

Heats for Combustion, Capacities, and Evaporation of Fresh Leaves and Their Relationships to Leaf Compositions

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Introduction

Fundamental thermal properties of fresh leaves that are essential to CFD modeling of leaf pyrolysis and flammability are related to leaf composition and moisture content. The focus of this paper is on measuring and providing functional relationships for the heat of combustion, specific heat capacity, and heat of moisture desorption for fresh leaves as they vary with moisture content and composition. With the leaves typically being within a fraction of a millimeter thick and having internal structures of petiole, veins, and blades filled with active living moisture and organic compositions that can also naturally degrade, specialized methods of thermal measurements were required. Heats of combustion were derived from leaf elemental formula for each leaf based on composition from ultimate analysis testing and an in-depth composition analysis for several fresh leaf varieties. Heat capacity was derived for the cut up and dried fresh leaves as function of temperature and corrected for mass loss during pyrolysis up to 440 °C utilizing a modulated Differential Scanning Calorimeter (DSC) and high resolution Thermogravimetric Analysis (TGA). Heat of evaporation was derived from the isothermic thermodynamic relationship with the leaf moisture desorption process obtained from a modern water activity meter with precise temperature and water activity measurements. The composition of a dozen and wide variety of leaf species from pine forests in the southern U.S. were recently determined for their content broken down into the following categories: lipid, fructose, glucose, protein, pectin, hemicellulose, starch, cellulose, phenols, lignin, and minerals. This summative analysis was recently completed and is currently being documented.

Composition of Fresh Leaves

The description of the live plant seedlings shipped to our laboratory from the nurseries are identical to that in the companion papers in this conference and elsewhere (Safdari *et al.* 2018). Because of the nature of measurements for this study, the plants were grown in large soil pots in an indoor greenhouse in Madison, WI that had southern sunlight exposure supplemented with LED diurnal plant lightings. These plants were watered twice during the week to provide fresh mature leaves on the unwatered days. Leaves were snipped with a scissors to fit in small sealed containers for the various tests. To assure leaf freshness, and to avoid initiating leaf rancidity, the various tests were begun immediately. The summative analysis paper being prepared describes in detail the wet chemistry resulting in the composition of 10 species shown in Figure 1, ordered in increasing lipid content.

