful, and potentially carcinogenic volatile organic compounds. This conjugated technique of analysis is typically used for thermal degradation pathways and mechanisms for pure compounds. For example, a sample of PVC, polyvinyl chloride, was analyzed during its thermal degradation pathway. The main thermal degradation pathway observed with PVC is the evolution of HCl(g), or hydrogen chloride. It was confirmed that the evolution could be tracked reliably due to the strong IR absorber of HCl(g). The article also suggests that other molecules that are also strong IR absorbers, like carbon dioxide and carbon monoxide, aid the characterization of thermal degradation pathways with TG-FTIR techniques more completely that that of TG alone.
CHAPTER 3: Justification and Methodology

Justification

Nearly four million acres of urban and wildlife forest suffered from the 2011 Texas wildfires, and nearly 5,600 homes and other structures were destroyed. Firefighters from over forty states traveled to Texas to help combat the raging wildfires. The wildfires would cost over $510 million dollars in insured damages.⁹

The damages also affected timber production and other crops in the state of Texas. The drought that year had already cost Texas nearly $3.2 billion from livestock losses alone. Cotton crops suffered with losses as high as $2.2 billion, and corn and hay production losses accrued nearly $750 million each. These figures were only made worse by the wildfires that would sweep across the state that and recovery of these agricultural industries was slow.⁹

Coupled with the conditions outlined by the Texas Forest Service, 94 % of the land in Texas is privately owned, meaning that land owners are free to manage their land as they see fit. With this privatization of land comes the potential increase of woody vegetation, changes in commercial crop production, vegetation overgrowth around communities, and residents living in and around previously rural areas.⁹ These factors impact wildfire occurrence and intensity and the growth of the wildlife urban interface (WUI), only makes matters worse. The WUI is the area in which heavily
populated urban areas encroach on natural wildlife and forested areas. It is at these junctions that a wildfire can have detrimental effects on urbanized environments that are heavily developed with public housing and economic centers. It is estimated that as much as 41 percent of Texas’s population lives in an area deemed as WUI.9

The fire models that are used to predict the behavior of wildfires in southeast Texas forest ecosystems are not sufficient to account for the temporal and spatial variability seen in present day ecosystems. In addition, current fuel models, based on the Rothermal fuel models, are not effective when considering periods of time other than the peak of the dry season, areas of fuel litter with grass or shrub understory, or high humidity areas.20 Since then, the understory plant composition has changed with the influx of exotic invasive species of plants.17 These invasive and exotic species yaupon, Chinese tallow, and Chinese privet, have proliferated throughout the East Texas area and were originally introduced as ornamental plants. However, the wildfire models have yet to be updated and proper wildfire prediction and wildfire management practices cannot be implemented accurately without updated fuel load data.13, 16, 17, 20

Analysis on the evolution of VOCs on yaupon, Chinese privet, and Chinese tallow will yield information about the mechanism of pyrolysis and combustion of the plant material with STA-IR. Analysis of these species using STA-IR to determine VOC and pyrolysis/combustion product formation have not been completed. Furthermore, with previous studies already showing temporal variation in yaupons’ thermokinetic data utilizing bomb calorimetry, the analysis of temporal chemical composition variation in
Chinese tallow and Chinese privet make for a good comparison as they are also invasive plant species prevalent in the southeastern United States and were also included in previous thermokinetic studies of yaupon.\textsuperscript{17}

Chemical composition variation temporally will be determined using GC-MS, which has not been completed in any of the target plant species leaves. This study will focus only on the foliage, or leaves, and VOC content will be assessed during the growth and dormant seasons. The temporal comparison will serve to compliment previous findings of temporal thermokinetic variation.\textsuperscript{17}
Methodology

Sample Collection:

A total of 35 samples were collected, prepared, and provided by Michael B. Tiller, Ph.D. candidate from the Arthur Temple College of Forestry and Agriculture, at Stephen F. Austin State University. Of the 35 samples, 15 samples were from the dormant season and 20 samples were from the growing season. For the dormant season, five separate samples were collected for each of the target species foliage of Chinese privet and yaupon, as well as five separate samples of stems for Chinese tallow since there are no dormant season leaves. Of the 20 samples collected for the growing season, five separate foliage samples were collected for Chinese tallow, Chinese privet, and yaupon, as well as five separate samples of Chinese tallow stems. Samples of yaupon, Chinese tallow, and Chinese were collected during two different seasons from the Texas A&M University Equine Center, classified as the Post Oak Savannah ecoregion (Figure 6) with the intention of determining if variations in chemical composition existed. All samples were collected in paper bags until they were transferred to the Arthur Temple College of Forestry and Agriculture Forestry lab, where initial open-air drying was completed to limit mold growth until samples were prepared for mesh screening. All trials for each sample were run in triplicate, with individual runs referenced as subsamples.
Figure 6. Satellite image of Texas A&M University Equine center, location of sample collection highlighted in red and Brazos County location in Texas provided by Esri, USGS, accessed Aug 2017.
**Sample Preparation:**

All samples, except for the Chinese tallow stems, were screened for moldy leaves and separated from the rest of the usable sample by hand. This process was not necessary for the Chinese tallow stem samples. A Wiley mill was utilized to reduce the Chinese tallow stems to arbitrary particle sizes which were screened with various sized mesh screens exactly like that of the foliage samples.

For foliage samples, liquid nitrogen was used to cryogenically and mechanically disrupt the foliage samples in a steel container with a metal spatula. Next, the frozen foliage samples were transferred to a General Electric single serve blender, Model #898695. The blender cup had small venting holes drilled in the top of it to prevent nitrogen gas buildup. The transfer of sample from the steel container to the blender cup was accomplished quickly to prevent thawing of sample. Quick transfer resulted in the transfer of small amounts of liquid nitrogen, hence the necessity for small venting holes. Once the foliage samples were blended, they were placed into small, labeled paper bags for the low temperature drying process. The Chinese tallow stems followed the same process as the foliage samples after they were ground with a Wiley mill. The drying process was done at 40 °C for 6-8 hours utilizing an air-convection oven until dry mass is stabilized. This temperature was chosen to avoid the loss of volatile compounds from high heat exposure and prevent the disruption of hygroscopic hemicellulose compounds present in the samples.\textsuperscript{73} Samples were then screened using various sized mesh screens. Mesh size No. 35 (0.500 mm) diameter screened samples were used in all analysis due to
the ease of loading samples into the platinum crucible, reproducibility of RSIT values at various heating rates, and high peak intensity relative to mass of sample from IR.

