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Thermal Decomposition of Vegetative Fuels

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Some of the data in this presentation has not been through the NIST review process and should be considered experimental and/or draft results.

engineering laboratory

The Wildfire Problem

- Increasing number of people moving to areas in or near fire prone wildlands[1]
- Accurate predictive modeling of wildland fires can mitigate the risk that these fires pose
- Physics based models[8] can better capture the controlling mechanisms of wildland fires, account for:
  - Variations in fuel species
  - Effect of fuel management (e.g., thinning)
  - Variable environmental conditions

Physics–based Modeling of Wildfires

- Comprehensive models require a large number of input parameters
- Parameters may be obtained by
  - Direct experiment
  - Literature search
  - Optimization techniques
- Thermal decomposition measurements are not readily available for a variety of common vegetative fuels[10]
  - Fuel properties that are available from such experiments can be subject to large uncertainty[10]

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Existing Measurements and Models of Vegetative Fuels

- Previous mg-scale measurements[11–20]
  - Philpot: Plant mineral content vs. pyrolysis behavior (rate, onset temperature, and residue yields)
  - Shafizadeh: Composition (cellulose, hemicellulose, and lignin) impact on thermal properties, decomposition pathways, species yields
  - Sussot: Temperature range of decomposition, heat of pyrolysis, total energy released
- "Standard Fire Behavior Fuel Models" [6]
  - Heat content prescribed as 18.6 kJ g^{-1} for all but one (of 40 available) fuel models
    - "Fuel Particle Heat Content" [BTU/lb]

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Focus of Study

- Perform thermal analysis experiments on a variety of common vegetative fuels
  - Extract thermal decomposition mechanisms + associated kinetics and heats of combustion
  - Store results in freely available database

- Conduct CFD simulations of wildfire flame spread using thermal decomposition models determined from experiments

- Quantify model sensitivity to measured variations in fuel decomposition behavior

Vegetative Fuels

- Six species commonly found in Western United States
  - Bulk sample (stems + leaves) picked from a series of randomly selected plants
  - Obtained between May and July of 2017

Vegetative Fuels

Introduction
- Background
- Focus of Study

Experimental
- **Vegetative Fuels**
- TGA Experiments
- MCC Experiments

Modeling
- Simulations of Wildfire Spread

Conclusions and Future Work

Origin	Scientific Name	Common Name
Pacific Southwest Research Station (California)	Adenostoma Fasciculatum	Chamise
	Arctostaphylos Glauca	Bigberry Manzanita
	Ceanothus Greggii	Desert Ceanothus
	Ceanothus Leucodermis	Chaparral Whitethorn
Rocky Mountain Research Station (Montana)	Pinus Contorta	Lodgepole Pine
	Pseudotsuga Menziesii	Douglas-Fir

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Thermal Analysis Experiments

- Thermogravimetric Analysis (TGA)
  - Degradation Reaction Mechanism
  - Thermal Degradation Kinetics (A_i, E_i)

- Microscale Combustion Calorimetry (MCC)
  - Heats of combustion of gaseous volatiles (ΔH_c)
  - Char Yields (μ_{char})

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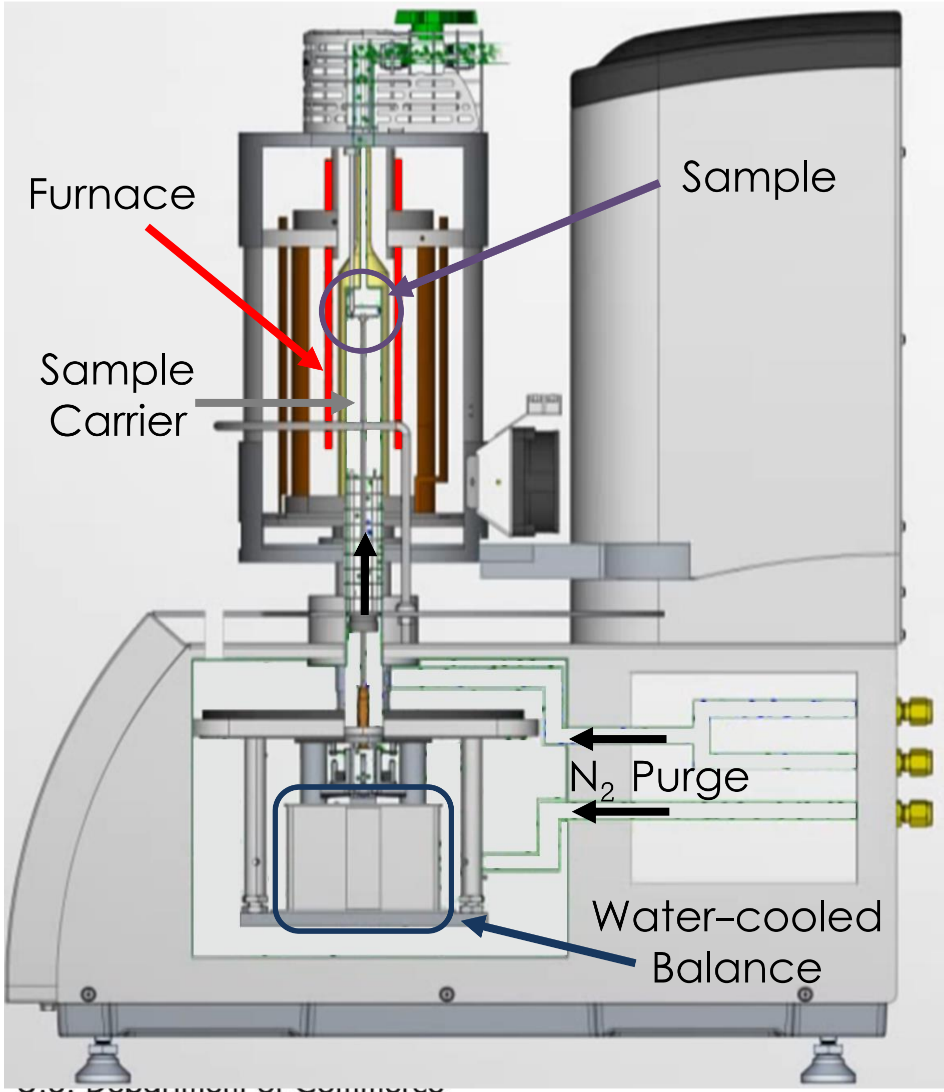
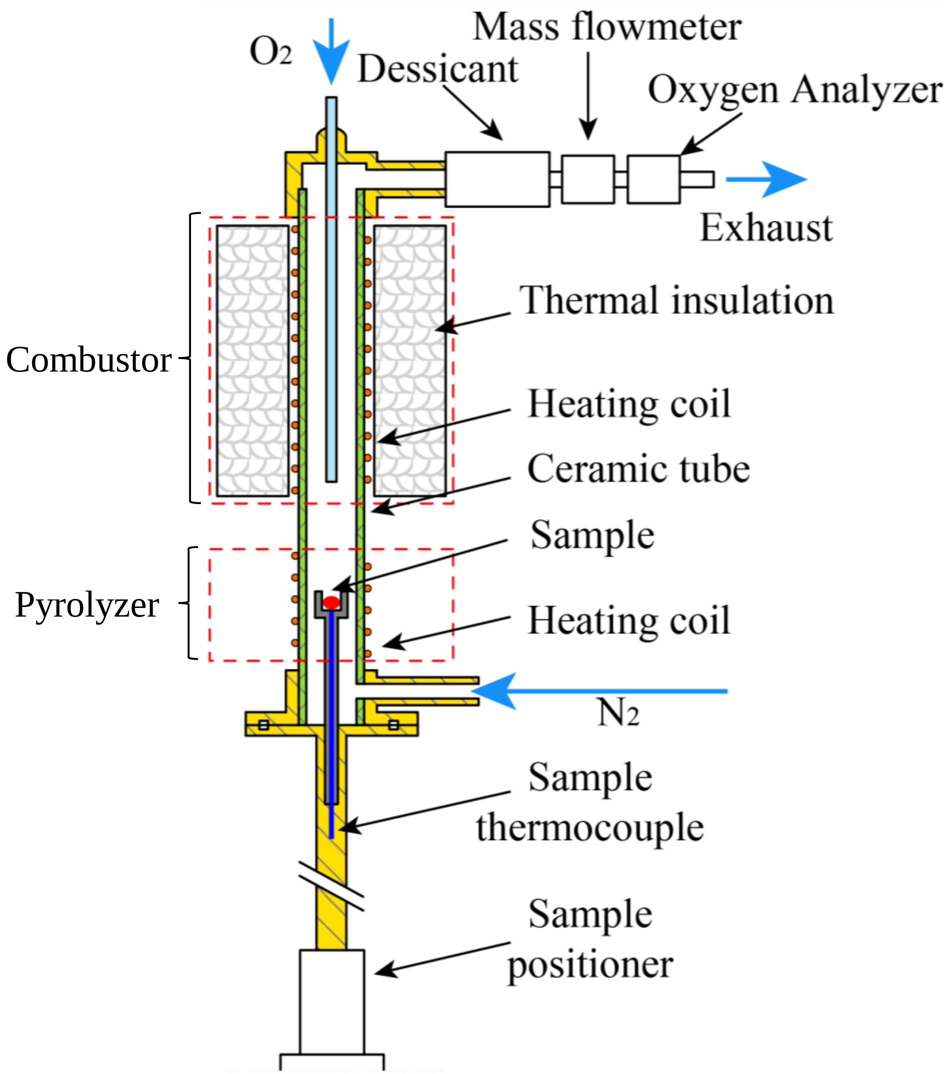
Thermogravimetric Analysis (TGA)



