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Thermal Degradation Modeling of Live Vegetation for Fire Dynamic Simulator

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Abstract: Fundamental pyrolysis thermal and kinetics properties for live vegetation that are essential to CFD modeling of pyrolysis and flammability were obtained from a series of small-scale tests for live and dead vegetation. The complexity of live leaf composition was recently documented allowing analysis of 12 crude compounds. Model simplification required a practical grouping into contents of (0) moisture, (1) lipids, (2) digestives (glucose, fructose, and protein), (3) hemicellulose (xylan and pectin), (4) glucan (cellulose and starch), (5) phenolic (lignin and tannins), and (6) inert (silicate and mineral), along with the use of higher reaction orders to accommodate the wide pyrolysis peaks, and of bi-production of volatiles (tar/gas) and char from each pyrolysis group. Extensive TGA tests in nitrogen and air were used to derive oxidative pyrolysis kinetics of the celluloses and of the char, which is also suitable for smolder modeling. Moisture desorption was based on phase change kinetics coupled with the moisture isotherm relationship and heat of desorption for bound water to add generality over that of the common first-order Arrhenius kinetics relationship. Extensive DSC tests in nitrogen flow provided leaf heat capacity and estimates of the exothermic heat of pyrolysis (primarily charring) reactions over a range of temperatures. The heat of combustion remains established as a correlation based on the oxygen consumption principle whether as a volatile or a char. Finally, the transport properties of leaf surface emissivity and convective heat transfer coefficient, in conjunction with a semi-theoretical expression for the leaf thermal conductivity varying with composition, temperature, moisture content, and material degradation was obtained via an inverse heat conduction approximation method with a specialized vegetation test using leaf surface thermocouples in the cone calorimeter. This paper provides the summary of such formulations and properties that could replace or supplement existing formulations in the vegetation module in the CFD modeling of wildland fires, e.g., Fire Dynamics Simulator (FDS).

Keywords: Pyrolysis Modeling, Live Vegetation, Leaf Components, Transport Properties

1. Introduction

The complexity of live leaf composition [1], in the order of increasing pyrolysis temperatures, is indicated by measurements of 12 crude compounds as lipids, glucose, fructose, protein, pectin, hemicellulose, starch, cellulose, phenolic, lignin, silicates, and minerals. Pyrolysis kinetics become difficult due to the variable percentage compositions of lipids, celluloses, and lignin among the different plant species and because each component has a wide range of pyrolysis temperatures.

With a practical grouping we simplified the crude compounds into similar functionalities, char fraction, and heats of combustion into contents of (0) moisture, (1) lipids, (2) digestives (glucose, fructose, and protein), (3) hemicellulose (xylan and pectin), (4) glucan (cellulose and starch), (5) phenolic (lignin and tannins), and (6) inert (silicate and mineral). The wide pyrolysis peaks for each group will need kinetics enhancements such as distributed energy approaches, sub-components, or higher reaction orders for better data fitting [2, 3], the latter of which was selected due to the simplicity of a single added parameter to fit the TGA data. Many models include the bi-production of volatiles (tar/gas) and char from each pyrolysis group, which is also adopted for this study [2-5]. Extensive TGA tests in nitrogen and air were also used to derive oxidative pyrolysis kinetics of the celluloses and of the char, as also suggested in the literature pertaining to oxidative pyrolysis [6-8], which is also suitable for smolder modeling.

TGA measurements were made of the leaves' drying for the 12 species with differing initial moisture content and temperature jump steps that demonstrated rapid drying without the associated boiling behavior at a boiling point. This motivated a review of the literature on moisture desorption (and adsorption) theories, in which we settled on the phase change kinetics [9] coupled with the moisture isotherm relationship for absorbed water [10, 11] to add generality over that of the common first-order Arrhenius kinetics relationship. Extensive measurements with the water activity meter for 12 vegetation species established a common empirical formula for the moisture isotherm relationship and the corresponding heat of moisture desorption as function of moisture content and temperature as derived with Clausius Clapeyron thermodynamic formulation [12, 13]. The Clausius Clapeyron equation is key in the equilibrium modeling, which was recently compared against the Arrhenius modeling, for moisture evaporation from biomass [14].

Extensive DSC tests in nitrogen flow provided leaf heat capacity and estimates of the exothermic heat of pyrolysis (primarily charring) reactions over a range of temperatures and an empirical relationship was developed and summarized for this paper [13, 15]. The stoichiometric heat of combustion remains established as a correlation based on the oxygen consumption principle whether the fuel is a volatile or a char [1]. In either smoldering or flaming, the combustion products of CO and soot implies the reduction of the heat release rate due to incomplete combustion [16].

To complete the pyrolysis modeling, extensive measurements with leaf surface temperatures on exposed and shaded side showed significant temperature differences after the leaves were dried during radiant heating, implying the important role of thermal conductivity as the leaf is degrading. Literature review for leaf thermal conductivity showed non-degrading heat exposed leaves with limited temperature and moisture content domain [17, 18], whereas for the live leaf in the current tests a full range of moisture content, temperatures, and degradation is expected and should be modeled. Since the leaf is heated by thermal radiation, a thorough study on the leaf surface absorptivity, transmittance, and reflectance (and thus also surface emissivity) has been done [19] for a few leaves, and the test method should be extended to other species. For the typical radiance from the cone calorimeter heater and most fires, surface emissivity of live leaves are about 0.9 and dry leaves are about 0.8. What is remaining is the use of an inverse heat conduction analysis to estimate the convective heat coefficient from the heat balance and of the overall thermal conductivity from the heat absorbed and lost from the leaf. Literature review has shown the possibility for theoretical relationship based on mixture of parallel and series structural elements [20, 21] as enhanced by the cellular thermosiphon of water [21], as discussed briefly in this paper.

All these properties and functional relationships were obtained independently from the computational pyrolysis modeling but can improve pyrolysis modeling in the Fire Dynamic Simulator (FDS) in various nuanced ways, and is suggestive of explaining fire behavior that has been elusive. The existing vegetation module in FDS as described in the Technical Guide, models the pyrolysis kinetically for three basic types of mass losses, which are (1) moisture loss, (2) overall fuel mass loss with simple kinetics into volatiles and char, and (3) mass loss with graphitic char oxidation. A simple formula for the leaf heat capacity and single constants for heat of moisture desorption and heat of pyrolysis are used. There is no thermal conductivity of the leaf provided as the leaf is assumed to be thermally thin. The ignition is based on a temperature criteria. There is just a single global reaction of the fuel that defines the overall combustion products, then treated as emissions. The heat of combustion is based on a correlation with the fuel elemental composition, so that the mass loss rate times the global heat of combustion is the heat release rate of a flame.

This paper provides the summary of new formulations and properties that could replace or supplement existing formulations in the vegetation module in FDS. Each individual physical process will be provided in detail in future companion publications. We note that forest litter loses some of the compositions of the live leaf, which means that property values may change without the need for changing the physical principles outlined if the chemical composition of the forest litter is known.