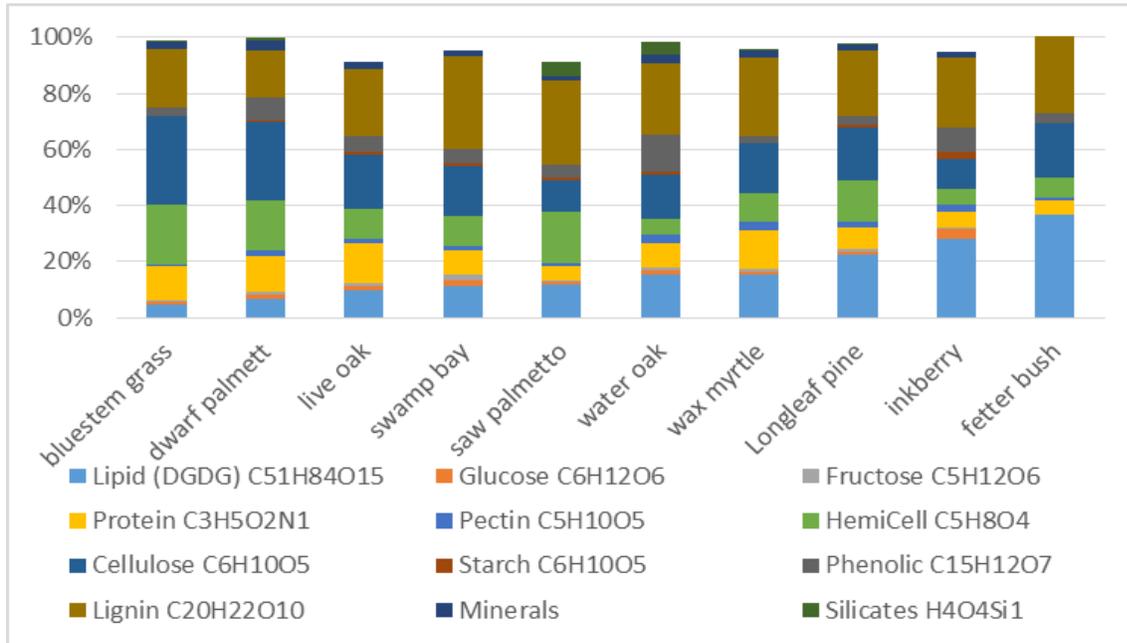


Figure 1. Composition of Fresh Leaves from US Southern Pine Forest Seedlings

Correlation for Leaf Elemental Formula and Heat of Combustion from Composition

Associated with each composition shown in Figure 1 is the elemental formula providing the opportunity to predict the ultimate analysis test results (Safdari *et al.* 2018) for the leaves on a dried and ash free basis. For proximate and ultimate analysis of the leaves as sent to a contract laboratory for standard testing, the hydrolyzed and/or peroxidized material had partially formed from the native material, despite the insertion of portable desiccants and oxygen absorbers in the shipped aluminized bags of the samples. Exposure to normal humidified air occurred both in the greenhouse preparation and in the contract laboratory, meaning that the presence of lipids, protein, pectin, and starch in the leaves was susceptible to rancidity, partly changing the native composition. The lipid formulation was particularly challenging to define a model compound for, and to specify a certain amount of peroxidation that occurs on the 6 double carbon bonds on the digalactosyldiacylglycerol (DGDG) lipid model compound chosen. Figure 2 shows prediction of the elemental mass formula on the dried and ash free basis (Equation 1) using the data in Figure 1 for comparison to the ultimate analysis data for the tested dried leaves, showing the native and peroxidized condition. Note that each f in Equation 1 is weighted by the composition mass fractions to obtain the overall mass fractions of each element in the leaves.

$$\begin{aligned}
 f_C &= n_C M_C / (n_C M_C + n_H M_H + n_O M_O + n_N M_N) \\
 f_H &= n_H M_H / (n_C M_C + n_H M_H + n_O M_O + n_N M_N) \\
 f_O &= n_O M_O / (n_C M_C + n_H M_H + n_O M_O + n_N M_N) \\
 f_N &= n_N M_N / (n_C M_C + n_H M_H + n_O M_O + n_N M_N)
 \end{aligned}
 \tag{1}$$

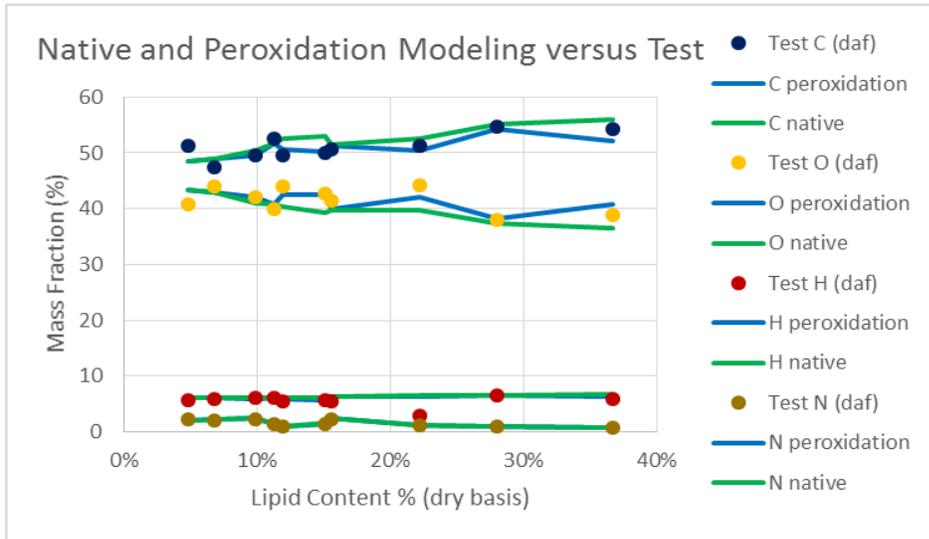


Figure 2. Elemental masses of C, O, H, and N for 10 leaves for native and peroxidized condition

Figure 3 shows the estimated level of lipid peroxidation mass added to each leaf species that seem reasonable as compared to the solid straight line of DGDG lipid fully peroxidized. The net and gross heat of combustion via the oxygen consumption correlation (Dietenberger 2002) for each composition element j , in the order of lipid, glucose, fructose, protein, pectin, hemicellulose, cellulose, starch, phenolic, lignin, minerals, and silicates, are,

$$H_{c,net,j} = 13.23 * \left(\frac{8f_{c,j}}{3} + 8f_{h,j} - f_{c,j} \right) \quad (2)$$

$$H_{c,gross,j} = H_{c,net,j} + 21.96 * f_{h,j} \quad (3)$$

The best accuracy was attained for glucose and small errors (<5%) were noted for the other composition elements. Summing these heats of combustion weighted by their composition element mass fractions obtains the overall heat of combustion. The comparison of the predicted gross heat of combustion to the higher heating value (HHV) (Figure 3) includes the native and peroxidized condition, indicated the consistency with elemental masses in Figure 2, and confirmed the use of Equations 2 and 3 for estimating heats of combustion of the leaf elements.