- Furnace
  - Continuously purged with N_2
  - Well-defined temperature program
- Measure
  - Mass of sample as a function of temperature
- Determine
  - Thermal degradation reaction mechanism
  - Associated kinetics (A_i, E_i)

Microscale Combustion Calorimetry (MCC)



- Pyrolyzer
  - Continuously purged with N_2
  - Well-defined temperature program
  - Gaseous pyrolyzates flows to combustion chamber
- Combustor
  - Gases react with excess O_2
  - HRR measured by oxygen consumption calorimetry
- Determine
  - Heats of Combustion of Gaseous pyrolyzates (ΔH_c)

Milligram–Scale Experiments

- Vegetative Fuel Samples
  - Stored in desiccator, minimum of 48 h
  - Whole leaf / stem samples < 0.75 mm thick
- Test Conditions
  - Sample mass: 4.5 to 6.5 mg
  - Initial isotherm: 20 minutes at 75 °C
  - Heating Rate: 10 K min^{-1}
  - Max Temp: 700 °C
  - Environment: Pure N_2
  - Crucible Type: Alumina
  - Replicate tests: TGA (5x), MCC (3x)
- Calibration
  - Temperature (156.6 to 961.8 °C): Within 3 months
  - TGA baseline, MCC O_2 sensor: Daily

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TGA Experiments

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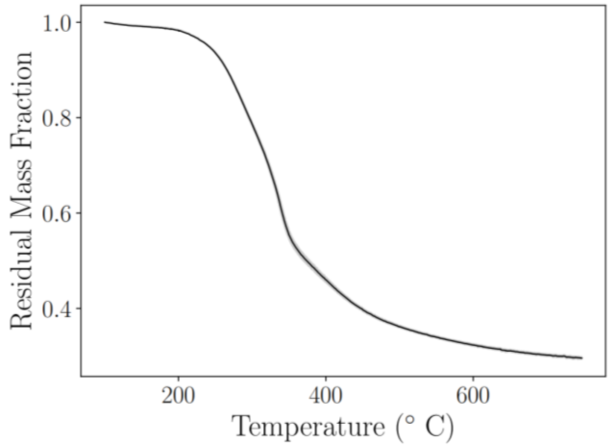
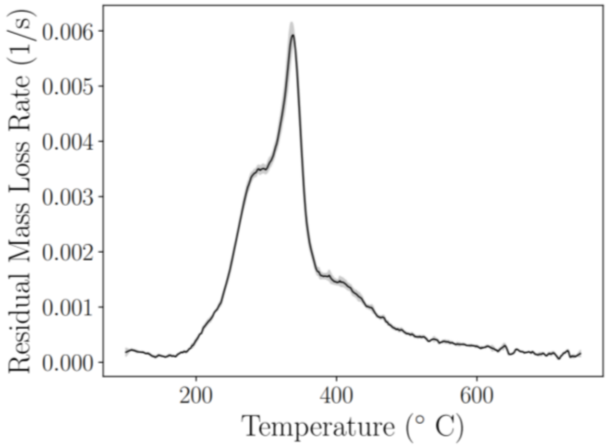
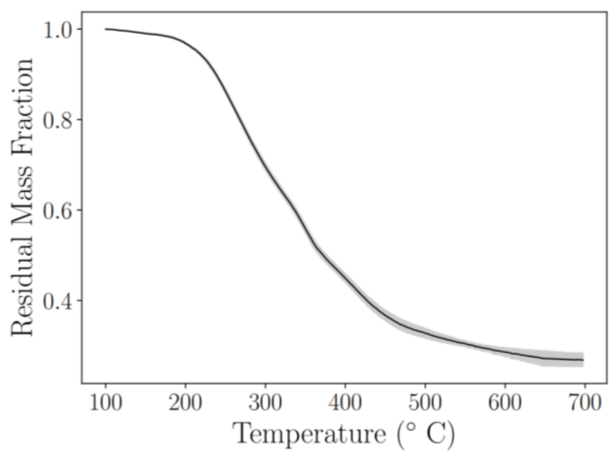
Conclusions and Future Work

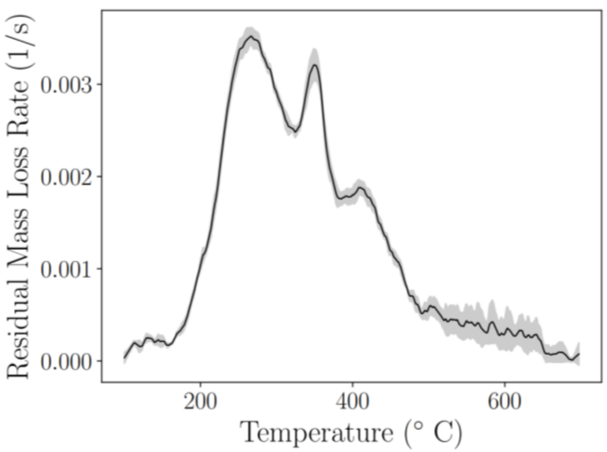
- Chamise Stem





- Big Berry Leaf





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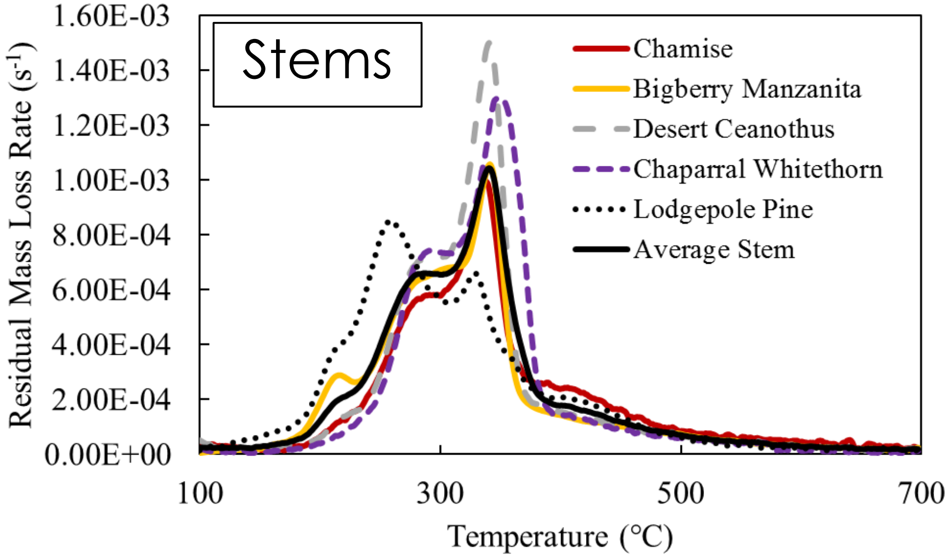

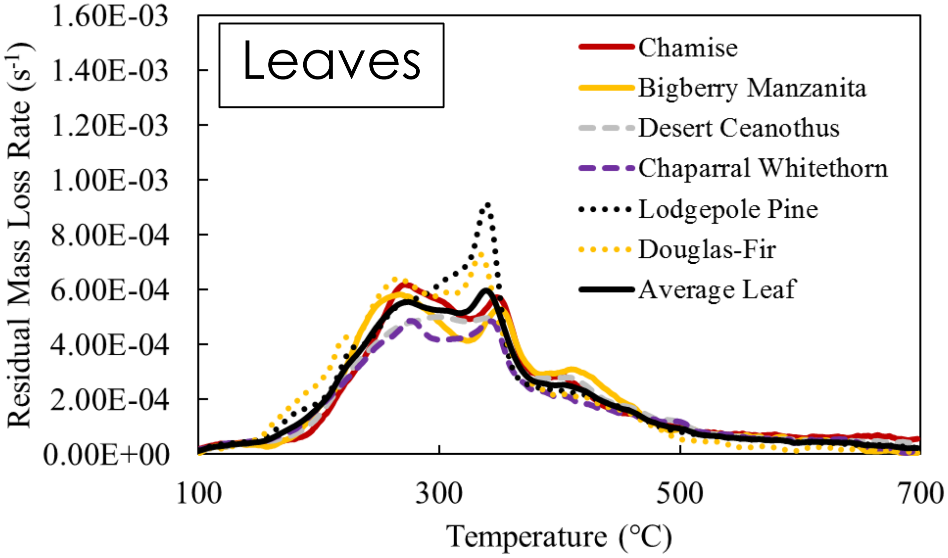

– Higher peak mass loss rate, little mass loss above 400 °C
– Typically two distinct mass loss peaks

– Decomposition occurs over a wider temperature range
– Multiple, overlapping reactions

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Thermal Decomposition Mechanisms

- Assumed degradation mechanism[12,14]
  - Parallel, first order, Arrhenius rate reactions

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -\sum_i (1-\nu_i) m_i A_i \exp\left(\frac{E_i}{RT}\right)$$

- m Total sample mass
- m_i Mass of component i
- T Sample temperature
- R Universal gas constant
- A_i, E_i Kinetic parameters describing the reaction
- Δm_i Mass lost as volatiles in reaction step i
- μ_{char} Char yield ($\mu_{char} = 1 - \sum_i \Delta m_i$)

- Kinetic parameters (A_i, E_i) and mass loss in each reaction step (Δm_i) determined using the algorithm developed in previous presentation [26]

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Experimentally–Measured and Model–Predicted TGA Data