2. Component pyrolysis kinetics for volatiles, oxidative depolymerization, and oxidation

Wet chemistry [1] provides initial mass fraction profiles of the grouped components on dry basis: (1) lipid, (2) digestible (as fructose, glucose and protein), (3) hemicellulose (as pectin and xylan), (4) glucan (as cellulose and starch), (5) polyphenol (as tannin and lignin) and (6) ash (as minerals and silicates). After achieving summative mass balance closure to within 95% or higher in this work, and for application to pyrolysis modeling, we renormalized the compositions so that their sum is unity,

$$\sum_{j=1}^{j=6} f_j = 1 \qquad (1)$$

where f_j represents the native mass fraction of the component j on the dry mass basis, noting that $j = 0$ is reserved for water. Extensive measurements with live and dried leaves in the TGA for the 12 species in both nitrogen and air flow indicated these grouping and ordering of components as based on their pyrolysis temperatures and charring behavior, and as in revealing the various pyrolysis peaks measured in the TGA as being correlated with known compositions from the wet chemistry (paper being prepared). During pyrolysis, each component has the potential for total volatile and total char, or

$$f_j = f_{v,j} + f_{c,j}\,, \quad j \geq 1 \qquad (2)$$

where subscripts v and c represent the volatilizing and charring parts of the native mass fraction, respectively. Normally the volatile matter fractions (aside from the initial water fraction) are reported under inert gas condition in a specialized TGA as ramped to very high temperatures that avoid reactions with the reacting chemicals such as oxygen and water (ASTM D7582) and then

the remaining char mass consist of "fixed carbon" and "ash", which is then combusted under air or pure oxygen at a somewhat reduced temperature that avoid ash melting reactions [1]. We postulate that under high enough heating rates, the volatiles can emit at a sufficient rate to prevent some penetration of reacting gases to the charring sample, thereby preserving the resulting char fractions without the need for inert gases environment. Many successful pyrolysis kinetics have been based on the assumption of an unchanging total char fractions (or unchanging volatile matter fraction) [2-5], even while the volatile matter data shows the decreasing ratio of bio-oil mass to that of the non-condensable gases with the increasing temperature or mineral contents. The well-known increase in certain minerals in some biomass can also increase the char fraction, and thus possibly vary with the plant species. But in the end, modeling the invariant char mass fractions for live leaf components and an invariant heat of combustion for the component volatiles (despite the possible varying ratio of bio-oil to combustible gases) was found suitable for the live leaves in this study [1, 4, and pyrolysis kinetics paper being prepared].

Once the volatile emissions start ceasing, the reacting gases can then penetrate easily the sample for surface reactions with the char, which result in further mass loss ultimately reaching the ash mass, which is described as oxidative pyrolysis. This means the event of volatilization has minimal or small overlap with the char surface oxidation for the leaf [22, paper being prepared], thus simplifying the pyrolysis kinetics modeling. With this definition of native mass fractions from Equation 2, the residual mass of live leaf at each time step, t_i, is:

$$m_{\mathrm{r},i} = m_{\mathrm{r},0} \sum_{j=0}^{j=6} (f_{v,j}\, \theta_{j,i} + f_{c,j}\theta_{7+j,i})/(1 + f_{v,0} + f_{c,0}) \qquad (3)$$

Whereas the theta is unity at time zero, $\theta_{j,0} = 1$ and is zero at time infinity, $\theta_{j,\infty} = 0$, for all such mass loss degradation processes. The theta remains at unity for the char components, $\theta_{7+j,i} = 1$, in inert gas exposures and has the potential to go to zero during char combustion in air. Ash is denoted by $j = 6$ in the equation 3 formulation.

Since absorb water does not normally char during pyrolysis, its "char theta" is zero, $\theta_{7+0,i} = 0$, and its char fraction is zero, $f_{c,0} = 0$. However, some of the absorb water can become chemically bound if the fresh leaf enzymes succeed in the hydrolysis of the digestible native material [1], which may in turn become an organic char upon further heating, still locking the moisture in the residual mass, thus in the end giving the absorb moisture some small contribution to the char mass. The moisture status of the initially heated leaf, which is, $f_{v,o} + f_{c,0}$, is typically different than of the native moisture content of the live leaf, which is f_0, which turns out to be an important factor in modeling moisture desorption or adsorption, as discussed later.

The lipids can also undergo the natural auto-oxidation known as lipid peroxidation [1], in which the diatomic oxygen is imbedded near the double carbon bonds in the various lipid structures, often resulting in rancidity in the case of fresh leaves used for food. Thus any rancidity in the leaves, particularly as fresh litter, should define a new "native" material by adjusting the initial empirical formula for the generic lipid [1]. In any case, the summation term in equation 3 is algebraically at unity at the initial time zero so that the residual mass at time zero, $m_{r,0}$, is the actual initial mass.

Kinetics Formulation

The mass loss rate at each time, t_i, is the time derivative of equation 3 with change of sign as:

$$\dot{m}_{v,i} = -\dot{m}_{r,i} = -m_{r,0} \sum_{j=0}^{j=6} (f_{v,j}\, \dot{\theta}_{j,i} + f_{c,j} \dot{\theta}_{7+j,i}) / (1 + f_{v,0} + f_{c,0}) \quad (4)$$

Where $\dot{\theta}_{j,i}$ can be modeled with an Arrhenius function ultimately as a set of ordinary differential equations (ODE) corresponding to a first-order system,

$$\dot{\theta}_{j,i} = -\sum_{k=0}^{n_k} a_{jk}\, \theta_{k,i}^{p_k} \sum_{l=1}^{n_l} r_{jkl} A_{jkl}\, T_i^{v_{jkl}}\, exp\left(\frac{-E_{jkl}}{RT_i}\right) \quad (5)$$

The Arrhenius expression has the usual activation energy, E_{jkl} (kJmol^{-1}), temperature at index i, T_i (K), exponent of temperature term, v_{jkl} , pre-exponential constant, A_{jkl} (K$^{-v_{jkl}}$ sec^{-1}), grouped component's reaction order, p_k, interaction matrix, a_{jk} , as providing dependence on other group's normalized degradation, $\theta_{k,i}^{p_k}$, and an adaptive factor, r_{jkl}, that can account for competing processes, oxidative conditions, process nonlinearities, or second order effects, and therefore requiring that $n_l > 1$.

Much of the literature on the pyrolysis kinetics of organic materials ignores the off-diagonal interaction terms and thus the interaction matrix, a_{jk} , is the unity matrix for a simplified model or is just ignored when interaction is not assumed, and thus having the potential for the analytical solutions to equation 5. We note that analytical solution to equation 5 with its matrix formulation can be obtained in special cases, such as when all the grouped component's reaction orders, p_k, is unity and applicable to certain prescribed temperature profile, such as piecewise linear temperature [23]. Analytical solution can also be obtained with the interaction matrix as a unity matrix and any non-unity reaction orders [4]. This latter analytical approach that was implemented readily in a spreadsheet allows for wide pyrolysis peaks for the grouped components, and is especially useful if there are already several components in the kinetic modeling. The other advantage to this approach is the derivation of thermodynamics parameters of enthalpy, Gibbs free energy, and entropy of chemical processes that are easily evaluated for each grouped component [4]. It is a viable and simpler alternative to the use of sub-components for the wide lipid, carbohydrate, and lignin degradation peaks that was used in the case of microalgae pyrolysis kinetics [2], or in the use of distributed activation energy approach to fitting wide pyrolysis peaks [3, 24].

