Automated Material Characterization for Fire Modeling

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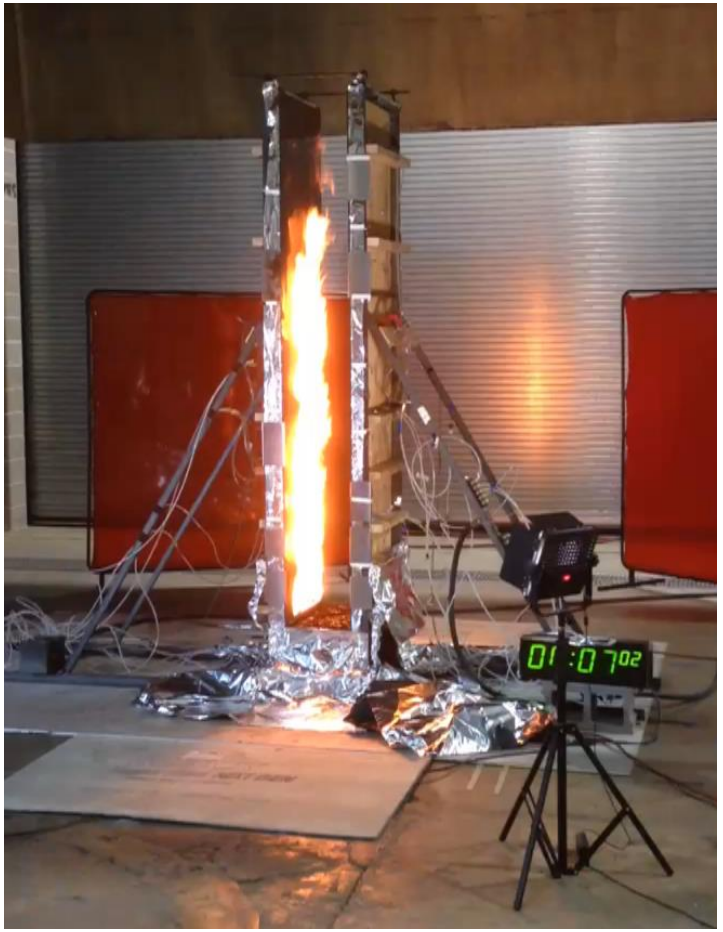
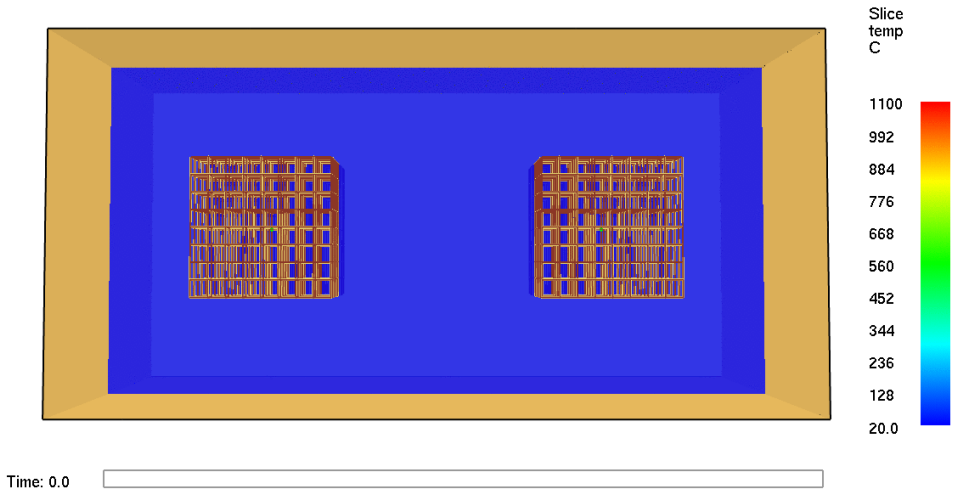
Predicting Fire Growth

- To engineer safer:
  - Buildings
  - Products
  - Materials
- Accurate predictions require **condensed phase pyrolysis models**