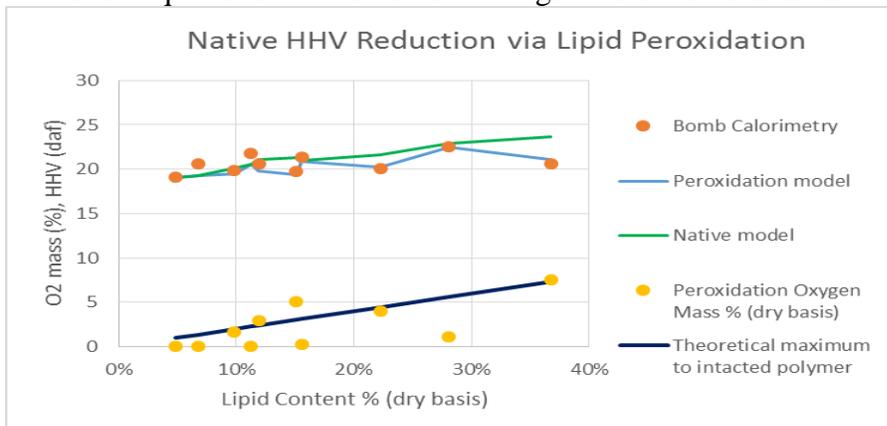


Figure 3. Higher heating value (HHV) for 10 plant species found in southern pine forests for native and peroxidized condition

Specific Heat Capacity Measurement and Correlations

For heat capacity of dried biomass, the literature provides considerable data for the standard elements of cellulose, hemicellulose, and lignin in the biomass. However, the fresh leaf also contains various other native constituents that places uncertainties on the heat capacity values, particularly as a function of temperature and degradation (Jolly *et al.* 2012). We have a modern DSC that has a modulating heat source that can provide a temperature range from the -90 °C temperature to 440 °C. Due to the tedious preparation of any sample for the DSC, and to assure very dry leaves during the heat capacity measurement, we developed a temperature curve in the DSC to pre-dry the material at 105 °C, and then bring it back to 0 °C to begin the modulating heat feature to determine the dried heat capacity. The results in Figure 4 for yaupon (*Ilex vomitoria* Aiton) and longleaf pine (*Pinus palustris* Mill.) needles (and not shown for other leaves that were within the boundaries of yaupon and longleaf pine) confirmed the proportionality to the absolute temperature as suggested in the literature for wood and its native constituents (Thybring 2014). The TGA provide the mass corrected value for the apparent specific heat capacity as function of temperature beyond the transition temperature of 225 °C. Xylan, the major hemicellulose component in leaves, is exothermic during degradation and likely the cause for initial leveling of the apparent heat capacity. There is X-ray Photoelectron Spectroscopy (XPS) data (private communication) showing the rearrangement of the carbon bonds becoming more and more like that of graphite. The graphite data obtained from the literature is shown in Figure 4 to indicate the reasonableness of the apparent heat capacity at high degradation temperatures, and to show that the so-called char heat capacity is not appropriate for pyrolysis modeling of the fresh leaf. Further details will be provided in a manuscript being developed to describe the heat capacity methodology for the fresh leaf.

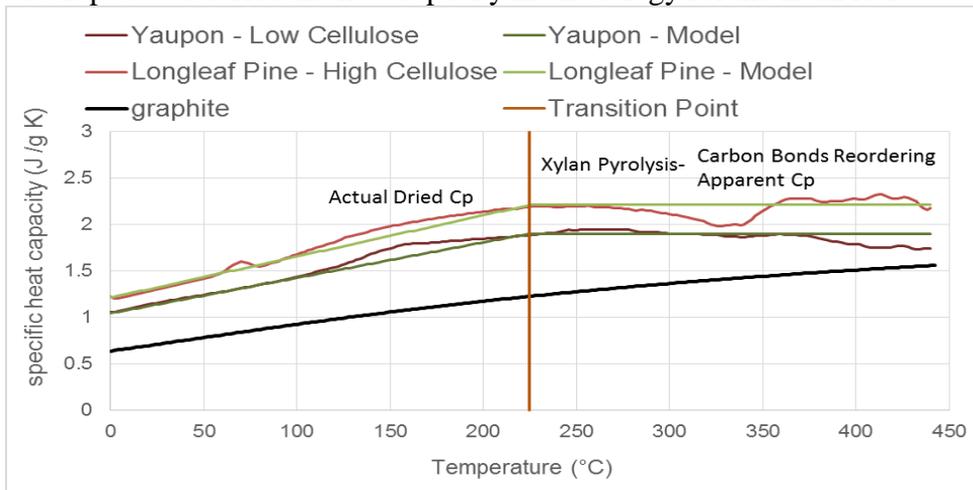


Figure 4. Specific heat capacity from modulating DSC and correlation with leaf composition