Introduction
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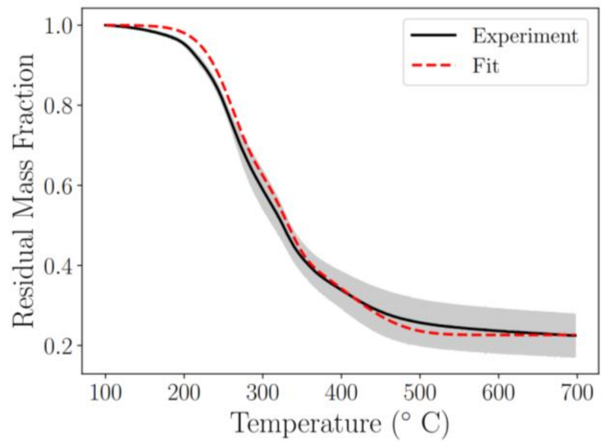
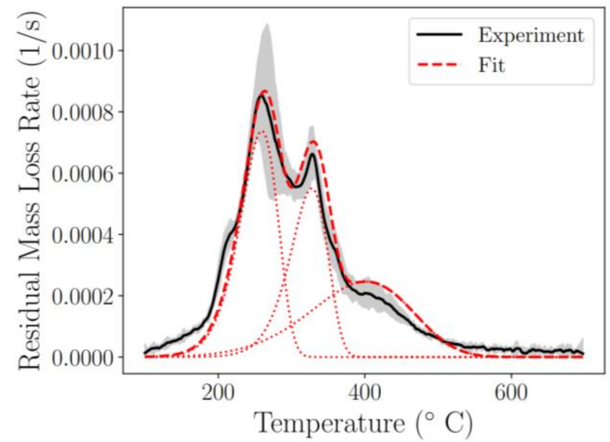
Conclusions and Future Work

- Lodgepole Pine Stem





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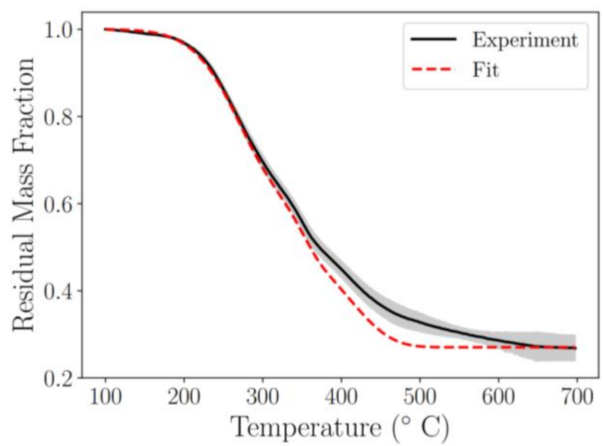

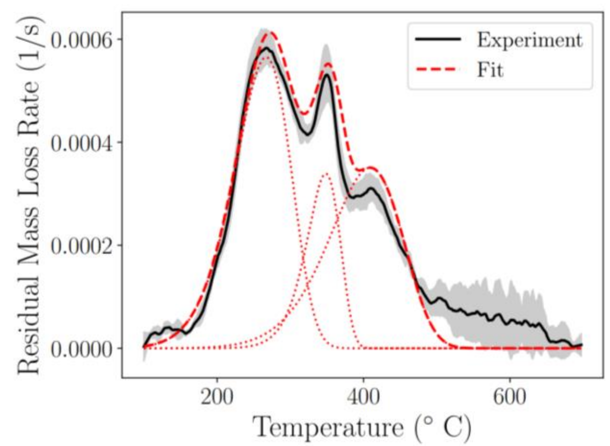

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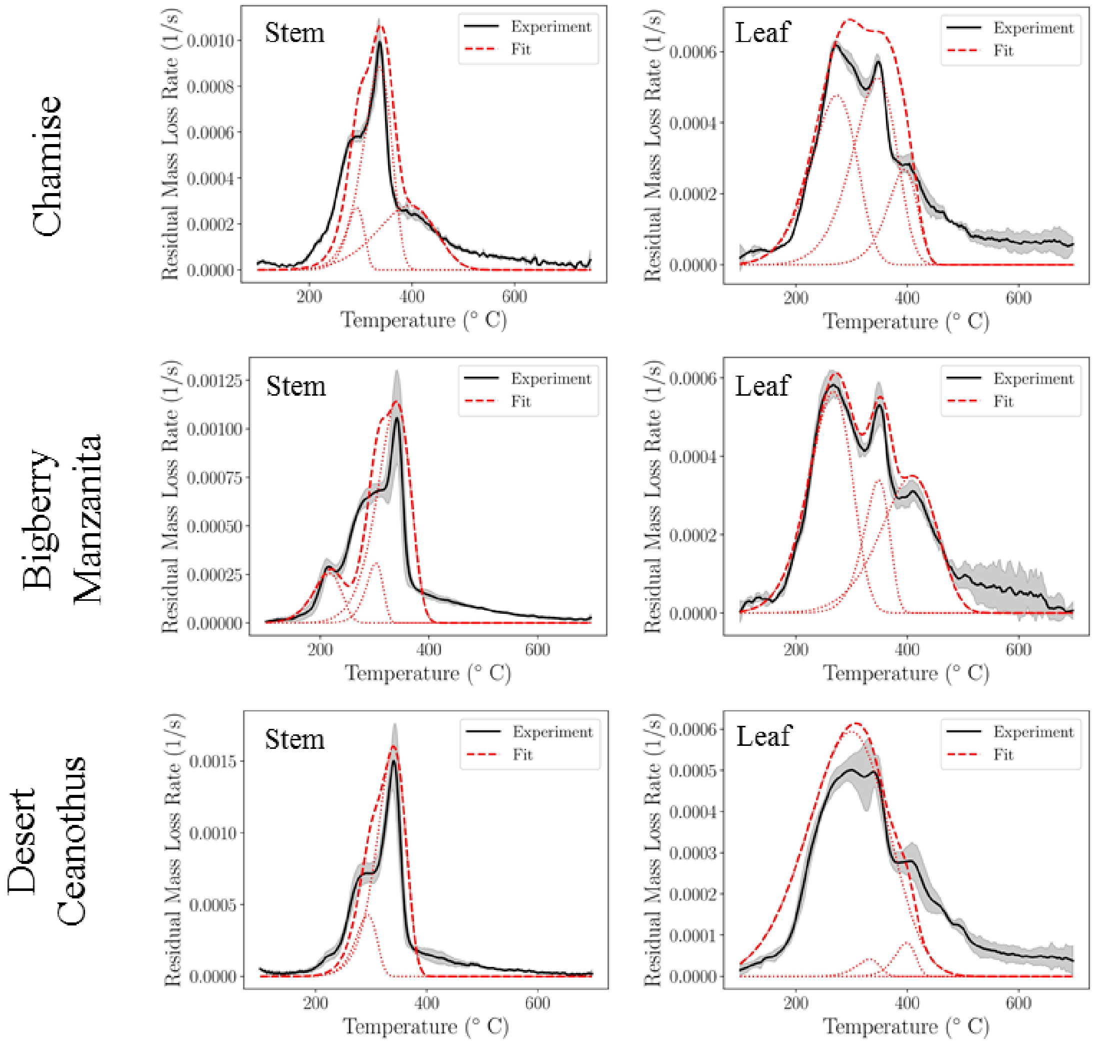

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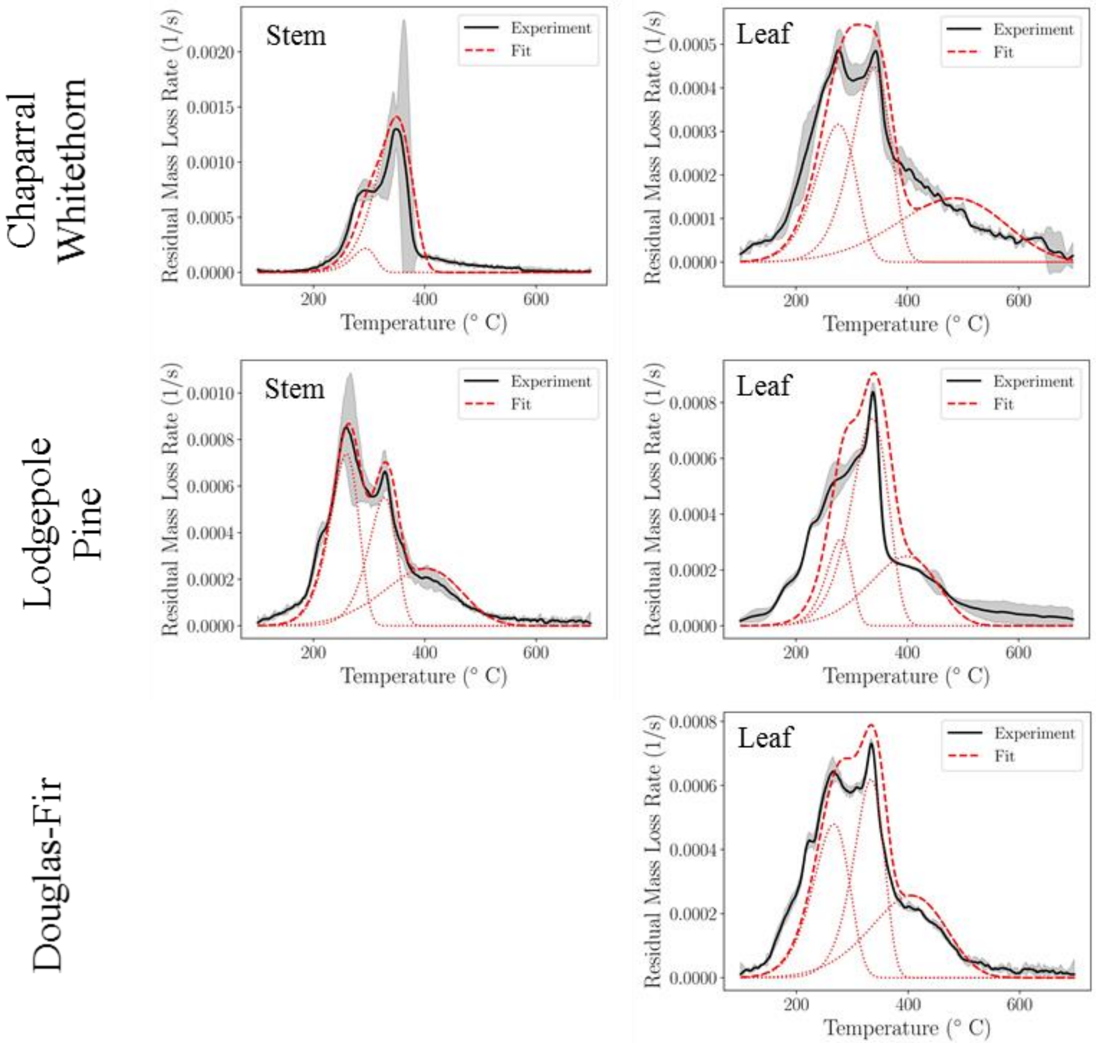