**Simultaneous Thermal Analysis/Infrared Spectroscopy (STA/IR):**

A Perkin Elmer simultaneous thermal analyzer 6000 was calibrated to manufacturer specifications by performance verification using calcium oxalate at a heating rate of 20°C/minute with nitrogen purge gas as is recommended by manufacturer specifications. Temperature calibration was completed using indium and silver reference metals.

**STA/IR Parameter Optimization**

The STA/IR coupled technique requires a gas flow from the STA and a separate pump flow from the pump control module. The gas flow from the STA provides the atmospheric environment during the heating of the sample being studied. The pump flow from the pump control module pulls the evolved gases from the STA, through the Silicosteel™ transfer line, into the gaseous IR cell, and through the waste gas line at the end of the diaphragm pump. The gas flow rate between the STA and the pump control module was optimized which resulted in maximized IR spectrum intensities, increased sensitivity of the IR, and improved detection/identification of small amounts of evolved gases. To determine the optimized gas flow settings, plant material from a randomly chosen sample of the 25 foliage samples were analyzed with settings of STA/Pump flow rates, respectively, of; 10/50 mL/min; 25/50 mL/min; 35/25 mL/min; 50/25 mL/min; 50/50 mL/min; and 100/50 mL/min. For optimization trials, growing season yaupon
sample #2 was used and analyzed in triplicate. The mass of sample used was typically maximized for the platinum crucible used in the STA, ~40-65 mg of the yaupon test plant material. Due to the variance in the sample loading mass, a ratio of IR peak intensity, or max absorbance against sample mass was calculated to determine the optimum gas flow parameters between the STA/IR coupled technique. The peak selected for this ratio comparison was the asymmetric stretching vibration peak for carbon dioxide around 2350 cm$^{-1}$, which is prevalent in the IR spectrum for plant materials at high temperatures, starting from ~200°C and continuing until the maximum temperature of 650°C.

The heating/ramp rate optimization was conducted using a randomly chosen sample out of the 25 foliage samples, and was growing season yaupon sample #1. Preliminary analysis used 11 different heating rates of 10, 20, 30, 40, 50, 75, 100, 125, 150, 175, and 200 ºC/minute and concluded that a heating rate of 50ºC/minute resulted in higher peak intensities for gaseous IR when compared to the IR spectra obtained under other lower heating rates but also maintained a high level of separation between the gas phase and solid phase combustion stages.

**STA/IR Data Collection**

All 35 blended/ground and dried samples were individually placed in a platinum crucible with sample masses ranging from ~40-65 mg and ran in triplicate. The variation in sample mass was highly dependent on how well the sample packed without excessive pressing and pushing with external tools, such as a cotton swab, and ultimately analyzed with a heating ramp of 50ºC/minute starting at 35 ºC and ending at 650 ºC in air. The
byproducts of oxidative combustion of plant species was analyzed with the Perkin Elmer Spectrum One FT-IR Spectrometer to identify volatile and gaseous products. Compounds such as volatiles that are evolved during different ramping periods of thermal degradation and combustion of plant samples can be observed during different heating stages. A heated Silicosteel™ tube (300°C) was used to transfer the evolved gaseous products from the STA to the heated gaseous IR cell (250°C). Spectra was compared to NIST vapor phase IR database for compound identification.

Gas Chromatography Mass Spectroscopy:

Analysis with a Varian 450 GC/Varian 240 MS instrument was performed using two different solvents for extraction: benzene/ethanol and diethyl ether due to the reported high yield of volatile compounds extracted from plant samples. An Agilent J&W VF-5ms capillary column, 5% phenyl-methyl, was used with the GC-MS. Different solvent systems were used to ensure extraction of different compounds, both polar and non-polar. A split/split-less method was utilized as the injection method. High resolution chromatographic profiles were obtained and compared to NIST/EPA/NIH mass spectral library profiles and identified with Nicolet/Aldrich vapor phase databases.

The identification of products of combustion using STA/IR is the first objective of this research. Additional analysis, such as GC/MS, was used to aid in the identification process in addition to the IR spectra obtained using STA/IR. The second objective was determination of the RSIT values of the target plant species during both the growing and dormant seasons accomplished solely utilizing STA/IR technique.
CHAPTER 4: Results and Discussion

Gas Flow Optimization:

Initial tests were completed to determine the optimum gas flow rates between the STA and IR to elicit the maximum IR response with a randomly choses sample. The gas flow parameters tested are suggested general operating parameters, parameters noted in the literature, and parameters presented by Perkin Elmer research technicians during a Perkin Elmer symposium in Houston Texas on November 2\textsuperscript{nd} 2017. Trials were run in triplicate of yaupon sample #2, that is the mean of three subsamples or trials. The first number represents the gas flow rate into the STA in mL/min and the second number is the gas flow rate from the pump control module of the IR in mL/min (Table 1).

Table 1. Mean signal to mass ratios of various gas flow parameters for optimization of IR peak for CO\textsubscript{2} for yaupon growing season foliage sample #2.

<table>
<thead>
<tr>
<th>Gas Flow STA/IR (mL/min)</th>
<th>10/50</th>
<th>25/50</th>
<th>50/50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Signal at 2350 (cm\textsuperscript{-1})</td>
<td>0.44987</td>
<td>0.39715</td>
<td>0.34354</td>
</tr>
<tr>
<td>Sample Mass (mg)</td>
<td>46.754</td>
<td>41.513</td>
<td>43.101</td>
</tr>
<tr>
<td>Signal/Mass Ratio</td>
<td>0.0096221</td>
<td>0.0095669</td>
<td>0.0079706</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Gas Flow STA/IR (mL/min)</th>
<th>35/25</th>
<th>50/25</th>
<th>100/50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Signal at 2350 (cm\textsuperscript{-1})</td>
<td>0.40053</td>
<td>0.37610</td>
<td>0.35422</td>
</tr>
<tr>
<td>Sample Mass (mg)</td>
<td>45.527</td>
<td>41.192</td>
<td>44.538</td>
</tr>
<tr>
<td>Signal/Mass Ratio</td>
<td>0.0087976</td>
<td>0.0091304</td>
<td>0.0079532</td>
</tr>
</tbody>
</table>

32
The gas flow rate chosen was 10 mL/min at the STA and 50 mL/min at the pump module/IR. This set of gas flow parameters gives the highest overall signal to mass ratio. It consistently generated the highest signal, but also the highest signal to mass ratio. This may be due to the negative pressure created with this set of parameters in which the STA pump is only pushing out 10 mL/min but the IR pump module is vacuuming out at a rate of 50 mL/min, creating a negative pressure and pulling the evolved gases from the STA through the transfer line and through the IR and out through the pump. The worst signal/mass ratio was seen at 100 mL/min at the STA and 50 mL/min at the pump. This may be due to evolved gases being pushed out of the STA venting hole due to the high positive pressure of gas flow generated from the STA while connected to the transfer line and IR. With essentially double the volume flow out to the transfer line, only half of the volume of evolved gases and flow gas are able to make it through to the transfer line through to the IR. The rest of the evolved gases are pushed out of the vent hole at the STA end due to the positive pressure.