The correlation equation for heat capacity utilizing the composition data in Figure 1 (Model curves in Figure 4) is,

$$C_{p,i} = \left(f_1 C_{p,max,,i,1} + \sum_{j=2}^n f_j C_{p,max,,j} \right) \min \left(\frac{T}{498}, 1 \right) \quad (4)$$

Of all the elements the lipid (as $j = 1$) is known to have higher heat capacity than the other components and is the most variable (for example in Morad *et al.* (1995) for triglycerides lipid), derived as the maximum specific heat capacities values that fitted the data for the differing species, i . The summation over the other elements, j , of the leaf include their maximum heat capacities (i.e. at 225 °C) that doesn't vary much among the species, except save possibly for the cellulose, whose heat capacities increases with cellulose amorphous levels (Thybring, 2014). We recommend use of Equation 4 for the dried component of the leaf in a computer model of pyrolysis and to zero out any heat of pyrolysis as it is implicitly in the apparent heat capacity.

Isoteric Heat of Moisture Desorption

The differential heat of desorption measurements uses a well-known isoteric formula from the food industry (Kaleemullah and Kailappan 2005) which has the material's water activity as a function of the pure water's heat of vaporization and pure water saturation vapor pressure:

$$\ln(h) = \left(\frac{\Delta H_{dif}}{\Delta H_{vap}} \right) \ln(P_{vap}) + C(m) \quad (5)$$

We programmed the water activity meter to provide temperatures at fixed increments (5 degrees increment as used for the longleaf pine needles), to provide water activity values as a function of temperature for a given moisture content within a single day period. The leaves' moisture content stayed constant as verified by before and after measurements in the activity meter of their weight. We then dried the leaves in the vacuum oven at 45 °C overnight to obtain the moisture content value on a dry basis. This temperature is much lower than the ASTM standard oven-dry temperature method for wood or cotton (Montalvo and Von Hoven 2008; ASTM D4442–16 2016). Water activity data shows a straight line when the log of water activity is plotted versus the log of pure water vapor pressure that varies with temperature for a given equilibrium moisture content (EMC). The slope (dimensionless) of the line is then the ratio of differential heat of desorption to the pure water heat of evaporation. Knowing the pure water heat of evaporation as function of temperature, the differential heat of moisture desorption can be solved for and plotted versus the leaf EMC as shown in Figure 5.

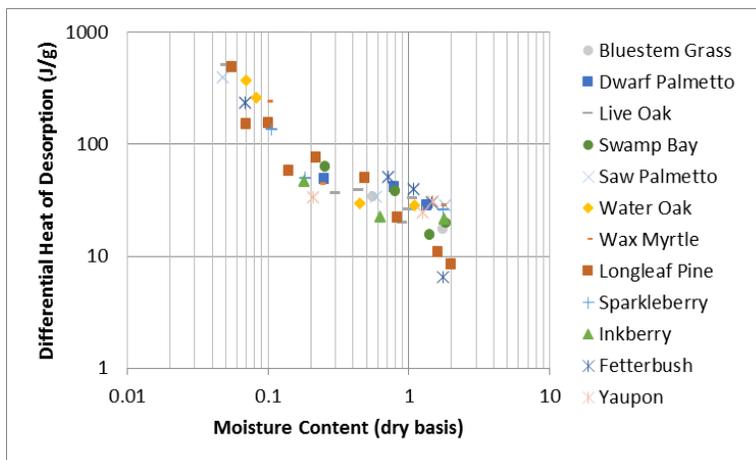


Figure 5. Differential heat of moisture desorption of 12 species via Equation 1.

The most important region at moisture content less than 0.3 (corresponding to water activity less than 0.9) provides a significant amount of desorption heat greater than that of pure water and shows no sign of a limit to the desorption heat as the moisture content approaches zero. It appears that all leaves tested behaved similarly within the experimental noise, meaning that it may not be possible to correlate the leaf composition with the heat of desorption.

Conclusion

The combined reporting of the 3 various heats measured for the essentially same 10 fresh plants during their native conditions is essentially complete for pyrolysis modeling, not even needing the heat of pyrolysis because that is implicit within the apparent heat capacity during pyrolysis. With the determination of 12 composition elements, we further obtained correlations involving weighted compositions' heat of combustion and compositions' specific heat capacity to agree with their observed composite values that show a generality implied for other foliage and biomass. The role of the lipids with the leaves highlighted in the thermophysical properties is uniquely obtained. The elusive heat of moisture desorption for the native leaves was obtained as function of moisture content and temperature along with the careful minimal conditioning time (by avoiding rancidity) of the leaf in the advanced water activity meter.

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