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Kinetic Parameters Describing Decomposition of Vegetative Fuels

Sample Name	A_1 (s^{-1})	E_1 (kJ $kmol^{-1}$)	Δm_1	A_2 (s^{-1})	E_2 (kJ $kmol^{-1}$)	Δm_2	A_3 (s^{-1})	E_3 (kJ $kmol^{-1}$)	Δm_3
Leaves									
Chamise	9.98×10^{2}	5.67×10^{4}	0.30	1.21×10^{4}	7.69×10^{4}	0.32	3.39×10^{8}	1.37×10^{5}	0.11
Bigberry Manzanita	2.12×10^{3}	5.91×10^{4}	0.34	3.64×10^{9}	1.39×10^{5}	0.12	1.07×10^{3}	7.23×10^{4}	0.27
Desert Ceanothus	2.22	3.32×10^{4}	0.64	9.99×10^{10}	1.52×10^{5}	0.01	3.80×10^{14}	2.14×10^{5}	0.02
Chaparral Whitethorn	9.85×10^{3}	6.68×10^{4}	0.17	1.15×10^{5}	8.68×10^{4}	0.24	1.53	4.36×10^{4}	0.21
Lodgepole Pine	2.38×10^{5}	8.99×10^{4}	0.38	2.85×10^{8}	1.12×10^{5}	0.11	6.39×10^{1}	5.67×10^{4}	0.23
Douglas-Fir	3.35×10^{4}	7.07×10^{4}	0.24	1.45×10^{7}	1.09×10^{5}	0.26	2.13×10^{1}	5.17×10^{4}	0.26
Stems									
Chamise	9.56×10^{6}	1.08×10^{5}	0.38	3.40×10^{12}	1.58×10^{5}	0.07	1.43×10^{2}	6.04×10^{4}	0.24
Bigberry Manzanita	4.85×10^{5}	7.41×10^{4}	0.10	2.14×10^{6}	1.01×10^{5}	0.53	2.06×10^{14}	1.79×10^{5}	0.07
Desert Ceanothus	1.16×10^{8}	1.20×10^{5}	0.64	5.05×10^{10}	1.39×10^{5}	0.13			
Chaparral Whitethorn	3.23×10^{9}	1.26×10^{5}	0.07	9.56×10^{5}	9.86×10^{4}	0.69			
Lodgepole Pine	3.45×10^{6}	8.91×10^{4}	0.30	5.97×10^{7}	1.15×10^{5}	0.22	1.51×10^{1}	4.96×10^{4}	0.26
Average Stem*	8.58×10^{5}	9.64×10^{4}	0.49	1.03×10^{16}	1.95×10^{5}	0.07			
Average Leaf*	1.22×10^{3}	5.75×10^{4}	0.23	2.46×10^{5}	9.03×10^{4}	0.23	1.32×10^{2}	6.02×10^{4}	0.25

* Effective values representing the thermal decomposition of a typical leaf or stem tested in this work

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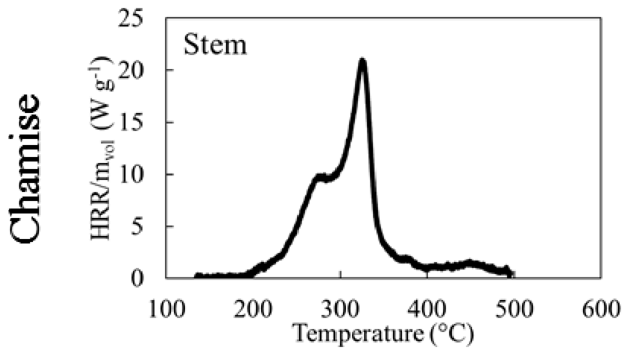

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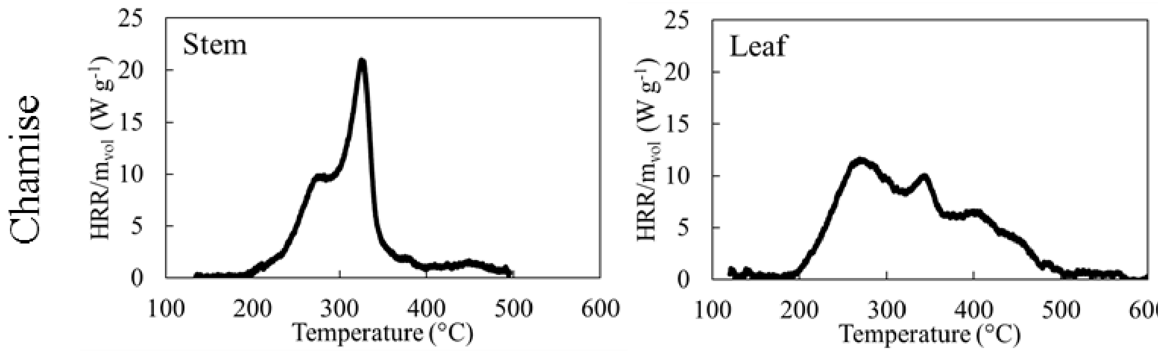

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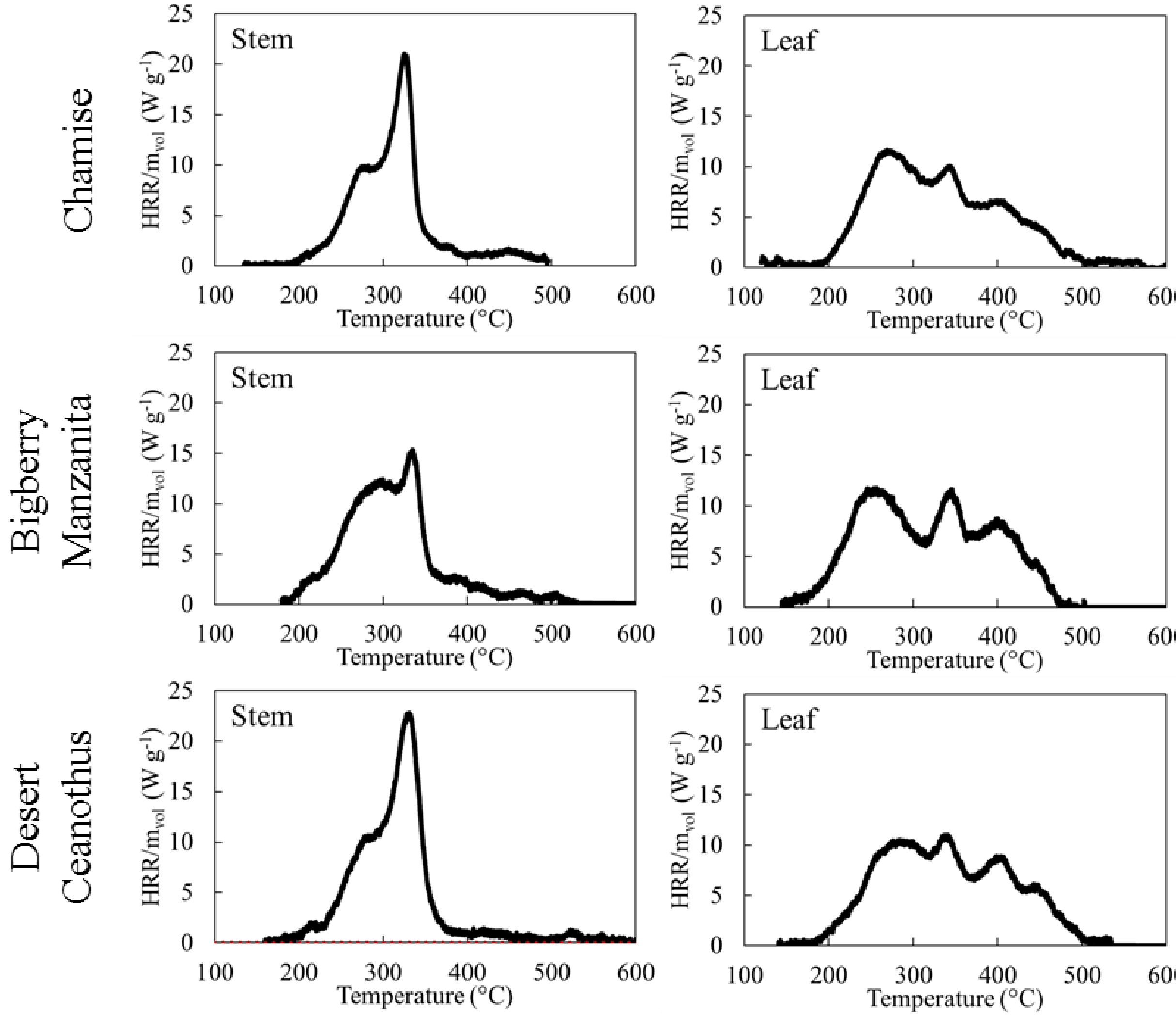