This theory is partly supported by the signal/mass ratios (Table 1), as the 10/50 and 25/50 negative pressure trials have the highest signal/mass ratios. However, they are not consistent in that the 50/25 positive pressure also shows a high signal/mass ratio. For the objective of RSIT determination utilizing the onset of CO₂ gas evolution from the thermal degradation of the plant species, the working gas flow parameters were chosen to be 10/50 mL/min (STA/IR).
**Heating/Ramp Rate Optimization:**

The heating rate optimization was determined by observing the highest IR absorbance at 2350 cm\(^{-1}\), a common peak for CO\(_2\), as well as observing the preignition mass loss as a percentage of sample mass from a randomly chosen sample of the 25 different foliage subsamples. Higher preignition mass loss means a greater amount of moisture and preignition volatiles are evolved prior to combustion. The end of the preignition mass loss curve plays a role in the onset of combustion, so separation between these two phases is important and can be increased by slower heating/ramp rates. A heating rate that is too fast will see a lot of overlap between the mass loss of the preignition stage and the exothermic ignition and subsequent combustion of gas phase molecules.

Figure 7 depicts the separated preignition mass loss portion (orange arrows) and the subsequent gas phase combustion mass loss portion (green arrows) of the thermogram along with the derivative curve (red) used to mark the end of preignition mass loss and the beginning of gas phase combustion process mass loss at 50°C/min. The derivative values are all negative due to the mass loss curve that it is based upon. The peak on the derivative mass loss curve separates the preignition mass loss from the gas phase combustion mass loss. As the preignition mass loss curve begins to slow down, less and less water and preignition volatiles are coming off until it hits a peak, representing the lowest mass loss rate. The points immediately following this peak are the increasing mass loss rates due to gas phase combustion processes. The minimum of the derivative
curve is the fastest mass loss rate that is observed during thermal degradation of the plant sample.

\[ \Delta Y = 9.034\% \]

Figure 7. Thermogram of mass loss/derivative curve with preignition and gas phase combustion phases at 50°C/min. Mass loss curve in blue, and derivative of mass loss curve in red. Also shown in the mass loss percentage from the beginning of sample heating until the onset of gas phase combustion, indicated by black line.

Figure 8 represents the same sample, but run at a heating rate of 150°C/min. With a heating rate this high, it was observed that the separation between preignition and gas phase combustion is difficult. There is an overlap between water and volatiles being evolved and the beginning of gas phase combustion processes. The observation is seen in the jumpy mass loss curve and derivative curve. Furthermore, to optimize the separation
of the preignition stage and the gas phase combustion phase, the mass loss percentage
during the preignition stage needs to be maximized.

Figure 8. Mass loss curve in blue with derivative curve in red of yaupon at 150°C/min.
Also shown is the mass loss percentage, which is significantly less than the same sample
of yaupon ran at a slower ramp rate.

Heating Rate and IR Response Optimization:

A slower heating rate allows for sufficient evolution of water and other volatiles
during the preignition stage of thermal degradation. Fast heating rates, as shown in Table
2, often results in less mass loss percentage during the preignition stage and an overlap in
the first two stages of thermal degradation. As the heating rate increases, there is a very
clear increase in absorbance maximum across every heating rate increase. However, there
is a slight deviation of the expected mass loss percentage for the heating rates of 10-50°C/min. In this range, the mass loss of the preignition stage fluctuates up and down, but higher heating rates see a large shift in decreasing mass loss of the preignition stage. The mass loss percentage of the preignition stage increases generally until the point of 50°C/min while having a moderate IR peak intensity.

Therefore, a more moderate heating rate of 50°C/min is ideal to maintain the separation of mass loss percentage between the two stages of preignition and gas phase combustion while providing a high IR peak intensity. A compromise is made between maximizing the IR response at 2350 cm\(^{-1}\) and maintaining a separation between the first two stages of thermal degradation. In terms of parameters, this means a moderate heating/ramp rate is required.

<table>
<thead>
<tr>
<th>Heating Rate (°C/min)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbance at 2350 cm(^{-1})</td>
<td>0.05850</td>
<td>0.08219</td>
<td>0.10947</td>
<td>0.12495</td>
<td>0.16430</td>
</tr>
<tr>
<td>Preignition Mass Loss (%)</td>
<td>7.164</td>
<td>6.982</td>
<td>7.156</td>
<td>7.200</td>
<td>7.388</td>
</tr>
</tbody>
</table>

Table 2. Relation of heating rate, absorbance, and preignition mass loss of growing season yaupon foliage sample #1, values shown are the mean value of all three subsamples

<table>
<thead>
<tr>
<th>Heating Rate (°C/min)</th>
<th>75</th>
<th>100</th>
<th>125</th>
<th>150</th>
<th>175</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbance at 2350 cm(^{-1})</td>
<td>0.23147</td>
<td>0.25340</td>
<td>0.30680</td>
<td>0.33713</td>
<td>0.40493</td>
<td>0.44093</td>
</tr>
</tbody>
</table>
Figure 9 shows the IR spectrum for gaseous carbon dioxide from the NIST/EPA vapor phase database. This sample has a partial pressure of 200 mmHg of CO$_2$ diluted to a total pressure of 600 mmHg with pure Nitrogen gas. Due to these different instrument parameters during collection of spectrum, SpectrumOne database matching software would often result in poor match results between 70-80%. To alleviate this issue, a spectrum of CO$_2$ was obtained using calcium oxalate, a standard used in TGA/IR. Calcium oxalate is used as a standard for TGA/IR because it has very well defined and distinct thermal degradation patterns.

![Infrared Spectrum](image)

**Figure 9.** Gas phase IR spectrum from NIST database, provided by Coblentz Society, peaks of interest are at 2350 cm$^{-1}$ and 650-700 cm$^{-1}$.