However, the absorb moisture as affecting the pyrolysis behavior is well known, giving second order effects via the off-diagonal interaction terms as follows. The presence of absorb moisture has been implicated in the steam "explosion" of the celluloses that convert the glucan to glucose [25]. Thermo-hydrolysis is a known method in sewage treatment in which the lipids are hydrolyzed at 130 ^{o}C, the protein hydrolyzed at 165 ^{o}C, and the cellulose hydrolyzed at 220 ^{o}C [26]. Given that the absorb moisture may affect volatilization process of all the major leaf components, would mean that the first row in the interaction matrix would be non-zero, and that any hydrolysis involves the loss of absorb moisture would mean that the first column of the interaction matrix is non-zero. These off-diagonal interaction terms for the moisture effect complicates the pyrolysis kinetics analysis and should be analyzed separately from the diagonal

terms, to make progress with modeling. To achieve this, our TGA test method involves the temperature profile that avoids the overlapping of the moisture desorption with devolatilization of combustible material, via a dryout stage at 105 °C for several minutes before the temperature ramping to very high temperature. Eventually, and in particular with moisture interaction, the off-diagonal terms should be addressed, via special tests, and with numerical methods, in a future work. Later, the moisture desorption in of itself is described in detailed for incorporation into the pyrolysis modeling.

Adaptive Factor for Oxidative Pyrolysis

In the first kind of oxidative pyrolysis, the amorphous polysaccharides (primarily hemi and alpha celluloses) undergoes depolymerization in air at 210 °C according to Zhou, et. al. [26], while the crystalline cellulose is unaffected by the oxygen molecule. Our data with TGA with both nitrogen and air flow indicates that the cellulose and/or hemicellulose are likely affected in this way in which the DTG peaks at around 350 °C for all species under nitrogen flow, that then shifts under air flow to a DTG peak at a lower temperature around 300 °C [paper being prepared]. This implies a lowered activation energy, as determined also in Tihay, et. al. [7] for oxygen effects on cellulose wadding, which has some amount of crystallinity. Xylan, as the model compound for hemicellulose, also undergoes an oxidative depolymerization, as found under 4 different oxygen levels with a TGA [8], for which the DTG peaks shifts to lower peak temperatures as the oxygen levels increases. The second kind of oxidative pyrolysis is the reaction of oxygen with the char that result directly in mass losses and large localized heat releases. This has resulted in the temperature rate bumps at around 450 °C for which the PID of the TGA had some difficulty in keeping the temperature rise rate at a constant value. Since the oxidative pyrolysis is associated with the modified native structure, the native adaptive factor is set to unity, $r_{jj1} = 1$, for inert gas flow and the oxidative pyrolysis factor for $l = 2$ is a power function of oxygen concentration,

$$r_{jj2} = (O_2/0.20946)^{u_j} \qquad (6)$$

The hemicellulose depolymerization corresponds to $j = 3$ and the glucan depolymerization corresponds to $j = 4$. If any of the volatilizing groups has char value greater than zero, $f_{c,j} > 0$, will then have the oxidative pyrolysis factors given by equation 6 for $j \geq 7$. It is known that the organic char can become graphitic (100% carbon) at temperatures significantly above 450 °C with further losses of H and O in the TGA under inert gases, which would introduce the native adaptive factor for char that accounts for these gaseous emissions. However, the cone calorimeter tests shows the leaf char as retaining the native (ie. lignin) empirical elemental formulation during the event of oxidative pyrolysis, or glowing combustion. This was proven by an effective heat of combustion at around 20 kJg^{-1} and the fuel reconstruction via examination of CO_2, CO, H_2O, O_2, and soot flow rates during the afterglow combustion. For simplicity and practicality all the individual grouped chars are considered a single composite char, with all char groups sharing the same values of activation energy, pre-exponential constant, and the exponent, u_j. The exponent u_j is set to 2 according to [8] as a best estimate as at present as we only have two oxygen levels corresponding to inert gas and air. In the future we can consider the dilution of oxygen in the air similarly to that done for Xylan-based hemicellulose [8]. Appendix A provides the calibrated values for the coefficients of the pyrolysis kinetics for longleaf pine

needles example, whereas the coefficients for the other species will be provided in a future publication being prepared.

3. Phase Change Kinetics for Moisture Desorption Varying with Plant Species

Extensive TGA measurements of leaf moisture desorption and extensive water activity meter measurements of the moisture isotherm for the 12 leaves offered an opportunity to investigate various moisture desorption theories available in the literature. We settled on a well-known relation for liquid to vapor transition, developed from the kinetic theory for ideal gases, that defines the maximum theoretical evaporation rate through a unit surface under vacuum conditions, but which involves a correcting factor to agree with experimental data. Eventually, the evacuated and enclosed environment will build up vapor pressure in countering the initial flow, resulting in the Hertz-Knudsen equation [9]:

$$F = \varepsilon\left(P_{veq} - P_v\right)\left(\frac{M_v}{2\pi RT}\right)^{1/2} \qquad (7)$$

where F is the interfacial mass flux (kg m^{-2} s^{-1}), P_v is the vapor pressure in the gas phase (Nm^{-2}), P_{veq} is the corresponding saturating vapor pressure (Pa) of the material, and T is the temperature of the liquid surface (K), and M_v is the molecular weight. The presence of the saturating vapor pressure term at the interface indicates maintaining the equilibrium conditions right at the interface at all times. The presence of molecular weight indicates that any real material that has a liquid/vapor interface follows the equation 7 for the vapor flux from the interface. At regions away from the nano-interface, as would happen in a porous material at the microscale, other processes for moisture flow could take place, via diffusion flux, Darcy vapor flux, or capillary liquid flux. In essence the leaf system is never quite in an equilibrium state, but the nano-interfaces of liquid and vapor are always in dynamic equilibrium.

Various theoretical and experimental research [9] has focused on the evaluation of the evaporation coefficient, ε , but will have an adjustment in relation to our TGA and Cone Calorimeter test results with the leaves. TGA has a dry environment and its sample pan requires cut-up leaves, thereby removing the resistance to moisture flow via orifices, porosity, or air vacuoles. That is, particularly in the TGA tests, the purge flow with dry gas will prevent build-up of water vapor pressure, and the act of reducing the sample dimensions to fit the sample pan, also meant that the vapor flow resistances due to orifices in the surface, or Darcy flow in porous bodies, or even diffusion flow in thick material as the processes that are minimized. In the case of water vapor, the phase change kinetics, as represented by Equation 7 would then provide the only resistance to the water desorption flow, as implied by the saturating vapor pressure of the material, P_{veq}. Since the interfacial material is liquid water as affected by dissolved minerals and sugars at high moisture content and by cell wall effects at low moisture content, means a differential Gibbs free energy adjustment to the saturation vapor pressure of pure water is as follows [10 and paper being prepared],

$$P_{veq} \approx T^{-2.5}\exp\left(35.293 + (-49.3 - \Delta G_{dif})/RT\right) \qquad \text{Pa or Jm}^{-3} \qquad (8)$$

which over the whole range up to close to the critical point Equation 8 is to within 3% error for pure water. The differential Gibbs free energy was correlated with leaf reversible moisture content and temperature from the extensive equilibrium tests with the water activity, a_w, apparatus as [11 and paper being prepared],

$$a_w = \frac{P_{veq}}{P_{vs}} = \exp\left(\frac{-\Delta G_{dif}}{RT}\right) \quad (9)$$

$$\Delta G_{dif} = \left\{\frac{m_c[1+\exp\,(A-B/T)]-C_1}{\exp(C_2)}\right\}^{\frac{1}{C_3}} - C \quad (10)$$