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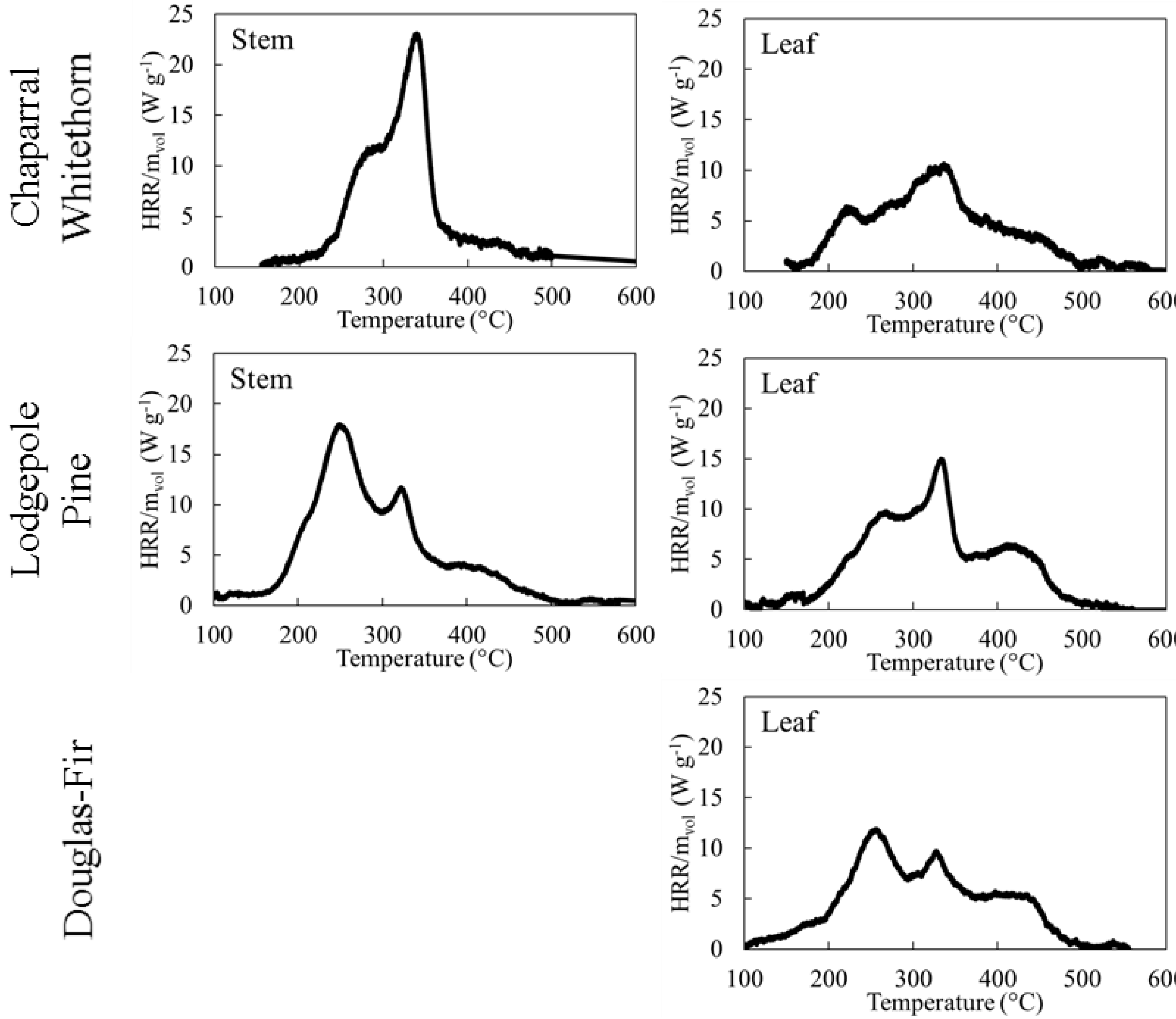

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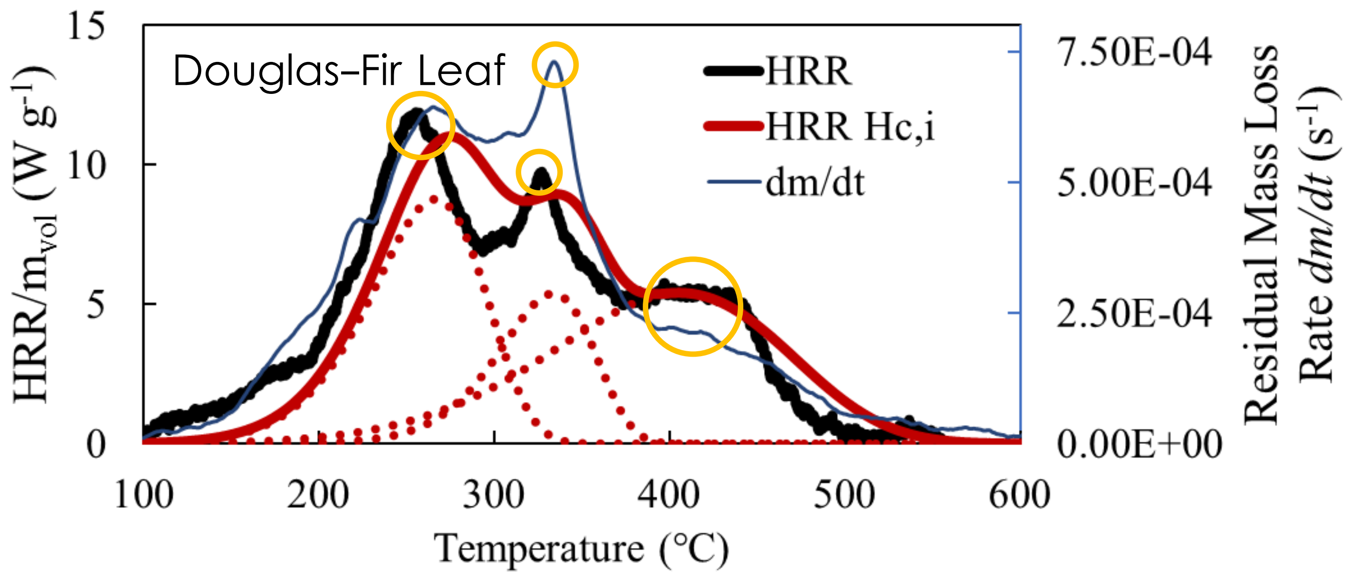
Heats of Combustion



- Simple analysis of MCC Data:
  - Heat of complete combustion, $\Delta H_{c,total}$
- Reaction-step specific heats of combustion, $\Delta H_{c,i}$
  - Consider relative peaks of <u>measured</u> HRR/m_{vol} and dm/dt
  - Use these peak values (measured) + relative fraction of volatiles released by each reaction step at peak (model)

$$\left.\frac{(HRR/m_{vol})_{exp}}{\left(\frac{dm}{dt}\right)_{exp}}\right|_{peak\ j} = \frac{\sum_{i=1}^{N_{rxns}}\left[\left(\Delta H_{c,i}\right)\times\left(\left.\frac{dm_i}{dt}\right|_{peak\ j}\right)\right]}{\sum_{i=1}^{N_{rxns}}\left[\left.\frac{dm_i}{dt}\right|_{peak\ j}\right]}$$

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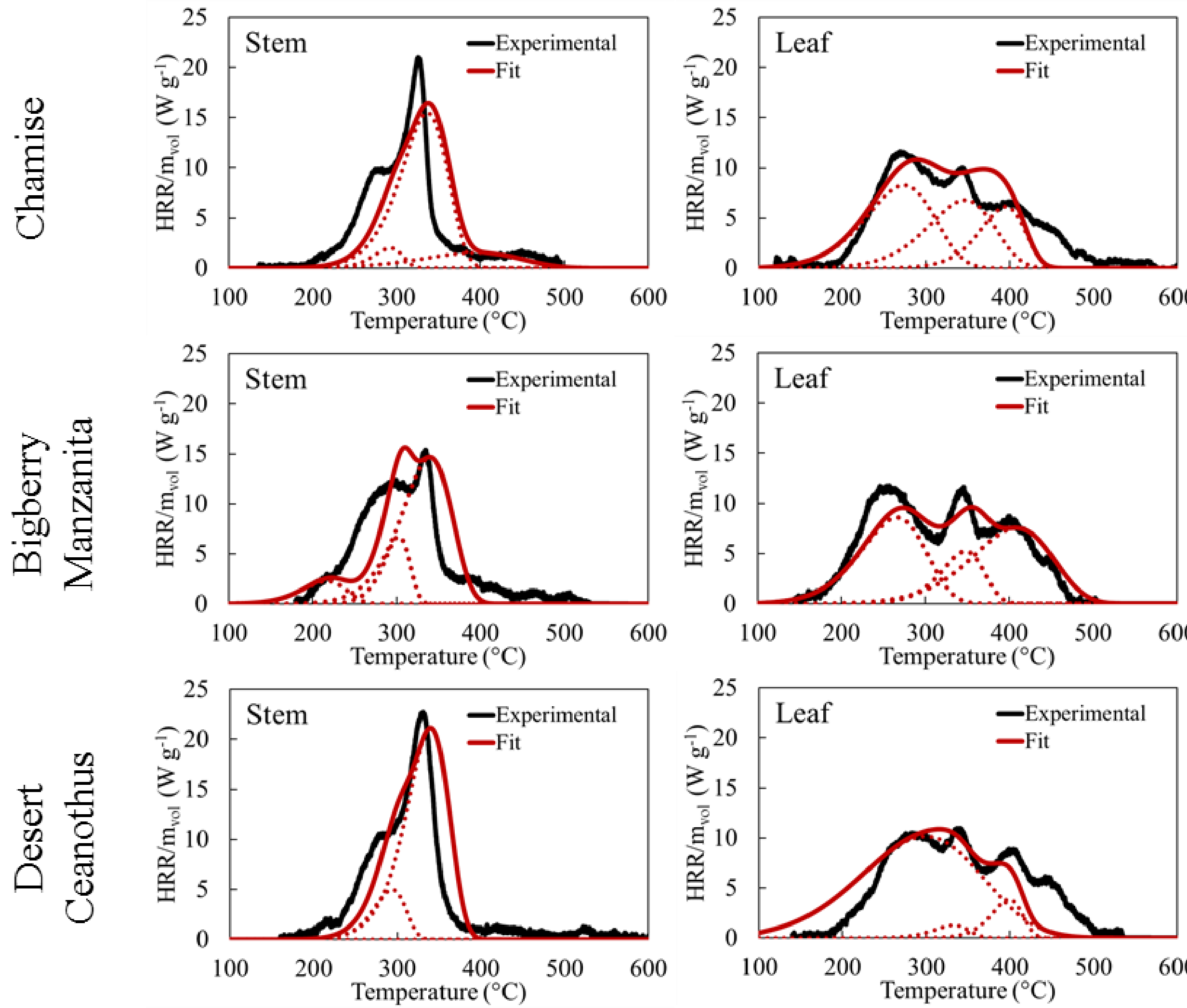