These patterns include initial evolution of water, subsequent evolution of carbon monoxide, CO, and finally, evolution of carbon dioxide, CO$_2$ as seen in the reaction given.
The IR spectrum generated from this experiment showed a much better match score from SpectrumOne software of around 90.2%. Figure 10 shows the comparison between the CO\textsubscript{2} IR spectrum profile typically generated from the thermal decomposition of calcium oxalate and a sample of Chinese tallow from sample #3. The IR spectrum from Chinese tallow is a typical IR response and is shown as a general representation of the IR spectrum observed during analysis. This comparison is important because it shows the comparison with spectra generated from instrumentation that is used for the entirety of the research. Using the CO\textsubscript{2} IR spectra from NIST database would result in poor spectrum match scores, and unexplained differences between the spectrum generated from the plant sample and that of the NIST IR spectrum (Figure 9).

\[ \text{Overall Reaction: } \text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O} \rightarrow \text{CaO} + \text{H}_2\text{O} + \text{CO} + \text{CO}_2 \]

1) \[ \text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O} \]

2) \[ \text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO} \]

3) \[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]
Figure 10. IR spectrum comparison between CO$_2$ generation from calcium oxalate standard and Chinese tallow sample using instrumentation at SFASU Department of Chemistry and Biochemistry. Important similarities at 2350 cm$^{-1}$ and 650-700 cm$^{-1}$ which are the same peaks from the NIST database IR spectrum for CO$_2$(g) as seen in Figure 9.

The two spectra in Figure 10 show many similarities, such as the intense, sharp peak at around 2350 cm$^{-1}$. The only difference between the two spectra at this specific asymmetric stretching vibration is the intensity of the peak. This peak is also observed in the NIST vapor phase IR spectrum for CO$_2$. Another similar peak, at around 650-700 cm$^{-1}$, is also present in all three of the spectrums, further confirmation that CO$_2$ is indeed the compound identified in the spectra. However, there are some key differences between the calcium oxalate spectra and the Chinese tallow spectra in Figure 10. One of these differences is the peak signature at 3600 and 3700 cm$^{-1}$. At these points, there are a lot of small peaks from both samples that make these two spectra look very different. Looking at Figure 9, it is apparent that there should be distinct, but small peaks for CO$_2$. However,
in Figure 10, this region is very distorted, even for the calcium oxalate CO$_2$ IR spectra. Some of the distortion in this region could be due to water. A recent Perkin Elmer publication has shown IR spectra that is observed during the thermal degradation of calcium oxalate monohydrate (Figure 11).$^{77}$

![Figure 11. IR spectra, top to bottom: H$_2$O(g), CO(g), and CO$_2$(g) during thermal degradation of calcium oxalate as it is heated from room temperature to 950°C. Initially, water is evolved, followed by carbon monoxide, and finally carbon dioxide.](image)

If atmospheric water makes its way to the IR, this distortion would be evident in the region from 3500 to 4000 cm$^{-1}$ where water shows many sharp intense peaks as seen in Figure 11. In Nacogdoches, Texas, where all experiments were conducted, a high level of humidity is a common occurrence. Desiccant packs are placed periodically in a certain location in the IR instrument to help absorb this natural atmospheric moisture. However, due to the high level of atmospheric humidity, these desiccant packs may have become
saturated, rendering them ineffective at removing atmospheric moisture. This could have led to water vapor contaminating the gaseous thermal degradation products, and distorting the IR spectra in the aforementioned region during the experiments. Also, a peak that is observed in the calcium oxalate CO$_2$ IR and Chinese tallow IR spectrums but not in the NIST CO$_2$ spectrum is at around 1050 cm$^{-1}$.

Numerous sources have determined this peak is also indicative of CO$_2$. It is unknown why the NIST vapor phase IR spectra for CO$_2$ does not have this peak, whereas other literature sources have reported this peak. One difference is the environment in which the spectra were obtained is different. The NIST spectra was done with a diluted CO$_2$ sample in a nitrogen atmosphere, whereas the other sources were done, and theoretically calculated, in atmospheric conditions. Regardless, the very sharp indicative peak at 2350 cm$^{-1}$ was used as a diagnostic peak for the beginning of combustion reactions and the sample temperature at this point was determined to be the RSIT.

Despite these differences, and evidence of additional products on the spectra, the spectral match was 90.2 percent for CO$_2$. The small, broad peaks for the Chinese tallow sample at 2900 and 1700 cm$^{-1}$ may represent other byproducts of combustion, but spectral analysis matching data resulted in extremely poor matches of cyanoacetic acid and carbon dioxide again, both of which were well below 50 percent matching. After confirming the initial carbon dioxide peaks and subtracting these peaks away, what is left is a spectrum that has many very small peaks that are indistinguishable. A spectrum taken from any time during the IR spectrum timeline has a lot of noise. The reason for this noise is the accumulation
of the data itself. The IR spectra must be collected in a quick manner, at a scan speed of 0.20 cm/s and a resolution of 32.00 cm\(^{-1}\). The scan speed allows for a full spectral analysis to be obtained about every 0.90 seconds. This allows monitoring of evolved gaseous products on a second-to-second basis. The drawback to this is a lot of noise in the spectra that rapidly shifts on a second-to-second basis, with only large intense peaks very clearly observed. Other, small, less intense peaks can be lost in the noise or be overwhelmed when spectral matching software analyses the spectrum. These small peaks often generate poor matches from the spectral matching software, sometimes as low as 30 percent, but usually never over 60 percent. For this reason, the peak at 2350 cm\(^{-1}\) was used due to its ideal sharp and intense peak during IR spectral collection. Figure 12 shows the onset of the CO\(_2\) peak at various times throughout the analysis of a typical sample of Chinese tallow. As the program temperature increases at a rate of 50°C/min, the evolution of the CO\(_2\) peak is observed as early as 346.41 seconds (s). As the sample temperature increases, the peak intensity increases, as does other peak associated with CO\(_2\), such as at 650 cm\(^{-1}\). Also, the other peaks at 1700 and 2900 cm\(^{-1}\) are also seen to increase proportionally to the diagnostic peak at 2350 cm\(^{-1}\).
Calcium Oxalate (CO₂) Compared to Chinese tallow Growing Foliage Sample 2, Subsample 1, at Various Times

![IR spectra graph]

**Figure 12.** IR monitoring of Chinese tallow growing foliage sample 2, subsample 1, at multiple points between its heating from 35-400°C.

 Certain regions of the IR spectra are inherently filled with noise, and this complicates peak identification in those regions and also spectral matching software. However, the peak at 2350 cm⁻¹ is in a region where the noise is exceptionally low and peak identification with spectral matching software such as SpectrumOne sufficiently identifies a spectrum with high match success of over 90 percent.