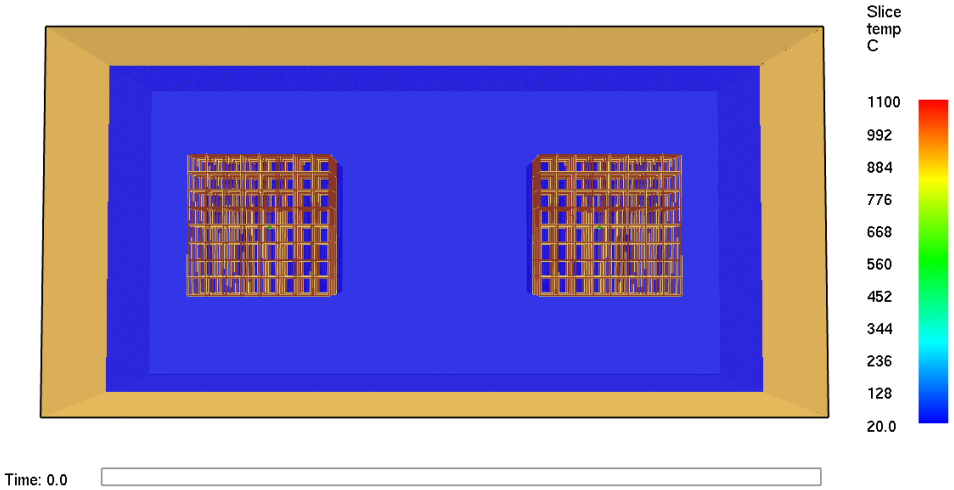


Condensed Phase Challenges



- Physics
  - Multiphase
  - Mechanical deformation
- Numerics
  - Gas phase coupling
  - Multiscale
  - Moving boundary
- Materials
  - Many parameters
  - Many materials

Condensed Phase Challenges



- Physics
  - Multiphase
  - Mechanical deformation
- Numerics
  - Gas phase coupling
  - Multiscale
  - Moving boundary
- **Materials**
  - Many parameters
  - Many materials

How Many Parameters?

$$\frac{\partial \rho_i}{\partial t} = \dot{m}_i''', \quad i = 1, \ldots N$$

$$\rho c \frac{\partial T}{\partial T} = \nabla \cdot (k \nabla T) + \dot{q}'''$$

$$\dot{m}_i''' = -A_i \rho_i \exp\left(-\frac{E_i}{RT}\right), \quad i = 1, \ldots, N$$

$$\rho c = \sum_{i=1}^{N} \rho_i c_i$$

$$k = f\left(\rho_1, \ldots, \rho_N, k_1, \ldots, k_N\right)$$

$$\dot{q}''' = -\sum_{i=1}^{N} \Delta h_i \dot{m}_i'''$$

$$\rho_i\left(t = 0\right) = \rho_{0,i}, \quad i = 1, \ldots, N$$

Neglecting
- Radiation
- Mass transport
- Charring
- Temperature dependence

At least ~$6N$ material property parameters need to be quantified

How many materials?

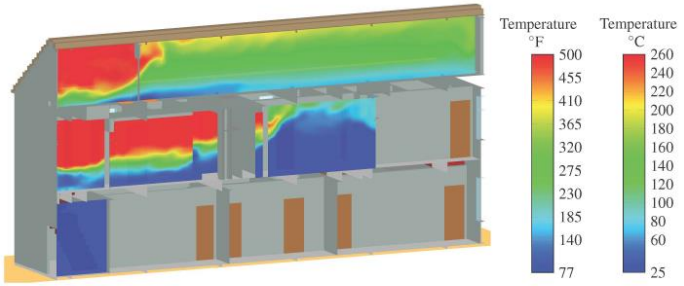
- NFIRS categorizes **38 distinct "types"** of solid materials "First Ignited"
- These "types" are extremely broad categories such as "Plastic", "Rubber", and "Plywood"
- For example, Lyon and Janssens (2005) contains data on **50 common plastics**
- Additional diversity due to processing variability, additives, blends, ageing, etc.