Within the experimental error of the water activity meter all the tested samples followed the same desorption isotherm, resulting in the values of the six isotherm coefficients as, $A = 4.884$, $B = 1985.6$ K, $C = 0.02706$ kJmol^{-1}, $C_1 = -0.01$, $C_2 = -1.825$, and $C_3 = -0.8469$. Since the water activity meter is able to maintain the leaf moisture content $m_c = f_{v,0}\theta_{0,i}$ as constant during its stepwise temperature changes, we applied the isoteric formulation for the differential heat of water desorption via the Clausius Clapeyron equation as applied directly to the data [12, 13]. The differential heat of water desorption decreases strongly with moisture content, meaning that the Clausius Clapeyron equation must also be applied to Equations 8-10, and found to have a good fit to the data, as the relationship,

$$\Delta H_{dif} = \Delta G_{dif} - \frac{\Delta G_{dif}+C}{C_3 T}\left[\frac{m_c B \exp(A-B/T)}{m_c[1+\exp\,(A-B/T)]-C_1}\right] \quad (11)$$

$$\Delta H_{veq} = 49.3 - 2.5RT + \Delta H_{dif} \quad (12)$$

Thus the heat of water desorption (Jmole^{-1}) is the sum of differential heat of desorption and the latent heat of pure water. By a slightly alternate selection of correlation constants in Equation 10, it is possible to achieve an infinite value of differential heat of water desorption as the moisture content approaches zero. This would mean the reversible absorb moisture would reach zero at infinite time, even at high temperatures, and could explain the cellulose "steam" explosion discussed earlier. However, the associated low relative humidity and low moisture content is beyond the water activity meter accuracy, and so the correlation is an extrapolation into the very low water activity regions until an improved instrumentation can be used for more measurements.

The final factors in formulating the moisture desorption is the porous nature of the leaves, in which the surface wetted area is not so simple, and the several pauses in moisture desorption due to erratic heating must be accommodated. For this a slight modification to phase change kinetics Equation 7 that would look like Equation 5 includes an effective θ that initializes at whatever pause level the process is at. The normalized water mass loss rate (s^{-1}) can be empirically related to a normalized moisture content to a power fraction, as in

$$d\left(\frac{f_{v,o}\,\theta_{o,i}}{f_0}\right)/dt = -\left(\frac{f_{v,o}\,\theta_{o,i}}{f_0}\right)^{p_o} A_w(F/\varepsilon) \quad (13)$$

where A_w is the fitted specific wetted area (m^{2}kg^{-1}) that are the characteristics of a hygroscopic material, and the reference (or native) moisture content is f_0 , and paused moisture content

is, $f_{v,o}$. Equation 13 fitted quite well the TGA data of fresh and dried live leaves, as subjected to various temperature profiles [paper being prepared]. Examination of Equation 5 provides the identification of the terms as, the activation energy, $E_{oo1} = 49.3 + \Delta G_{dif}$ (kJmol^{-1}), exponent of temperature term, $v_{oo1} = -3$, pre-exponential constant, $A_{oo1} = A_w \exp(35.293) \left(\frac{M_v}{2\pi R}\right)^{1/2}$ or , $A_{oo1} = A_w(3.948E + 16)$, grouped component's reaction order, p_o, interaction matrix element, $a_{oo} = 1$, and an adaptive factor, $r_{oo1} = \left(\frac{f_{v,o}}{f_0}\right)^{(p_o-1)}$. The reversible reaction of moisture adsorption has the following additional terms, activation energy, $E_{oo2} = E_{001}$ (kJmol^{-1}), exponent of temperature term, $v_{oo2} = v_{001}$, pre-exponential constant, $A_{oo2} = A_{001}$, and adaptive factor, $r_{002} = (-P_v/P_{veq})\, r_{001}$. These equations proved their value in the cone calorimeter tests of leaf drying of several species. It is interesting that the moisture isotherm relation in Equation 10 has unvarying empirical constants among the 12 plant species tested (within experimental errors of the water activity meter). While the coefficients for moisture desorption process, which are specific wetted area, desorption reaction order, and native moisture content vary considerably with the plant species. An obvious application can be made to assessing the condition of fresh litter diurnally, in addition to their flammability potential.

4. Specific Heat Capacity and Exothermic Heat of Charring varying With Components

The data for the 12 dried leaf species from a modulated DSC and a calibrated TGA has provided their specific heat capacity and exothermic heat of charring that may be correlated with composition, temperature, and degraded mass. The resulting correlation for specific heat to within experimental errors is [13, 14, and paper being prepared],

$$C_{p,dry} = C_{max} \left[\frac{T}{T_{max}}\right]^n \text{while } T < T_{max} \qquad (14)$$

C_{max} is a fit parameter which is the maximum specific heat which occurs when the temperature in Kelvin exceeds that of T_{max} , which is another fit parameter. n is near unity. Clearly the material composition is changing after T_{max} , but the overall specific heat, neglecting the heat of reaction, is nearly constant for all our leaf species. Although the fit parameters has been derived for each plant species, it was useful with a small loss of predictability to correlate $C_{max,j}$ with the specific heats of the 12 components of the leaf as weighted by their mass fraction and setting $T_{max,j}$ and n_j to constants among all species. The specific heat of water (for j = 0) is included in the pyrolysis modeling via the formula (air is ignored as being such a small mass even in comparison to ash),

$$C_{p,i} = \left[\sum_{j=0}^{j=6} C_{p,j,i}(f_{v,j}\,\theta_{j,i} + f_{c,j}\theta_{7+j,i})\right] / \sum_{j=0}^{j=6} (f_{v,j}\,\theta_{j,i} + f_{c,j}\theta_{7+j,i}) \qquad (15)$$

Where the index i represents evaluating the expression at temperature, T_i. We note that the specific heat of water has a different temperature dependency than that of the dry leaf. Equation 15 then shows the dominance of moisture on the heat capacity of live leaf at initial time, and then ends up after full degradation, the heat capacity of lignin char at high temperatures. Since the organic char is not fully graphitic, it can be expected to have the temperature dependency that of

Equation 14, which is in contrast to that used for char in the literature. Finally, as the organic char is oxidized the leaf is left with the ash, and its specific heat.

The heat of pyrolysis reactions was determined as the difference between the overall heat process and the heat capacity, and had slight positive values at less than 200°C and generally negative values at the higher temperatures of degradation [paper being prepared]. It is postulated that the positive values at low temperatures were due to melting of some components prior to their devolatilization, and that negative values at high temperatures were due to charring reactions of various leaf components. The overall exothermic H_p heat of pyrolysis reactions (Jg^{-1}) has been determined for each plant species. However, with the availability from pyrolysis kinetics modeling for the component mass losses with temperature, the individualized exothermic heat of pyrolysis $H_{p,j}$ was also estimated for each degrading components, as there were peaks in the exothermic heat values that correspond to the peaks in mass loss rate values.