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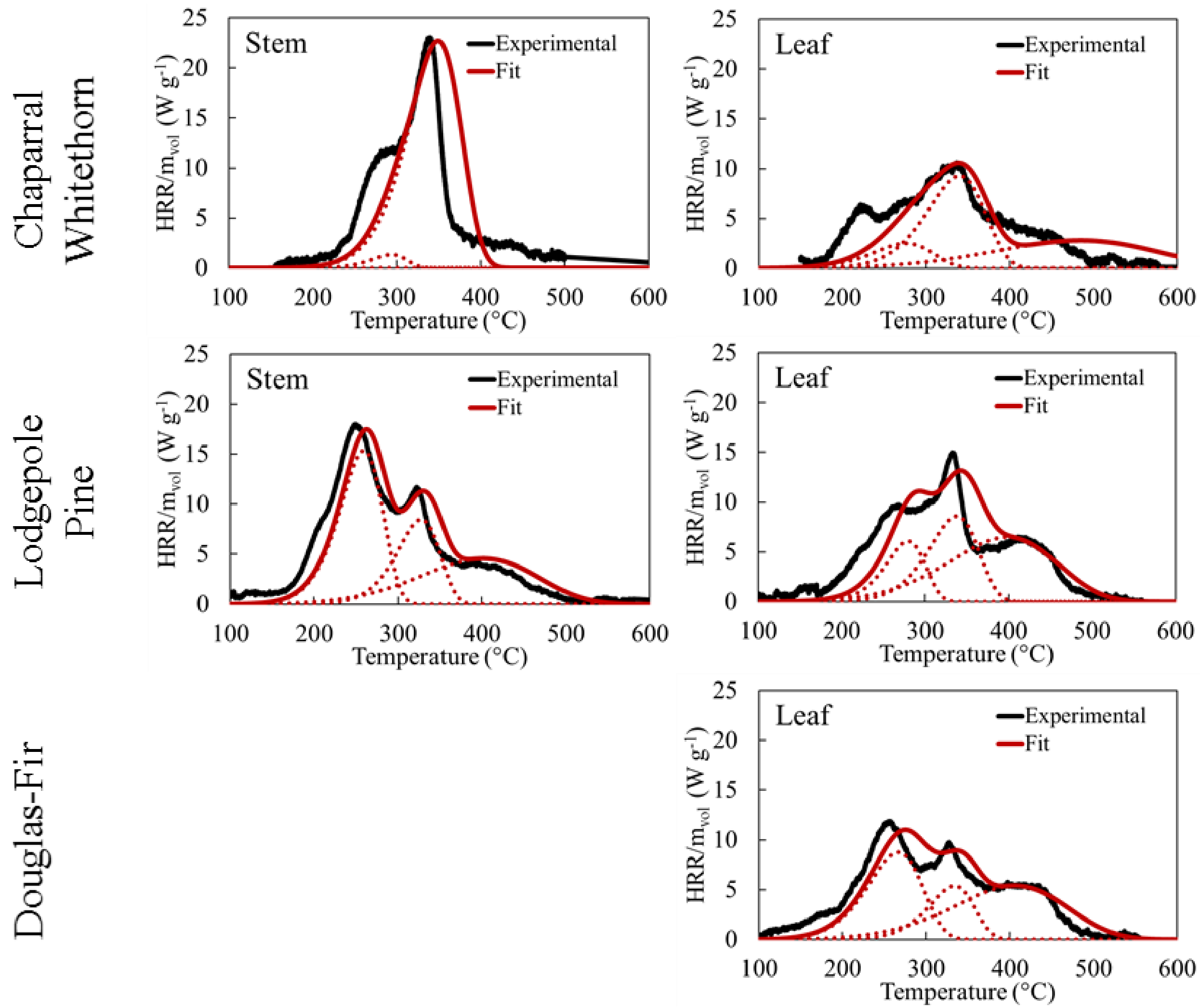

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Heats of Combustion and Char Yields of Vegetative Fuels

Sample Name	$\Delta H_{c,1}$ (kJ g^{-1})	$\Delta H_{c,2}$ (kJ g^{-1})	$\Delta H_{c,3}$ (kJ g^{-1})	$\Delta H_{c,\ total}$ (kJ g^{-1})	μ_{char} (-)
Leaves					
Chamise	13.0±2.0	9.7±1.5	17.2±2.6	11.7±1.2	0.25±0.04
Bigberry Manzanita	12.0±1.8	11.6±1.7	17.0±2.6	12.4±0.9	0.22±0.06
Desert Ceanothus	11.6±1.7	20.9±3.1	32.2±4.8	12.3±1.1	0.32±0.03
Chaparral Whitethorn	5.3±0.8	13.9±2.1	12.7±1.9	10.4±1.8	0.33±0.04
Lodgepole Pine	8.2±1.2	12.2±1.8	17.9±2.7	12.6±0.6	0.24±0.04
Douglas-Fir	13.7±2.1	6.5±1.0	15.8±2.4	12.2±0.6	0.25±0.04
Average Leaf *	-	-	-	11.9±0.8	0.27±0.05
Stems					
Chamise	12.8±1.9	5.3±0.8	4.0±0.6	8.9±0.6	0.27±0.04
Bigberry Manzanita	5.7±0.9	8.1±1.2	13.8±2.1	9.6±1.3	0.37±0.06
Desert Ceanothus	9.9±1.5	8.8±1.3	-	9.1±0.5	0.25±0.06
Chaparral Whitethorn	4.7±0.7	12.4±1.9	-	11.5±2.6	0.23±0.05
Lodgepole Pine	16.2±2.4	12.0±1.8	14.5±2.2	14.4±2.0	0.22±0.04
Average Stem*	-	-	-	10.7±2.3	0.27±0.06

*Calculated as the mean value of $\Delta H_{c,total}$ or μ_{char} measured for all stem or leaf species

- $\Delta H_{c,\ total}$ varies between 8.9 and 14.4 kJ g^{-1}
- $\Delta H_{c,\ total}$ is 17% greater for leaves than for stems
  - Excluding Lodgepole Pine stems for which $\Delta H_{c,\ total}$ is 42% greater than the average of all other stems tested

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Numerical Simulations of Wildland Fires

- Simulations of wildfire spread conducted in the NIST Fire Dynamics Simulator (FDS)
  - FDS version 6.7.1[29]

- Case study:
  - Controlled burn of a 100 m by 100 m plot of kerosene grasslands[30]
  - Repeat simulations using the reaction mechanisms, associated kinetics (A, E), and heats of combustion ($\Delta H_{c,i}$) determined for all vegetative fuels tested in this work

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Numerical Simulations of Wildland Fires

- Computational domain
  - 120 x 120 x 20 m
  - 36 meshes, 0.5 m cubic cells
- Lagrangian particles simulate grass
  - Modeled as slender cylinders
  - Rigidly fixed, perpendicular to the wind and the source of thermal radiation
  - One simulated blade of grass per cell; weighting factor applied to match measured bulk mass per unit area

Numerical Simulations of Wildland Fires

- Ignition defined to match experimental conditions[9]
- All relevant soil, vegetation, and combustion parameters are taken from a recent modeling study[9] are typical of wood or cellulosic fuels

Measured properties of CSIRO Grassland Fire Case C064 [30]

Property	Value
Wind Speed	4.6 m s^{-1}
Ambient Temperature	32 °C
Surface Area to Volume Ratio	9770 m^{-1}
Grass Height	0.21 m
Bulk Mass per Unit Area	0.283 kg m^{-2}
Moisture Fraction	6.3%

Assumed Fuel and Soil Properties for Wildfire Simulations [9]