Figure 13 depicts a Gram-Schmidt plot (red) in comparison to the mass loss curve (blue) from the thermogram of the same sample. A Gram-Schmidt plot graphically represents the total amount of absorbance occurring at any time during IR spectra collection. The initial mass loss of water and low amounts of volatiles is initially so low, that little is shown on the Gram-Schmidt plot except for noise, as indicated by the jagged total absorbance curve from 0-380 seconds. Once the temperature increases to the RSIT,
the mass loss curve decreases greatly due to the initiation of combustion. Consequently, the combustion results in a large increase in evolved gaseous products that is observed in the increase in total absorbance of the Gram-Schmidt profile.

![Graph of Growing privet Foliage Sample 4, Subsample 3 Mass Loss vs. Gram-Schmidt Profile](image)

**Figure 13.** Gram-Schmidt profile (red) from TimeBase software of sample 4, subsample 3, of Chinese privet growing foliage compared to its mass loss curve (blue) from Pyris software. The correlation between the significant mass loss and overall IR response is observed by the decreasing blue curve and simultaneous increase of the red curve.

It can be seen that the Gram-Schmidt profile decreases as the time exceeds 500 seconds. At this point, the majority of cellulose and hemicellulose have decomposed, and the remaining lignin is beginning to undergo thermal degradation as well. Lignin thermal degradation occurs at much higher temperatures than that of cellulose and hemicellulose. It is observed in Figure 14, where a second phase of
combustion is observed after the preignition mass loss phase and the gas phase combustion mass loss phase (red circle).

Figure 14. Mass loss curve (blue) with mass loss derivative (red) of Chinese privet foliage sample 5 subsample 1 from 35-650°C. Red circle indicates high temperature lignin decomposition beginning overlapping with the end of gas phase combustion.

The derivative mass loss curve in Figure 14 changes at around 475°C. This temperature is very high for the beginning of lignin thermal decomposition which has been reported to begin around 280°C and reach its maximum rate at a temperature range of 350-450°C.\textsuperscript{46,82,83} Instead of marking the beginning of thermal degradation of lignin, which may have been covered up by the cellulose and hemicellulose mass loss portion,
this could mark the point of which the main component degrading switches from cellulose/hemicellulose to lignin.

The sample in Figure 14 was run at a higher temperature range, 35-650°C, in initial testing experiments. When it was determined that RSIT occurs at a much lower temperature, this range was decreased to a maximum temperature of 400°C to shorten the run time of samples. The change in maximum temperature also reduced the amount of char and oily residue which made cleaning of the platinum crucible and transfer line much easier.

**RSIT Determination from CO₂ IR Peak Onset:**

Relative self-ignition temperature, or relative spontaneous ignition temperature, is the lowest temperature a substance requires to initiate ignition without an external flame source. This ignition is the beginning of combustion reactions that leads to runaway heating of the sample through exothermic reactions of combustion. One of the major components of combustion is carbon dioxide. As a sample is heated, it gradually evolves gases. Initially, water moisture is evolved along with low concentrations of volatiles. Once the RSIT temperature is reached, carbon dioxide is evolved from the sample and this evolution can be monitored with continuous real-time IR spectra. When a small peak is observed at 2350 cm⁻¹, such as the blue spectra in Figure 12, the time that this occurs is recorded. This time can be referenced in Pyris software to then determine the sample temperature at the time that the IR spectra confirmed the presence of CO₂ and therefore confirmed the beginning of combustion, Figure 15.
Figure 15. Sample temperature of 211.15°C determined in Pyris software with observed time of CO$_2$ onset of 5.829 minutes from IR spectrum from TimeBase software of Chinese privet foliage growing sample 3 subsample 2.

Table 3 shows the RSIT results from all samples of yaupon from samples 1-5 during the growing season. The mean of all 15 subsamples have been determined to give the Overall Average, Overall Standard Deviation (STD.DEV), and the Overall Relative Standard Deviation (RSD).
Table 3. RSIT, CO₂ onset time, and mass loss % for yaupon foliage growing season samples 1-5 with respective subsamples. Included are the overall average, standard deviation, and relative standard deviations.