On the order of 10^3 distinct materials relevant to fire growth predictions

$(10^1$ Parameters) × $(10^3$ Materials)
= **10^4 Properties for reliable fire growth predictions**

A **Material Property Database** is needed

Material Property Database



- Being developed at NIST
- Adopting “Hierarchical” approach
- Critical components
  1. Standard formatting
  2. Standard metadata
  3. **Analysis tools**

Global Approach

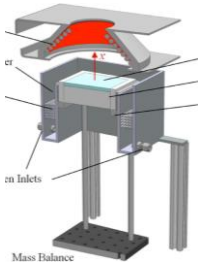
$$A_i, E_i, c_i, k_i, \Delta h_i, \rho_{0,i}$$

Fire Model

Hierarchical Approach

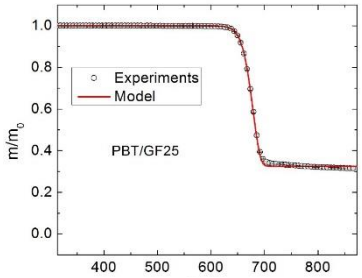
$$A_i, E_i, \rho_{0,i}$$

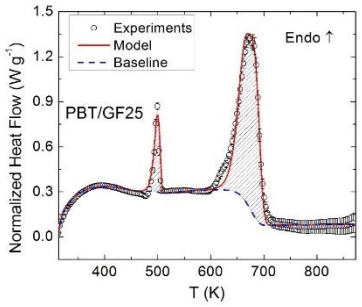
$$c_i, \Delta h_i$$

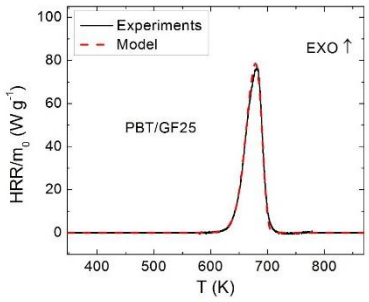


$$k_i$$

Model Parameterization: Framework







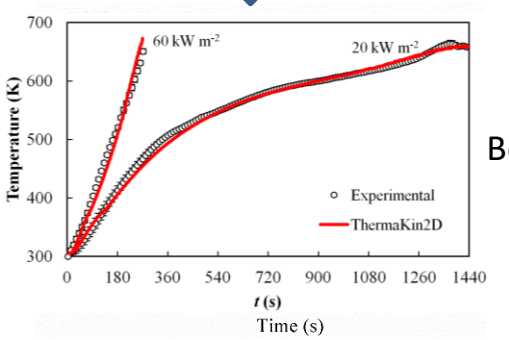
mg-scale testing

Analysis tools

Thermophysical properties

$$A \quad E \quad \nu$$
$$c_p \quad h_i \quad \Delta H_c$$
$$k \quad \rho$$
$$\alpha \quad \varepsilon$$

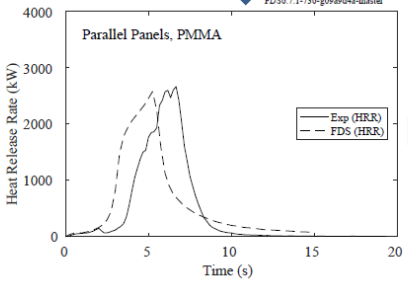
Computational Model



Bench scale experiments for model calibration

Computational Model

Full scale testing for model validation



Quantitative prediction of fire growth

Users

- FPEs
- Researchers
- Materials Companies
- Investigators
- Product Designers

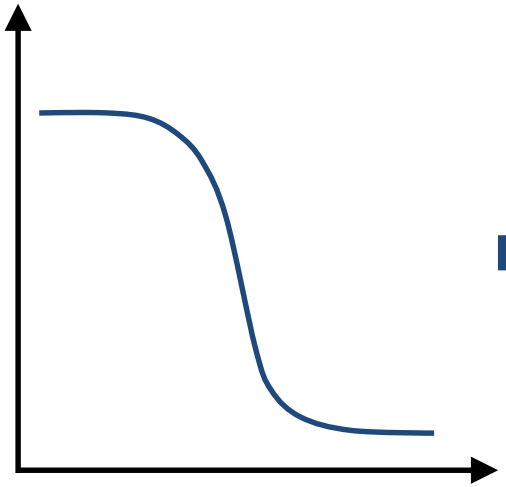
Model Parameterization

- Experimental approach
  - Conduct as few physical tests as possible
  - Isolate parameters through each test
  - Validate model across a range of scales, outside of calibration conditions

- Focus of this presentation: Analysis of TGA and MCC data for
  - Reaction mechanism
  - Kinetics
  - Heats of combustion

Analysis of TGA Data

How should we estimate pyrolysis kinetic parameters from raw TGA data?