5. Thermal Conductivity, Surface Emissivity, and Convective Heat Transfer

With data from thermocouples attached to leaf surfaces in the cone calorimeter tests and with data obtained earlier, an approximate inverse heat conduction analysis was used to estimate thermal conductivity and convective heat transfer coefficient with test time. Surface emissivity of the leaf has been well studied as a function of source wavelength, moisture content, and foliage density [19]. With the cone heater set at 35 kWm^{-2} it was determined its dominant wavelength result in the live leaf emissivity of approximately 0.9 and for a dried leaf the emissivity of approximately 0.8. So the radiant energy absorbed is about 31.5 kWm^{-2} initially, and then after dryout, the radiant energy absorbed is about 28 kWm^{-2}. The actual energy absorbed is calculated from the summation of (1) heat capacity (from Equation 15) times averaged temperature rise rate (from the thermocouples), (2) the moisture heat of desorption times moisture mass loss rate, and (3) pyrolysis heats of reactions times pyrolysis mass loss rate. The difference between the radiant energy absorbed and actual energy absorbed are the energy losses from the exposed leaf surface to the ambient via convection and emitted radiation, and from the back leaf surface to the ambient as mediated via heat conduction in the leaf. The presence of smoldering and flaming adds an additional heat source, which was only approximated because CFD models were not being used in the spreadsheet. Assuming convective heat transfer to the ambient to be similar on both sides of the leaf, the convective heat transfer coefficient had a reasonable value of approximately 0.04 $kWK^{-1}m^{-2}$. This helped confirm a reasonable contact of thermocouples to the leaf surfaces.

The thermal conductivity evaluation can be subject to large errors, as it relies on good thermocouple contacts to the leaf surfaces, is dependent on other parameters that are also error prone, can vary with depth in the leaf, and is constantly changing due to temperature, moisture, and degradation. These factors make thermal conductivity modeling very challenging, but must be addressed because the surface thermocouples show a large temperature gradient within the dried leaves, potentially affecting their fire behavior. To overcome these difficulties, there are theoretical and literature considerations. As one example the live leaves provide the advantage of high moisture content (very small void space) and cell wall components that have some well-known values of thermal conductivity, which initially will mean the thermal conductivity of around 0.55 $Wm^{-1}K^{-1}$ [20] for most live leaves.

In the case of 40 tobacco leaves stacked on top of each other and subject to impulse heating on one side and measured with the interlayers of thermocouples in an insulated cylinder pan, show via a transient inverse conduction analysis, a thermal conductivity of dried leaves of ~0.1 $Wm^{-1}K^{-1}$ that change little with temperature, and values up to ~0.32 $Wm^{-1}K^{-1}$ for higher moisture (34%) and high temperature values (373°K) [17]. Since moisture is the only factor in enhancing the heat flow through thermal conductivity, and using water thermal conductivity of 0.61 $Wm^{-1}K^{-1}$ only brings the leaf thermal conductivity up to 0.23 $Wm^{-1}K^{-1}$ for a moisture content of 34% as a theoretical maximum in a parallel matrix structure. One must then postulate a cellular water thermosiphon within the void space of the individual cells to enhance the thermal conductivity by at least 0.09 $Wm^{-1}K^{-1}$, a concept that was successfully introduced in a generalized correlation of the water frost thermal conductivity [21]. The semi-theoretical model developed for the leaf is a weighted average of series and parallel structures that includes volumetric contributions of leaf components, water, and air, with the void space heat transfer being enhanced by the heat of desorption driven by water vapor diffusion flux within the relatively sealed cells. The effective air thermal conductivity with the thermosiphon effect is [21],

$$k_{a,eff} = k_a + \left(\frac{D_{vs}\, P_{veq}}{\tau_s T}\right)\left(\frac{P_{atm}}{P_{total}}\right)\left(\frac{\Delta H_{veq}}{RT}\right)\left(\frac{\Delta H_{veq}}{RT} - 1\right) \qquad (16)$$

Where the air thermal conductivity, diffusion coefficient and tortuosity formulations are,

$$k_a = 0.00272\ T^{0.5} / \left[1 + (300 / T)\ 10^{(-23.4\ /\ T)}\right] \quad Wm^{-1}K^{-1} \qquad (17)$$

$$D_{vs} = 0.00001198\ T^{1.75} \quad m^2s^{-1} \qquad (18)$$

$$\frac{1}{\tau_s} = \text{minimum}\left[1, \left(\frac{f_{v,o}\ \theta_{o,i}}{f_{o,tsp}}\right)^b\right] \qquad (19)$$

Equation 19 for tortuosity was fitted to the cone calorimeter data for the drying of longleaf pine needles (paper being prepared). Material matrix volume that decreases with time t_i for thermal conductivity is the sum of the component masses as divided by their corresponding component density $\rho_{j,i}$ as in,

$$V_{r,i} = \sum_{j=0}^{j=6} V_{r,j,i} + V_{r,7+j,i} = \sum_{j=0}^{j=6} m_{r,0}(f_{v,j}\,\theta_{j,i}/\rho_{j,i} + f_{c,j}\theta_{7+j,i}/\rho_{7+j,i})/(1 + f_{v,0} + f_{c,0}) \qquad (20)$$

The internal air volume displacing the loss in moisture or material volume is,

$$V_{a,i} = V_{r,0} - V_{r,i} \qquad (21)$$

It is interesting that the cone calorimeter tests of very thin wood slab indicate a linear shrinkage of around 10% in all wood physical dimensions at high temperatures of around 375°C or higher. Assuming that matrix components are not able to increase in densities, this could mean a shrinkage of initial volume by 37%, which means the air volume will shrink even further as following Equation 21. This effect would be responsible for cracking in thick wood undergoing

charring, and would predict the leaves curling in the direction of the heat, if not restrained and especially with a low dried thermal conductivity. Overall thermal conductivity is weighted between parallel and series parts [18, 20, and 21],

$$k_i = (1-B)\left(\frac{k_{aeff,i}V_{a,i}}{V_{r,0}} + \sum_{j=0}^{j=13}\frac{k_{j,i}V_{r,j,i}}{V_{r,0}}\right) + B\Big/\left(\frac{V_{a,i}}{k_{aeff,i}V_{r,0}} + \sum_{j=0}^{j=13}\frac{V_{r,j,i}}{k_{j,i}V_{r,0}}\right) \quad (22)$$

In this semi-theoretical expression there are only three coefficients, which are B, b, and $f_{0,tsp}$ that need defining with fitting the data. All the other coefficients have been determined in the other tests or in the literature. The temperature variation of thermal conductivity is a built-in effect of the cellular thermosiphon due to the temperature dependency of the saturated water vapor pressure of the moist material and of the water vapor diffusion coefficient. Literature review has indicated the temperature dependency of the air itself, and that of thermal radiation of the fibers, are not enough to account for the measured thermal conductivity rise with the increase in temperature during moisture evaporation. Once the material is dried and the temperature continues to rise, the pyrolysis of the components will result in the decrease in the thermal conductivity that is evidently predicted with Equations 20 to 22, except in the event of material shrinkage. Even during char oxidation the thermal conductivity continues to decrease, as the air portion is increasing. This process is consistent with the wide temperature differences between exposed surface and shaded surface during pyrolysis, but a very small temperature difference in the case of moisture evaporation of live leaves, during the cone calorimeter testing. Eventually, to overcome the various errors in the thermal conductivity measurements, a new kind of thermal conductivity apparatus needs to be developed to accommodate thin materials with moisture and pyrolysis features along with their temperature dependency.