<table>
<thead>
<tr>
<th>Yaupon 1 G Leaves</th>
<th>CO₂ onset (s)</th>
<th>IR RSIT est. (°C)</th>
<th>Mass loss %</th>
<th>Yaupon 4 G Leaves</th>
<th>CO₂ onset (s)</th>
<th>IR RSIT est. (°C)</th>
<th>Mass loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subsample 1</td>
<td>380.72</td>
<td>247.32</td>
<td>8.847</td>
<td>Subsample 1</td>
<td>357.01</td>
<td>224.59</td>
<td>8.505</td>
</tr>
<tr>
<td>Subsample 2</td>
<td>375.25</td>
<td>240.21</td>
<td>9.129</td>
<td>Subsample 2</td>
<td>364.95</td>
<td>230.82</td>
<td>8.621</td>
</tr>
<tr>
<td>Subsample 3</td>
<td>365.28</td>
<td>229.63</td>
<td>9.062</td>
<td>Subsample 3</td>
<td>365.05</td>
<td>232.04</td>
<td>8.595</td>
</tr>
<tr>
<td>Average</td>
<td>373.75</td>
<td>239.05</td>
<td>9.0127</td>
<td>Average</td>
<td>362.337</td>
<td>229.15</td>
<td>8.5737</td>
</tr>
<tr>
<td>STD.DEV</td>
<td>7.8285</td>
<td>8.902</td>
<td>0.14733</td>
<td>STD.DEV</td>
<td>4.6133</td>
<td>3.996</td>
<td>0.06087</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>2.0946</td>
<td>3.724</td>
<td>1.6347</td>
<td>RSD (%)</td>
<td>1.2732</td>
<td>1.744</td>
<td>0.71</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Yaupon 2 G Leaves</th>
<th>CO₂ onset (s)</th>
<th>IR RSIT est. (°C)</th>
<th>Mass loss %</th>
<th>Yaupon 5 G Leaves</th>
<th>CO₂ onset (s)</th>
<th>IR RSIT est. (°C)</th>
<th>Mass loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subsample 1</td>
<td>356.25</td>
<td>218.49</td>
<td>8.297</td>
<td>Subsample 1</td>
<td>365.89</td>
<td>233.94</td>
<td>8.724</td>
</tr>
<tr>
<td>Subsample 2</td>
<td>355.08</td>
<td>218.78</td>
<td>8.386</td>
<td>Subsample 2</td>
<td>366.13</td>
<td>235.03</td>
<td>8.669</td>
</tr>
<tr>
<td>Subsample 3</td>
<td>366.88</td>
<td>229.63</td>
<td>8.252</td>
<td>Subsample 3</td>
<td>365.97</td>
<td>233.99</td>
<td>8.717</td>
</tr>
<tr>
<td>Average</td>
<td>359.403</td>
<td>222.29</td>
<td>8.312</td>
<td>Average</td>
<td>365.997</td>
<td>234.32</td>
<td>8.7033</td>
</tr>
<tr>
<td>STD.DEV</td>
<td>6.5014</td>
<td>6.332</td>
<td>0.0682</td>
<td>STD.DEV</td>
<td>0.1222</td>
<td>0.615</td>
<td>0.02994</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>1.8089</td>
<td>2.849</td>
<td>0.82</td>
<td>RSD (%)</td>
<td>0.03339</td>
<td>0.263</td>
<td>0.344</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Yaupon 3 G Leaves</th>
<th>CO₂ onset (s)</th>
<th>IR RSIT est. (°C)</th>
<th>Mass loss %</th>
<th>Yaupon G Leaves Overall</th>
<th>CO₂ onset (s)</th>
<th>IR RSIT est. (°C)</th>
<th>Mass loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subsample 1</td>
<td>366.83</td>
<td>233.87</td>
<td>8.387</td>
<td>Overall Average</td>
<td>366.031</td>
<td>232.269</td>
<td>8.583</td>
</tr>
<tr>
<td>Subsample 2</td>
<td>364.31</td>
<td>232.25</td>
<td>8.304</td>
<td>Overall STD.DEV</td>
<td>6.9833</td>
<td>7.9203</td>
<td>0.28168</td>
</tr>
<tr>
<td>Subsample 3</td>
<td>374.86</td>
<td>243.48</td>
<td>8.254</td>
<td>Overall RSD (%)</td>
<td>1.9078</td>
<td>3.41</td>
<td>3.28198</td>
</tr>
<tr>
<td>Average</td>
<td>368.667</td>
<td>236.533</td>
<td>8.312</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STD.DEV</td>
<td>5.5096</td>
<td>6.0703</td>
<td>0.0713</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Most of the samples had RSIT values for all 3 subsamples that were fairly close to each other, as evidenced by the low standard deviation and relative standard deviations for samples four and five, RSD of ~0.6 and 1.7%. Samples one through three had higher deviations with RSD values ranging from 2.6 - 3.7%. The deviations are expected to be substantial due to the use of natural product analysis, but deviations presented in this research are fairly low. Other literature sources have published on the energy content and ignition temperature of natural products, specifically plant material, with an acceptable percent error of over three percent. The overall RSD for all fifteen subsamples, across all five samples, was ~3.4% for yaupon during the growing season. This would seem to be an acceptable RSD, but there is no percent error calculation possible because there is no literature accepted value for the RSIT of any of these plant species. The RSIT value for yaupon leaves during the growing season was determined to be 232.3°C with an overall preignition stage mass loss of 8.583%. Out of all three species, yaupon had the highest RSIT value and also the highest preignition stage mass loss. The correlation between the high RSIT value and the high mass loss during the preignition stage could be a high amount of preignition volatiles that make yaupon more flammable overall. Higher proportions of volatiles could lead to yaupon being more ignitable, as this is justified in the high RSIT temperature. In literature, it has been stated that high RSIT values often correlate to have low pilot ignition temperatures. This means that when a flame source is available, a substance with high RSIT temperature will tend to have a lower pilot ignition
temperature, making said substance a more ignitable fuel and burn more easily by flame.\textsuperscript{56, 85, 86}

Table 4 contains the overall results for growing season Chinese privet, Chinese tallow, and also Chinese tallow stem. Chinese tallow does not have leaves during the dormant season, so for a comparison between dormant and growing season, the stem was also analyzed.

Table 4. Growing season Chinese privet foliage and Chinese tallow foliage/stem overall RSIT, time to ignition, and mass loss of samples 1-5.

<table>
<thead>
<tr>
<th></th>
<th>CO2 onset (s)</th>
<th>IR RSIT est. (°C)</th>
<th>Mass loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Privet G Leaves</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Overall Average</td>
<td>347.213</td>
<td>210.057</td>
<td>6.226</td>
</tr>
<tr>
<td>Overall STD.DEV.</td>
<td>7.9350</td>
<td>7.6838</td>
<td>0.3340</td>
</tr>
<tr>
<td>Overall RSD (%)</td>
<td>2.2853</td>
<td>3.6579</td>
<td>5.364</td>
</tr>
<tr>
<td><strong>Tallow G Leaves</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Overall Average</td>
<td>341.008</td>
<td>208.399</td>
<td>7.841</td>
</tr>
<tr>
<td>Overall STD.DEV.</td>
<td>3.9354</td>
<td>5.3239</td>
<td>0.5132</td>
</tr>
<tr>
<td>Overall RSD (%)</td>
<td>1.1540</td>
<td>2.5547</td>
<td>6.546</td>
</tr>
<tr>
<td><strong>Tallow G Stem</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Overall Average</td>
<td>375.856</td>
<td>250.281</td>
<td>8.346</td>
</tr>
<tr>
<td>Overall STD.DEV.</td>
<td>2.7115</td>
<td>2.7595</td>
<td>0.3150</td>
</tr>
<tr>
<td>Overall RSD (%)</td>
<td>0.72141</td>
<td>1.1206</td>
<td>3.774</td>
</tr>
</tbody>
</table>
Following yaupon, Chinese privet is the next most ignitable plant species with an RSIT of 210.1°C. Finally, Chinese tallow leaves are the least ignitable plant species of the three target species with an RSIT of 208.4°C. This ranking is the same that was observed in Tiller’s work, albeit much different values due to a different method of RSIT determination with different working parameters. The RSD values of these three sample groups were either similar or better than those observed with the yaupon data set.¹⁷

Chinese tallow stem showed a very high RSIT value, even higher than that of yaupon, with an RSIT of 250.3°C. The woody stem of Chinese tallow has high ignitability characteristics in contrast with that of its leaves that have the lowest ignitability out of the three target species. This is the same conclusion that Tiller presented in his research.¹⁷ When observing the mass loss during preignition of Chinese privet and tallow (excluding stem), the higher RSIT Chinese privet, albeit not by much, has substantially less volatiles lost during this phase of thermal degradation. This may discredit the correlation between mass loss during preignition phases and plant ignitability. However, it may be a result of the difference in composition of the preignition mass loss. If the preignition mass loss composition between two different species is less water and more volatiles, such as essential oils, waxes, and terpenoids, then one species may have significantly higher ignitability and flammability characteristics even with the same mass loss percentage during the preignition stage.¹³,²⁶,²⁷,⁴⁰ This may warrant further studies and additional types of analysis, such as GC-MS to identify these preignition volatiles.
Table 5 includes all species analyzed during the dormant seasons, which include Chinese tallow stem, Chinese privet, and yaupon. Observed here is that yaupon maintains the highest RSIT value and overall mass loss percentage, although its mass loss percentage has dropped from 8.6 to 7.7 percent. This is not surprising as literature has reported that terpenoid content alone may change as much as 1.2 percent from 0.6 to 1.8 percent from the dormant to the growing season, respectively. Although this amount may see insignificant, accounting for less than two percent of the overall mass of the plant, the flammability may be altered by as much as 30 percent. This warrants determination in the amount and proportions of volatiles such as terpenoids, waxes, and essential oils evolved during the preignition mass loss phase.