Property	Value
Fuel Properties	
Chemical Composition	$C_6H_{10}O_5$
Radiative Fraction	0.35
Soot Yield	0.015
Specific Heat	1.5 kJ kg^{-1} K^{-1}
Conductivity	0.1 W m^{-1} K^{-1}
Density	512 kg m^{-3}
Heat of Pyrolysis	418 kJ kg^{-1}
Soil Properties	
Soil Specific Heat	2.0 kg^{-1} K^{-1}
Soil Conductivity	0.25 W m^{-1} K^{-1}
Soil Density	1300 kg m^{-3}

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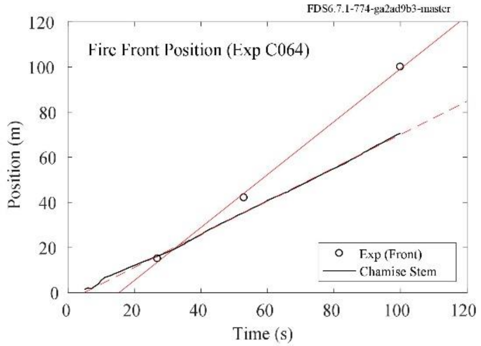

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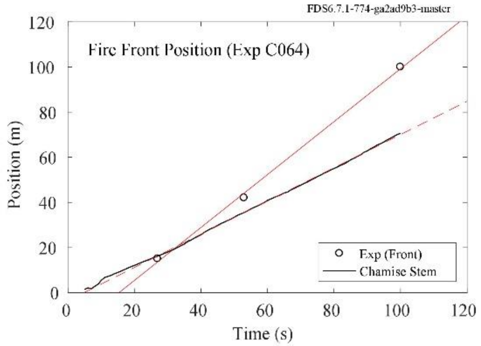

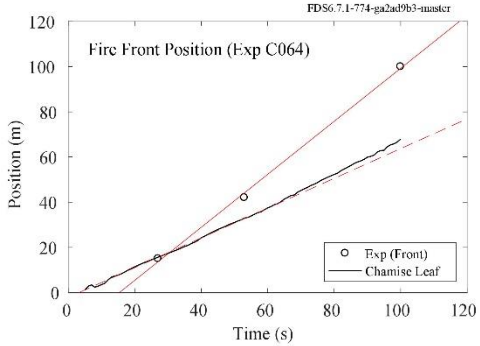

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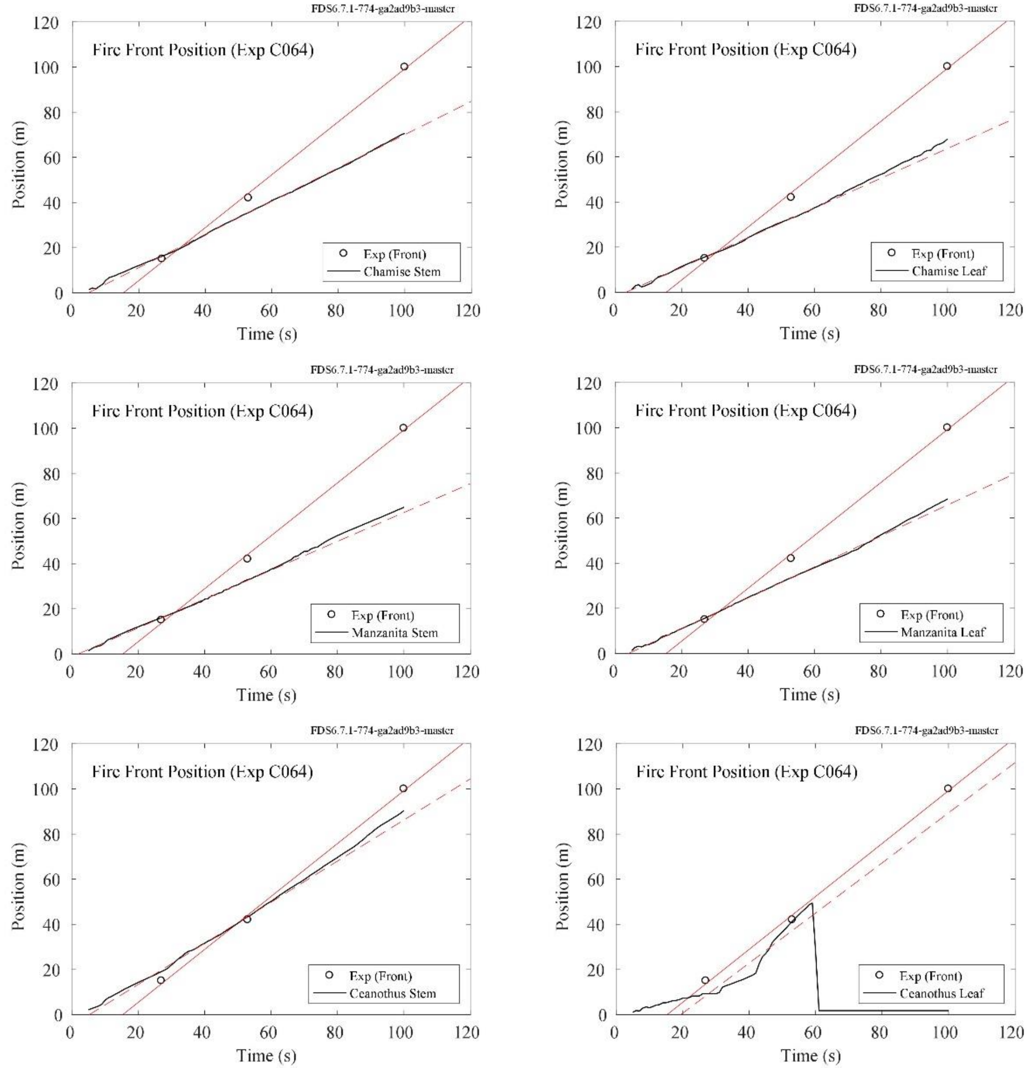

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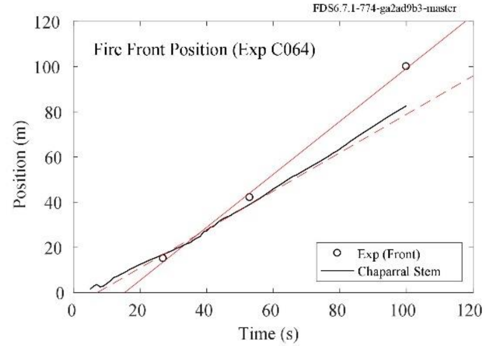
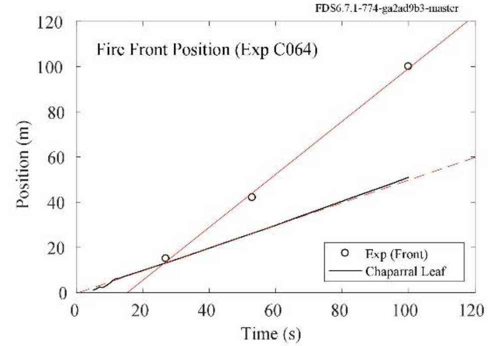
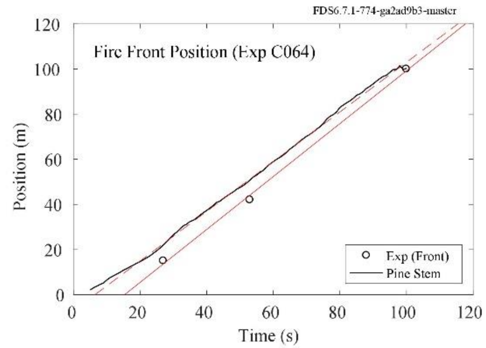
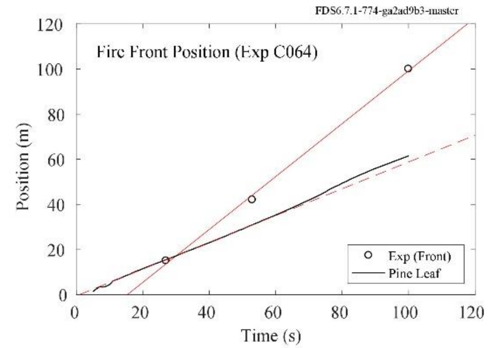
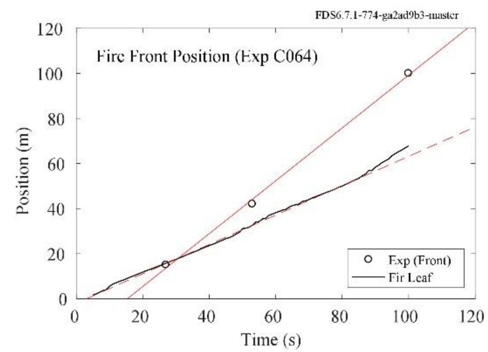
Conclusions and Future Work