6. Modeling Ignition for Smoldering and Flaming via Heat Release Rate (HRR)

By having oxygen consumption data with the cone calorimeter in the leaf pyrolysis tests in which the CO2 and CO data mirrors O2 consumption profile [28, paper being prepared], means that smoldering oxidation of organic char is the main source of CO2 and CO, even as low as 200°C in which the lignin begins charring and exposes reactive carbon to the air. There is then the expectation of simultaneous char oxidation that eventually peaks at around 450°C as measured in the TGA in the presence of air. The heat of combustion of the organic char in the cone calorimeter was measured to be ~20 kJg^{-1}, which correspond to that of the virgin lignin. The overall chemical HRR can be given by the expression that includes some of the volatiles being caught in combustion as,

$$\dot{H}_{net,i} = \frac{-m_{r,0}}{(1+f_{v,0}+f_{c,0})}\sum_{j=0}^{j=6}\left(f_{v,j}\,\dot{\theta}_{j,i}e_jH_{c,j} + f_{c,j}\dot{\theta}_{7+j,i}e_{7+j}H_{c,7+j}\right) - 32.8\dot{m}_{soot} - 10.1\dot{m}_{CO} \quad (23)$$

The stoichiometric net heat of combustion, $H_{c,j}$, of the component j is available from the ultimate analysis [1]. The net heat of combustion of water vapor and minerals are zero. We note that since the cone calorimeter tests show the organic char still retains the empirical elemental formula of the parent components, so that for the most part we have, $H_{c,j} = H_{c,7+j}$, helping to simplify the smoldering kinetics and combustion. In the case of longleaf pine, the capturing of

8% volatiles into smoldering combustion, has the evaluation, $e_j = 0.08$ (and is 1.0 during flaming combustion), and the combustion of organic char, has the evaluation $e_{7+j} = 1$, for its complete combustion, as found in the cone calorimeter tests in burning completely to ash. Since the cone calorimeter provided measurements of CO and soot mass flow rate, Equation 23 includes their effects on the incomplete combustion of the process, which we express as chemical HRR, for comparison with the cone calorimeter's measurements of HRR.

The incorporation of such oxidative heat release, along with the other properties obtained earlier, should provide the CFD pyrolysis model a prediction of smoldering that may continue until ashes. For prediction of sustained flaming ignition, all the combustion capturing factors are set to unity, $e_j = 1$, the production of soot and CO are set to zero in Equation 23, and then calculate if the virtual ignition net HRR flux, as

$$\left(\dot{H}_{net,i}/A_p\right) \geq \dot{H}''_{ignite} = 24\ kWm^{-2} \qquad (24)$$

is satisfied [29] in the presence of an ignition source such as glowing, spark plug, flame-tip, fire brands or hot-air plasma. If such flaming ignition criteria is not met, then the process continues naturally as smoldering (which for our purposes is the simultaneous events of volatile production and escaping and oxidation of organic char), and providing that the heat balance as calculated by the CFD keeps the temperature high enough for pyrolysis. Even though all plant species remained smoldering to the end of the tests at the irradiance of 35 kWm^{-2}, there were some species that transitioned from smoldering to flaming at the higher irradiant exposure of 50 kWm^{-2} in the cone calorimeter. This was easily determined as the appearances of the diffusion flame and conversion of white smoke to black smoke that coincided with sudden increases in CO_2 production and O_2 consumption. With various kinetics and properties that were identified and derived in this paper without the benefit of using CFD pyrolysis modeling, it would then be the opportune moment for the CFD pyrolysis prediction for the smoldering to flaming transition, as well as some other three dimensional fire effects implied, such as leaf curling during heating. Other situations for ignition of vegetation [30, 31] can benefit from this more general criteria of ignition that should be applicable to any moisture status of the foliage.

Having emissions measured with NDIR, FTIR, and GC2xTOFMS helps establish combustion efficiencies for determining the heat release rate and for volatiles that escape smoldering and flaming. The role of CO_2 (and CO), although in the end a large emission source, offered a surprising profile that mirrors the O_2 consumption profile [28, paper being prepared], leading to greater role for smoldering than originally thought. Literature review of microalgae pyrolysis, combustion, and gasification with a TGA-DSC linked with MS, showed the very small role for H_2O, CO, and CO_2 for the lipid, protein, and carbohydrate contents of the microalgae during pyrolysis in inert gases [32]. In addition to these three contents, the leaves also have hemicellulose, tannin, and lignin contents, from which CO_2 is also not easily produced from the native composition during pyrolysis in inert gases [4]. The cone calorimeter FTIR is limited to low molecular weight gases, the largest production rates of which are CO_2, H_2O and CO, but for trace gases the largest production is methane CH_4 [28, paper being prepared], which itself is a small molar fraction of CO concentrations, a summary that was echoed in Yokelson, et.al. [33] for their study of smoldering emissions of forest floor material. This has also been confirmed by

Qiao [4] using fast pyrolysis TGA with FTIR on the composition basis as from castor oil, corn starch, soy protein, lignin, xylan, and cellulose.

With the remaining trace gases in the noisy ppm range of the cone calorimeter FTIR, the focus for emissions shifted to investigating the contents of white smoke during leaf pyrolysis at the irradiance of 35 kWm^{-2}, which had high molecular weights gases (light tar) and aerosols (heavy tar), as indicated from preliminary measurements with the GC2xTOFMS, showing the compounds attributed to cellulose, hemicellulose, and lignin compositions [5], as well many more compounds from other compositions (i.e. lipids and protein) and many others that previously were undetectable, even with a high resolution FTIR [28, 32]. A great majority were ketones, alcohols, and phenols. These are the compounds that can be captured into the flame sheet and be combusted by O_2 into CO_2, CO, H_2O, and soot measured with the cone calorimeter, and that will otherwise escape into the atmosphere in the absence of the flame sheet, and become a problem when cooled.

7. Conclusions

On the basis of the results from the cone calorimeter tests of the single layer of live leaves in varying conditions and environments are able to reveal the shortcomings of the existing model that is remedied with an updated vegetation model that is more detailed, and can be accommodated with today's computer technology. Moisture desorption, via the new phase change kinetics coupled with the universal moisture isotherm relationship, can start at any moisture level, and be dried to any moisture content, but at the limit of the equilibrium moisture content. As environmental conditions changes the moisture can be reabsorbed to the appropriate equilibrium moisture content. However, the moisture isotherm also applies to high temperatures associated with pyrolysis, meaning that the moisture desorption occurring at the same time as fuel pyrolysis will affect the heat of combustion of the volatile mixture. The fuel pyrolysis itself is now based on five grouped degrading components, which are lipids, digestible, hemicellulose, glucan, and phenolic, as based on extensive TGA data, and which the components have varying pyrolysis temperatures, charring, and heat of combustions. Since the flaming ignition can be reliably based on a critical virtual heat release rate, the differing flammability and ignitability among the various species has the potential of being explained with the new pyrolysis and combustion model.