**Table 5. Dormant season overall RSIT values, mass loss percentages, and time to ignition for Chinese tallow stem/foliage, and yaupon and Chinese privet foliage.**

<table>
<thead>
<tr>
<th>Tallow Stem D</th>
<th>CO2 onset (s)</th>
<th>IR RSIT est. (°C)</th>
<th>Mass loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall Average</td>
<td>353.162</td>
<td>227.383</td>
<td>7.3001</td>
</tr>
<tr>
<td>Overall STD.DEV.</td>
<td>12.3093</td>
<td>2.8945</td>
<td>0.35329</td>
</tr>
<tr>
<td>Overall RSD (%)</td>
<td>3.48544</td>
<td>1.2730</td>
<td>4.8396</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Yaupon D Leaves</th>
<th>CO2 onset (s)</th>
<th>IR RSIT est. (°C)</th>
<th>Mass loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall Average</td>
<td>365.122</td>
<td>237.792</td>
<td>7.6922</td>
</tr>
<tr>
<td>Overall STD.DEV.</td>
<td>3.6124</td>
<td>4.3320</td>
<td>0.22658</td>
</tr>
<tr>
<td>Overall RSD (%)</td>
<td>0.98936</td>
<td>1.8218</td>
<td>2.9455</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Privet D Leaves</th>
<th>CO2 onset (s)</th>
<th>IR RSIT est. (°C)</th>
<th>Mass loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall Average</td>
<td>336.804</td>
<td>211.761</td>
<td>6.7625</td>
</tr>
<tr>
<td>Overall STD.DEV.</td>
<td>4.307</td>
<td>4.8530</td>
<td>0.31611</td>
</tr>
<tr>
<td>Overall RSD (%)</td>
<td>1.279</td>
<td>2.2917</td>
<td>4.6744</td>
</tr>
</tbody>
</table>
Chinese privet had the lowest RSIT value during the dormant season, but this was not a direct comparison between the leaves across all three species as it was during the growing season, so the proper ranking order cannot be determined. What can be noted is that the RSIT value between the growing and dormant seasons for Chinese privet did not change very much, having values of 210.1°C and 211.8°C respectively. Even though the mass loss percentage during the dormant season was greater than that of the growing season, 6.8 to 6.2 percent respectively. Again, this could call for the aid of GC-MS analysis during the preignition mass loss phase to help determine the proportions of water versus volatiles evolved in this region.

Yaupon resulted in higher RSIT values during the dormant season than in the growing season, 237.8°C to 232.3°C respectively. This result was not expected, these values are much closer than the values determined from previous temporal studies, a difference of 5.5°C compared to a difference of 15.8°C in Tillers’ research. Again, yaupon had a lower mass loss during the preignition mass loss phase during the dormant season and still yielded higher RSIT values. It is possible, although unknown, if the growing season contains more water content, and that residual water content in the growing season after the sample preparation drying period has any effect on the RSIT determination method. Again, GC-MS analysis could prove beneficial to solve this issue or at least offer a more definite explanation.

The Chinese tallow stem RSIT value during the dormant and growing season was 227.4°C and 250.3°C respectively. The mass lost during the preignition mass loss phase
was also less during the dormant season when compared to the growing season samples, of 7.3 and 8.3 percent respectively. These results are to be expected based on previous literature.\textsuperscript{3, 17, 26, 27} Chinese tallow stem was expected to have a high RSIT value due to its high fibrous content. With higher fibrous content than leaves, lignin proportions are much higher and more difficult to breakdown.\textsuperscript{87-89} Also, wood tends to be really homogenous in nature when compared to other forms of plant biomass, such as the leaves, roots, and bark, which may explain the low RSD values that were obtained from analysis of the Chinese tallow stems during both the growing and dormant seasons of only 1.1 and 1.3 percent respectively.

\textit{GC-MS Analysis of Extracts:}

Diethyl ether extracts of roughly a gram of plant material were analyzed with GC-MS. However, due to technical difficulties and instrument failures, data was lost and results were insufficient to draw any conclusions or identify any substances. Only two samples were run with GC-MS and neither of the spectra from the MS were able to identify even the solvent from the NIST library database which does include diethyl ether. The inability to identify even the solvent used during the analysis was a call for concern and due to this factor, further analysis with GC-MS during the timeline of this research was not accomplished. Future research of compound identification would prove beneficial in many aspects regarding this research, specifically in identifying low concentration volatiles during preignition phase mass loss.\textsuperscript{23, 24, 26-33} However, it is very difficult to find an instrument that is able to heat up a non-extract plant sample at a
programmable temperature and inject into a GC-MS. Ideally, an STA-GC-MS would be the perfect hyphenated instrumentation technique that could elicit the data needed. Purge and trap GC-MS would also be useful in this type of analysis, especially with a heated sampler purge tubes. These are able to heat samples, reportedly, to around 200°C with dynamic headspace analysis.⁹⁰
CHAPTER 5: Conclusions and Future Research

Conclusions

STA/IR analysis of plant material was successful in identifying, quite effectively, the onset of carbon dioxide evolution from the thermal degradation of yaupon, Chinese tallow, and Chinese privet. This evolution of CO$_2$ marked the beginning of combustion without a flame source, a phenomenon called Relative Spontaneous Ignition Temperature, or RSIT. Although STA/IR analysis was used successfully in carbon dioxide onset detection, it has its limitations. Specifically, at current operating parameters, not all of the peaks that appear in the IR spectrum can be identified using the STA/IR analysis technique. It shows a high spectral match of 90.2 percent from database matching software, SpectrumOne, for carbon dioxide, but shows extremely low spectral matches for other molecules as low as 30 percent matching and rarely over 60 percent. These other matches include cyanoacetic acid, 9,10-dihydroanthracene, and thiophenol to name a few. With spectral matches this low, there is no conclusive evidence to say that the spectral matches are accurate. This makes the first overall objective for this research only partially accomplished. After extensive literature review, it became apparent that this technique was undervalued, especially considering that there was virtually no literature that related the relative spontaneous ignition temperature to the mass loss peak in STA and IR analysis. More sensitive detectors are now readily available, such as the mercuric cadmium telluride, MCT, detector that is hundreds of times more sensitive than
the lithium tantalate, LiTaO$_3$ detector used in this research. This type of detector is good for kinetic studies as it does not work like typical thermal detectors. The MCT detector is a quantum detector, unlike that of the thermal detectors which operate under the constraints that the signal is inversely proportional to the data collection speed.