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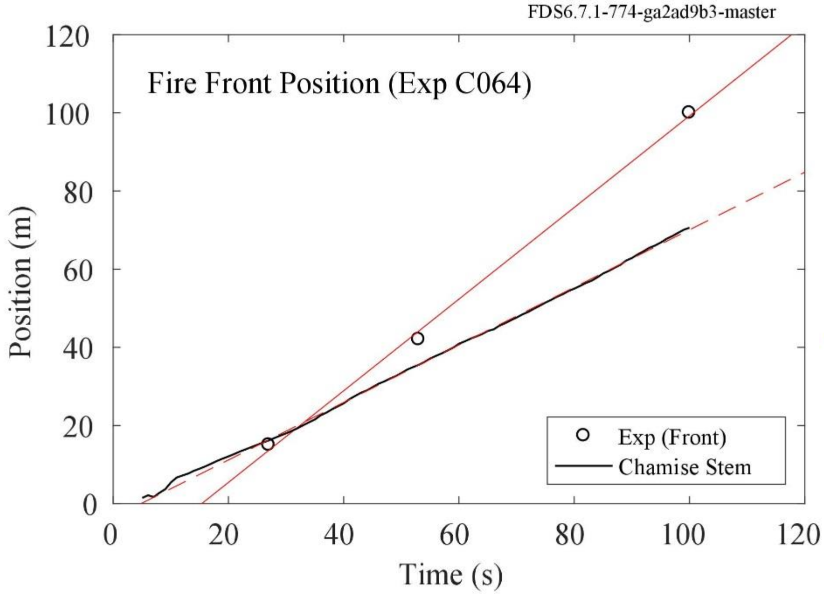
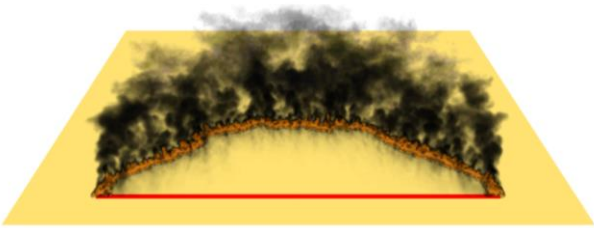
Numerical Simulations of Wildland Fires





Representative snapshot of FDS simulation of a CSIRO Grassland Fire

- Fire front location
  - Location of the maximum gas temperature
- Propagation occurred at constant rate, R
  - **For all fuels: 0.50 ≤ R ≤ 1.11 m s^{-1}**
  - Spread rate faster for leaves than stems
  - $\Delta H_{c,\,total}$ vs. $\Delta H_{c,i}$
    - For each fuel, R changes by −27% to + 66%

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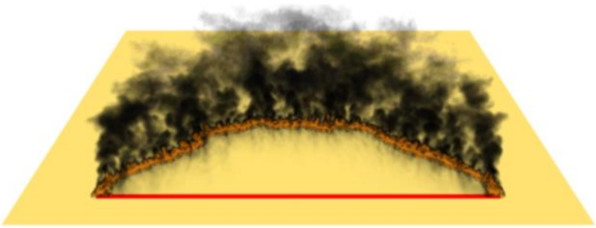
Numerical Simulations of Wildland Fires

Sample Name	Spread Rate (m s^{-1}) $\Delta H_{c,i}$	Spread Rate (m s^{-1}) $\Delta H_{c,total}$
Leaves		
Chamise	0.82	1.20
Bigberry Manzanita	1.11	0.85
Desert Ceanothus	0.91	0.66
Chaparral Whitethorn	0.66	0.58
Lodgepole Pine	0.74	0.51
Douglas-Fir	0.50	0.83
Average Leaf		0.53
Stems		
Chamise	0.65	0.79
Bigberry Manzanita	0.69	0.65
Desert Ceanothus	0.64	0.77
Chaparral Whitethorn	0.59	0.75
Lodgepole Pine	1.10	1.07
Average Stem		0.85



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Conclusions

- Measured thermal degradation behavior of stem and leaf samples of six vegetative fuels commonly found in the United States
- Thermogravimetric Analysis (TGA)
  - Thermal decomposition mechanisms
    - Parallel, first order, Arrhenius rate reactions
  - Associated kinetic parameters (A_i, E_i)
- Microscale Combustion Calorimetry (MCC)
  - Heats of complete combustion of *all gaseous pyrolyzates* released by sample, $\Delta H_{c,total}$
    - $\Delta H_{c,\,total}$ varies between 8.9 and 14.4 kJ g^{-1}
  - Heats of complete combustion of gaseous species produced in *each reaction step*, $\Delta H_{c,i}$

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Conclusions

- Distinct variations in degradation behavior of different fuels
  - Onset temperature of degradation
  - Number of apparent reactions
  - Peak measured mass loss and heat release rates
    - Reaction step peaks observed between 220 and 485 °C.
  - Stems: higher peaks, narrower temperature range
  - Leaves: overlapping reactions over a wider temperature range, higher heats of combustion
- Model-predicted wildfire spread rate sensitive to measured variations in decomposition behavior of these fuels
  - Significant dependence on fuel decomposition mechanism: Predicted wildfire spread rate varied between 0.5 and 1.11 m s^{-1}
  - Spread rate faster for stems than leaves

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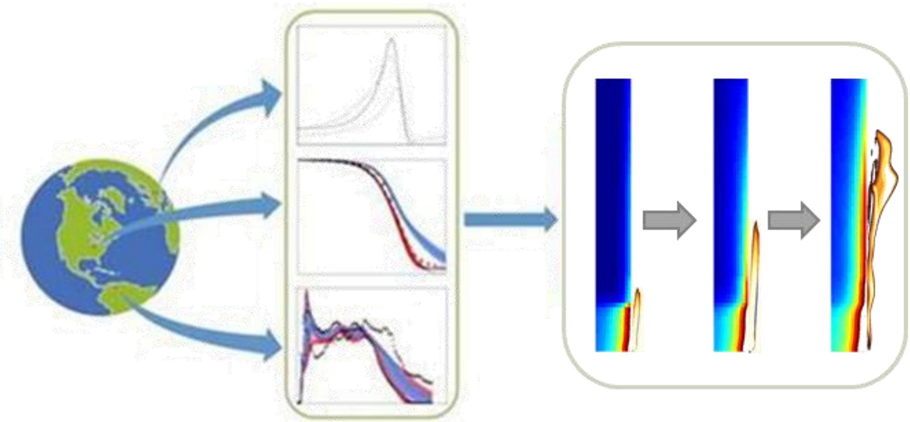
The 2020 MaCFP Condensed Phase Workshop

Workshop Objectives

- To catalogue current approaches used to parameterize pyrolysis models;
- To quantify the interlaboratory variability for comparable experimental datasets;
- To assess the impact of the variability of model parameters on predictions of sample burning rate;
- To present a rigorous analysis of these results in the *Fire Safety Journal*



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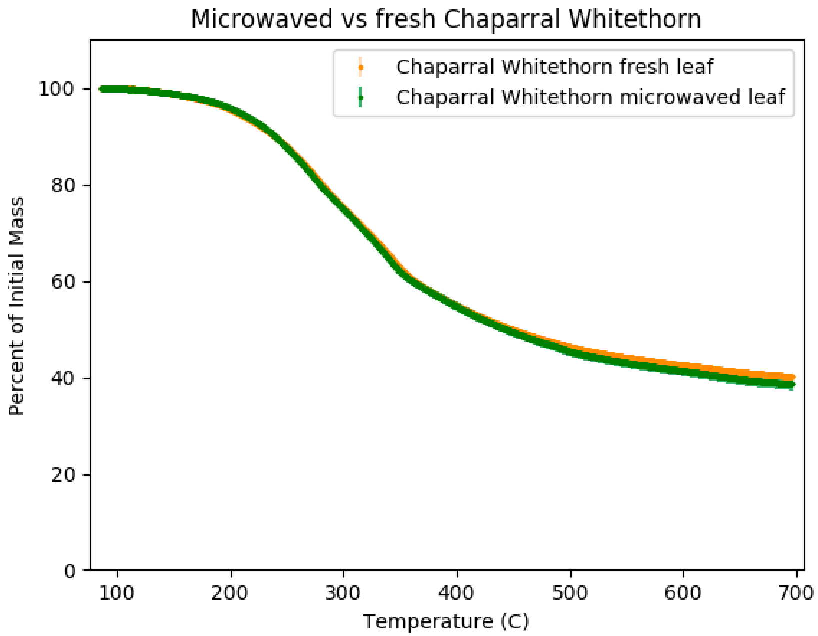
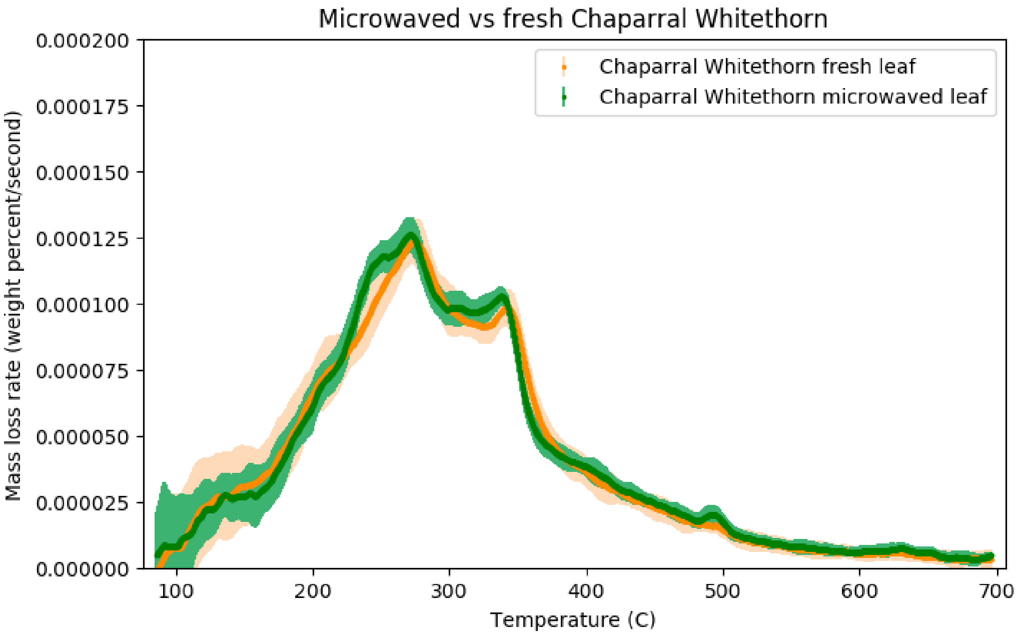
Validation of microwaving samples for preservation





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