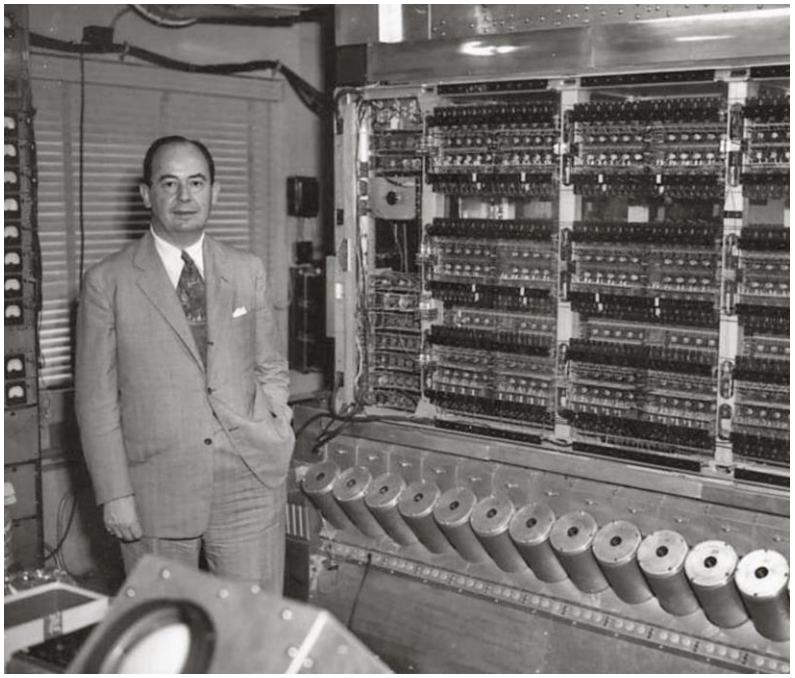


$A_i, E_i, \rho_{0,i}$

Method Requirements

1. Parameters predict data → **Accurate**
2. Many different materials → **Efficient**
3. Many different behaviors→ **Robust**
4. Parameters do not vary → **Consistent**