Temporal variations were observed for all three plant species, although these were mainly from the thermogravimetric data collected alone. Growing season samples of Chinese privet had a small difference in RSIT value from the dormant season, 210.1°C and 211.8°C, despite a significant mass loss differential during the preignition phase between the growing and dormant seasons, 6.3 to 6.8 percent respectively. Samples of yaupon had growing season RSIT values and mass loss percentages of 232.3°C and 8.6 percent. The dormant season of yaupon saw a small increase in RSIT value to 237.8°C despite a decrease in mass loss to 7.7 percent. Chinese tallow samples were only temporally examined for the stem due to the lack of leaves during the dormant season. The growing season for Chinese tallow stem had RSIT values of 250.3°C and a mass loss of 8.3 percent during the preignition phase of thermal degradation. By contrast, the dormant season of Chinese tallow stem saw an expected decrease in both RSIT and mass loss to values of 227.4°C and 7.3 percent.

The second objective of this research was completed entirely as every plant species RSIT values were determined during both the growing and dormant seasons using the IR detection of CO$_2$ onset to mark the event of spark source deficient ignition. Table
6 shows the RSIT and mass loss results of all species during both the growing and dormant seasons comparison.

Table 6. Overall temporal comparison of RSIT and mass loss for all target species.

<table>
<thead>
<tr>
<th></th>
<th>Privet</th>
<th>Tallow</th>
<th>Yaupon</th>
<th>Tallow Stem</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Growing RSIT °C</strong></td>
<td>210.1</td>
<td>208.4</td>
<td>232.3</td>
<td>250.3</td>
</tr>
<tr>
<td><strong>Growing Mass Loss (%)</strong></td>
<td>6.3</td>
<td>7.8</td>
<td>8.6</td>
<td>8.3</td>
</tr>
<tr>
<td><strong>Dormant RSIT °C</strong></td>
<td>211.8</td>
<td>--</td>
<td>237.8</td>
<td>227.4</td>
</tr>
<tr>
<td><strong>Dormant Mass Loss (%)</strong></td>
<td>6.8</td>
<td>--</td>
<td>7.7</td>
<td>7.3</td>
</tr>
</tbody>
</table>
**Future Research**

This completed project is one part of an overall study. The results and conclusions of this project will benefit the overall study and additional techniques and types of analyses may be used to accomplish goals of the overall study. An easily achievable goal is to increase the signal observed throughout the IR spectrum collection. In order to accomplish this, a much slower heating rate would be ideal, as well as a decrease in the scan rate of the IR to as low as possible. This would maximize the signal peaks that are observed from the IR without worry of missing out on the ignition of the material. Slowing down the heating rate allows for the ignition of the material to be spread out over a longer period of time, allowing for the IR to capture this moment even if it only takes a scan every 20-30 seconds. By comparison, the parameters of this research yielded a spectral scan every 0.90 seconds. The issue that may arise from this slower scan rate and heating rate is that the concentration of the evolved gaseous products may be too low to be detectable over the background noise. Potentially, the strong IR absorbing CO$_2$ may be unaffected by this change in parameters, however, there is no way to be sure until the experiment is run. If the low concentration of the evolved gases becomes problematic, another detector, with higher sensitivity may be ideal.

A mercuric cadmium telluride, or MCT, detector is up to 600 times more sensitive than that of the lithium tantalate detector used. It is, however, ideal for low
throughput experiments, with less than 20% of the IR beam reaching the detector. This can be resolved however by limiting the beam of energy that reaches the MCT detector to prevent saturation. Limiting the energy of the beam is easily accomplished with neutral density filters or optical screens.

Other future work stems on GC-MS analysis of the target species of plants. Utilization of GC-MS analysis would aid in characterization of molecules present in the plant species, which may aid in identifying key components that affect the plant ignitability, combustibility, and overall flammability. Furthermore, within the literature review, multiple techniques of component separation and subsequent analysis give the potential for easier characterization of components. The issue with GC-MS is that typically a sample must be in solution and injected, unless using a different technique such as static headspace GC-MS. Few instruments allow for heating and thermal degradation of solid matter to be analyzed, but a hyphenated technique of STA-GC-MS would be ideal for this situation, especially if static headspace analysis was used. The STA would heat the sample, gases would be evolved, the static headspace analysis would collect the evolved gases and they would be injected into the GC-MS for characterization of the evolved gases.

Additional research of plant samples from other locations would also be beneficial. This research focused only on the samples collected from the Post Oak Savannah ecoregion, but other ecoregions of plant matter were collected, such as the samples from the Blackland Prairie. Comparison between ecoregions would show
potential variations that could expand to other ecoregions and eventually covering much of the southeastern United States, where these invasive species of plant are very persistent. To accomplish this, the samples simply need to be analyzed, as the samples have already been collected.
References


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27. Zakaria, H.; Youssef, M.; Khalid, A. J. In *Variation in Yield and Composition of Essential Oil in Pelargonium sp During the Vegetative Stage*, International Conference on Chemical, Environmental and Biological Sciences, Dubai (UAE), 2015.


Vita

Antonio David Trevino attended Robert M. Shoemaker High School in Killen, Texas and graduated in June 2009. In the fall of that same year, he began his undergraduate degree, B.S. Chemistry with a minor in biology, at Stephen F. Austin State University in Nacogdoches, Texas. He graduated from SFASU in December of 2014 and was married in June of the following year to Kelsey Marie Nixon, a fellow alumni of SFASU. By fall of 2015, he accepted a full-time teaching position at Gladewater High School as a chemistry teacher. In spring of 2016, Antonio finished the academic year at Gladewater High School and accepted a graduate teaching assistantship at his old alma mater. He entered the Graduate School at Stephen F. Austin State University seeking a Master of Natural Science with a focus on chemistry. He is expected to graduate in August 2018.

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