There is also the possibility for the modeling of smoldering in a way that could not be previously achieved. This comes especially with the changing heat for moisture desorption, leveling of the specific heat around 200^{o}C, presenting the exothermic heat of pyrolysis, the insulating effect of the lowered thermal conductivity due to pyrolysis, and the lowered temperature for char oxidation with its heat release rate, all of which promote smoldering and a possible temperature run-away process to reach flaming ignition. All these physical processes has been observed and quantified in separate tests, but ultimately it is their incorporation into the CFD pyrolysis modeling that will show the various promising features, such as leaf curling towards the heat, or the unusual features of leaf ignitions reported in the literature.

Flammability and emission are still treated separately in the fire models, as the content of the white smoke has not yet been clearly established to allow for any significant gas phase kinetics

analysis. For estimating emissions one would just determine the total mass of CO2, CO, H2O, and soot as combustion products and divide by the fuel dry mass for their emission factors, and the total mass of trace gases (from a high resolution FTIR) can be referenced to the total mass of CO. The mass of the white smoke can be obtained by the difference between the fuel mass loss and the fuel mass volatized/combusted as low molecular weight gases (as mass of CO2, CO, soot, trace gases, and H2O minus that of consumed mass of O2). The white smoke developed in the cone calorimeter unpiloted experiments and currently being measured with the GC2xTOFMS process (currently estimated at 71% of dry mass in the case of longleaf pine needles), can be treated as emissions when it mixes with the exhaust combustion plume, but is also coincidently providing perhaps the better example of primary pyrolysis products in the real world outside of the TGA experiments with inert gases.

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9. References

[1] F. Matt, M. Dietenberger, and D. Weise, Summative and Ultimate Analysis of Live Leaves from Southern U.S. Forest Plants for Use in Fire Modeling, Energy Fuels (2020) 34, 4, 4703-4720, https://doi.org/10.1021/acs.energyfuels.9b04107

[2] Q.V. Bach, W.H. Chen, A comprehensive study on pyrolysis kinetics of microalgal biomass, Energy Conversion and Management 131 (2017) 109–116.

[3] Q.V. Bach, W.H. Chen, Pyrolysis characteristics and kinetics of microalgae via thermogravimetric analysis (TGA): A state-of-the-art review, Bioresource Technology 246 (2017) 88–100.

[4] Yingyun Qiao, Bo Wang, Yaoyao Ji, Fanfan Xu, Peijie Zong, Jinhong Zhang, Yuanyu Tian, Thermal decomposition of castor oil, corn starch, soy protein, lignin, xylan, and cellulose during fast pyrolysis, Bioresource Technology 278 (2019) 287–295.

[5] Chenxi Zhao, Enchen Jiang, Aihui Chen, Volatile production from pyrolysis of cellulose, hemicellulose and lignin, Journal of the Energy Institute 90 (2017) 902-913.

[6] Xiaowei Zhou, Wenjun Li, Ross Mabon and Linda J. Broadbelt, A mechanistic model of fast pyrolysis of hemicellulose, Energy Environ. Sci., 2018, 11, 1240.

[7] Virginie Tihay, Christophe Boulnois, Philippe Gillard, Influence of oxygen concentration on the kinetics of cellulose wadding degradation, Thermochimica Acta 525 (2011) 16–24.

[8] Dekui Shen, Lanqing Zhang, Jiangtao Xue, Shipian Guan, Qian Liu, Rui Xiao, Thermal degradation of xylan-based hemicellulose under oxidative atmosphere, Carbohydrate Polymers 127 (2015) 363–371.

[9] Anne-Laure Lozano, Fabien Cherblanc, Bruno Cousin, Jean-Claude Benet, Experimental study and modelling of the water phase change kinetics in soils. European Journal of Soil Science, Wiley, 59 (5), (2008) 939-949.

[10] V.L. Snoeyink, and D. Jenkins, Water Chemistry. (1980) John Wiley & Sons, New York.

[11] Alberto Schiraldi, Dimitrios Fessas, Marco Signorelli, Water Activity in Biological Systems – A Review, Pol. J. Food Nutr. Sci., Vol. 62, No. 1, (2012) 5-13.

[12] D.F. Othmer, Correlating vapor pressure and latent heat data. J. Industrial Eng. Chem., Vol. 32, (1940) 841-856.

[13] M.A. Dietenberger, C.R. Boardman, and D. Wiese, Heats for Combustion, Capacities, and Evaporation of Fresh Leaves and Their Relationships to Leaf Compositions, Proceedings for the 6th International Fire Behavior and Fuels Conference, April 29 – May 3, (2019) Albuquerque, New Mexico USA.

[14] P. Rahimi Borujerdi, B. Shotorban, S. Mahalingam, and D. R. Weise. Modeling of water evaporation from a shrinking moist biomass slab subject to heating: Arrhenius approach versus equilibrium approach. International Journal of Heat and Mass Transfer, Vol. 145, (2019) 118672.

[15] E.E. Thybring, Explaining the heat capacity of wood constituents by molecular vibrations. Journal of Materials Science 49, (2014) 1317–1327. doi:10.1007/s10853-013-7815-6.

[16] M.A. Dietenberger, Update for combustion properties of wood components, Fire and materials. Vol. 26 (2002) 255-267.

[17] T. Kuroiwa, N. Araki, and Y. Nakanishi, Y., Measurement of Thermal Conductivity of Cured Tobacco Material, Food Sci. Technol. Res., 14 (2), (2008) 124 – 131.

[18] M. Chandrakanthia, A.K. Mehrotrab, J.P.A. Hettiaratchi, Thermal conductivity of leaf compost used in biofilters: An experimental and theoretical investigation, Environmental Pollution 136 (2005) 167-174.

[19] B. Monod, A.Collin, G.Parent , P.Boulet, Infrared radiative properties of vegetation involved in forest fires, Fire Safety Journal 44 (2009) 88–95.

[20] J. Hunt, H. Gu, P. Lebow, Theoretical Thermal Conductivity Equation For Uniform Density Woods Cells, Wood and Fiber Science, 40(2), (2008), 167– 180.

[21] M.A. Dietenberger, Generalized Correlation of the Water Frost Thermal Conductivity, Int. J. of Heat Mass Transfer, 26, (1983) 607-617.

[22] T. Barboni, L. Leonelli, P.A. Santoni, V. Tihay-Felicelli, Aerosols and carbonaceous and nitrogenous compounds emitted during the combustion of dead shrubs according to twigs' diameter and combustion phases, Fire Safety Journal 113 (2020) 102988, https://doi.org/10.1016/j.firesaf.2020.102988

[23] Vadim Mamleev, Serge Bourbigot, Jacques Yvon, Kinetic analysis of the thermal decomposition of cellulose: The main step of mass loss, Anal. Appl. Pyrolysis 80 (2007) 151–165.

[24] Amini, Elham. 2020. "Characterization of Slow Pyrolysis Behavior of Live and Dead Vegetation." Ph.D. thesis, Provo, UT: Brigham Young University.

[25] Wenjie Sui and Hongzhang Chen, Effects of water states on steam explosion of lignocellulosic biomass, Bioresource Technology 199 (2016) 155–163.