How to be Consistent

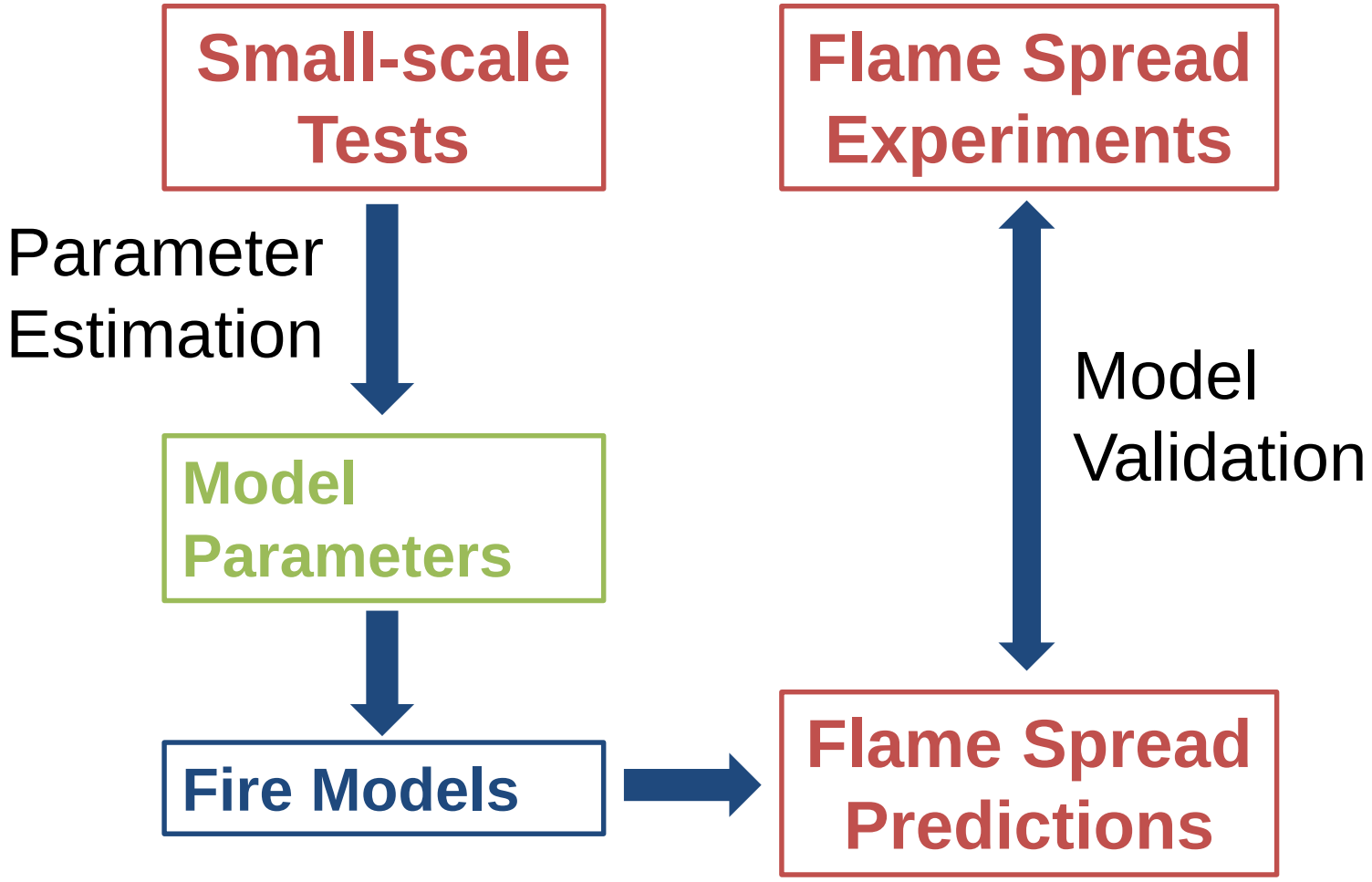


“With four parameters I can fit an elephant, and with five I can make him wiggle his trunk.”

~John von Neumann

1. **No free parameters**
2. **No random numbers**

For given data, the method should always produce the same parameters



The quality of any **parameter estimation** algorithm is ultimately determined in **model validation**

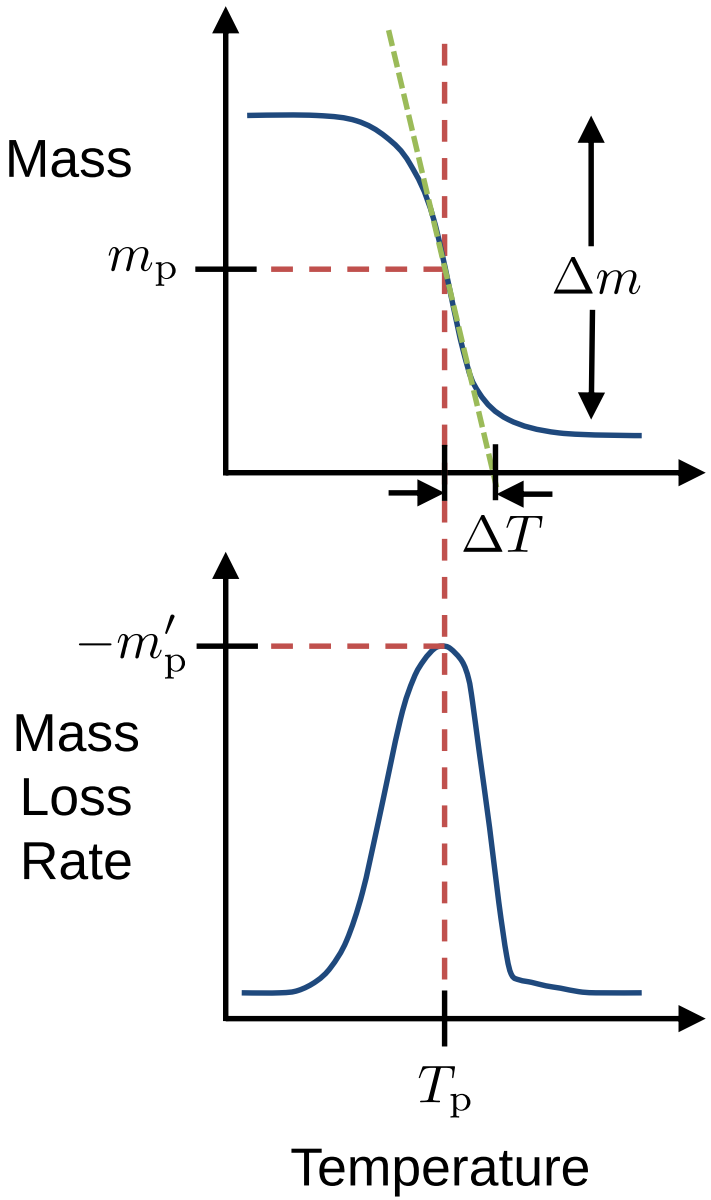
Pyrolysis Model: Independent Unimolecular Reactions