[26] C.A. Wilson, J.T. Novak, Hydrolysis of macromolecular components of primary and secondary wastewater sludge by thermal hydrolytic pretreatment, Water Research 43 (2009) 4489-4498.

[27] Lipeng Zhou, Xiaomei Yang, Jiaolong Xu, Meiting Shi, Feng Wang, Chen Chen and Jie Xu, Depolymerization of cellulose to glucose by oxidation–hydrolysis, Green Chem., (2015), 17,1519. DOI: 10.1039/c4gc02151g

[28] T.Fateh, F. Richard, B. Batiot, T. Rogaume, J.Luche, J. Zaida, Characterization of the burning behavior and gaseous emissions of pine needles in a cone calorimeter – FTIR apparatus, Fire Safety Journal 82 (2016) 91–100, http://dx.doi.org/10.1016/j.firesaf.2016.03.008

[29] R.E. Lyon, J.G. Quintiere, Criteria for piloted ignition of combustible solids, Combustion and Flame, Volume 151, Issue 4, December (2007), 551-559.

[30] Lamorlette, A., M. El Houssami, and D. Morvan. 2018. "An Improved Non-Equilibrium Model for the Ignition of Living Fuel." *International Journal of Wildland Fire* 27 (1): 29–41. https://doi.org/10.1071/WF17020.

[31] Fletcher, Thomas H., Brent M. Pickett, Steven G. Smith, Gregory S. Spittle, Megan M. Woodhouse, Elizabeth Haake, and David R. Weise. 2007. "Effects of Moisture on Ignition Behavior of Moist California Chaparral and Utah Leaves." *Combustion Science and Technology* 179 (6): 1183–1203. https://doi.org/10.1080/00102200601015574.

[32] L. Sanchez-Silva, D. López-González, A.M. Garcia-Minguillan, J.L. Valverde, Pyrolysis, combustion and gasification characteristics of Nannochloropsis gaditana microalgae, Bioresource Technology 130 (2013) 321–331.

[33] Robert J. Yokelson, Ronald Susott, Darold E. Ward, James Reardon, and David W. T. Griffith, Emissions from smoldering combustion of biomass measured by open-path Fourier transform infrared spectroscopy, J. of Geophysical Research, Vol. 102, No. D15, (1997) 18,865-18,877

Appendix A: Coefficients of Vegetative Pyrolysis Model for Longleaf Pine

Table A1: Live longleaf pine needle pyrolysis kinetics coefficients (Interaction matrix is unitary $a_{jk} = [\![1]\!]$), Units are mol, m^3, s, kJ, K.

Element j,k,l	Component	f_j	$f_{v,j}$	p_k	r_{jkl}	A_{jkl}	v_{jkl}	E_{jkl}
0,0,1	Desorption	1.87	input	0.622	$\left(f_{v,o}/f_0\right)^{(p_o-1)}$	5.42E+12	-3	$49.3+\Delta G_{dif}$
0,0,2	Adsorption	1.87	input	0.622	$\left(-P_v/P_{veq}\right)r_{001}$	5.42E+12	-3	$49.3+\Delta G_{dif}$
1,1,1	Lipid Tar	0.227	0.227	7.01	1	3.20E+12	0	145.1
8,8,1	Lipid Char Oxy	Eq. 2	Eq. 2	-	-	-	-	-
2,2,1	Digest Tar	0.099	0.099	4.47	1	5.83E+08	0	112.7
9,9,1	Digest Char Oxy	Eq. 2	Eq. 2	-	-	-	-	-
3,3,1	Hemi Native Tar	0.174	0.174	6.63	1	7.40E+18	0	226.0
3,3,2	Hemi Depoly Tar	0.174	0.174	6.63	$(O_2/0.20946)^{u_3}$	1.13E+16	0	201.5
10,10,1	Hemi Char Oxy	Eq. 2	Eq. 2	-	-	-	-	-
4,4,1	Glucan Native Tar	0.201	0.181	6.86	1	4.47E+19	0	269.0
4,4,2	Glucan Depoly Tar	0.201	0.181	6.86	$(O_2/0.20946)^{u_4}$	3.48E+17	0	221.3
11,11,1	Glucan Char Oxy	Eq. 2	Eq. 2	0.874	$(O_2/0.20946)^{u_{11}}$	1.10E+09	0	156.2
5,5,1	Phenolic Tar	0.272	0.0887	1.428	1	5.37E+17	0	231.2
12,12,1	Phenolic Char Oxy	Eq. 2	Eq. 2	0.874	$(O_2/0.20946)^{u_{12}}$	1.10E+09	0	156.2
6,6,1	Ash Tar	0.0262	0	-	-	-	-	-
13,13,1	Ash Residue	Eq. 2	Eq. 2	0	1	1	0	0

The following are approximated until more data is obtained: $u_3 = u_4 = 1$ and $u_{11} = u_{12} = 2$

Table A2: Live longleaf pine needle: thermal coefficients

Element j	Native Component	$C_{max,j}$ ($Jg^{-1}K^{-1}$)	$T_{max,j}$ (K)	n_j	$H_{p,j}$ (Jg^{-1})	$\rho_{j,0}$ ($g(cm)^{-3}$)	$k_{j,0}$ ($Wm^{-1}K^{-1}$)	B	b	$f_{o,tsp}$
0	Moisture	4.176	-	-	Eq. 12	1.003	0.61	0.3	5	0.44
1	Lipid	2.7	498	1.15	0	1.00	0.41			
2	Digestible	2	498	1.15	-450	1.56	0.41			
3	Hemi Cellulose	1.9	498	1.15	-450	1.54	0.41			
4	Glucan	2.1	498	1.15	-450	1.54	0.41			
5	Phenolic	2.2	498	1.15	-450	1.36	0.41			
6	Ash	1.1	498	1.15	0	2.17	2.5			
11	Glucan Char	2.1	498	1.15	0	1.54	0.41			
12	Phenolic Char	2.2	498	1.15	0	1.36	0.41			
13	Ash Char	1.1	498	1.15	0	2.17	2.5			

Table A3: Live longleaf pine needle: elemental formula (mass), net heat of combustion (dry basis), and smolder capture factors

j	Fuel Component	C	H	O	N	S	Min	Mass Sum	$H_{net,j}$ (kJg^{-1})	e_j
0	Water Vapor	0	0.2015	1.5996	0	0	0	1.8011	0	0.08
1	Lipid Tar/Gas	0.1486	0.0205	0.0582	0	0	0	0.2273	29.2	0.08
2	Digest Tar/Gas	0.0407	0.0059	0.0402	0.0122	0	0	0.0990	17.6	0.08
3	Hemi Tar/Gas	0.0783	0.0103	0.0858	0	0	0	0.1744	15.6	0.08
4	Glucan Tar/Gas	0.0804	0.0112	0.0893	0	0	0	0.1809	15.7	0.08
5	Phenol Tar/Gas	0.0507	0.0045	0.0336	0	0	0	0.0888	20.6	0.08
11,12, 13	Char (Glucan, Phenolic, Ash)	0.1137	0.0109	0.0833	0	0.0018	0.0199	0.2296	19.5	1
	Sum (no water)	0.5124	0.0633	0.3904	0.0122	0.0018	0.0199	1 (dry)	20.3	Dry leaf