$$\text{Reactant} \xrightarrow{k} \nu\text{Char} + (1-\nu)\,\text{Gas}$$

$$k = \left(\frac{A}{\beta}\right)\exp\left(-\frac{E}{RT}\right)$$

$$m' \equiv \frac{\mathrm{d}m}{\mathrm{d}T} = -(1-\nu)\,km, \quad m(T_0) = m_0$$

Appropriateness to be determined by ability to predict fire growth.



Characteristic temperature and mass changes:

$$\Delta T \equiv \frac{m_\mathrm{p}}{-m'_\mathrm{p}}$$

$$\Delta m \equiv m_0 \left(1 - \nu\right)$$

Analysis of peak condition yields:

$$E = \frac{RT_\mathrm{p}^2}{\Delta T}$$

$$A = \frac{\beta}{\Delta T} \exp\left(\frac{T_\mathrm{p}}{\Delta T}\right)$$

Estimating Parameters

TGA Data

$$T_{\mathrm{p}}$$
$$m'_{\mathrm{p}}$$
$$m'''_{\mathrm{p}}$$

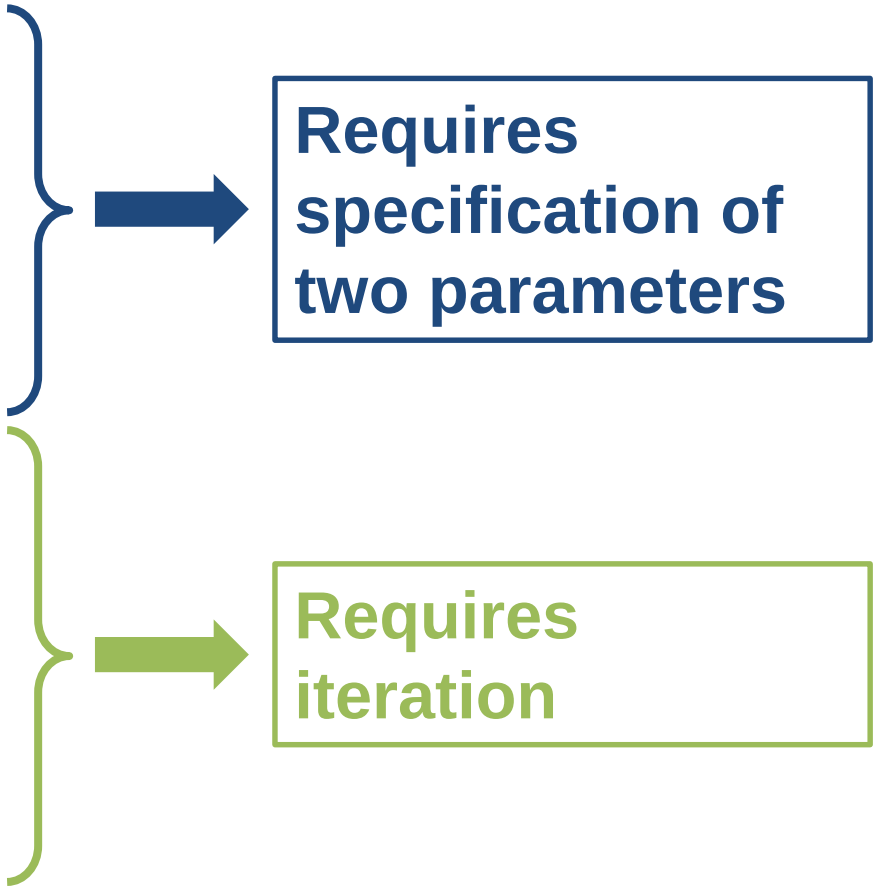
Approximate Solution

$$\Delta T = \sqrt{\frac{-m'_{\mathrm{p}}}{m'''_{\mathrm{p}}}}$$

$$\Delta m = -\mathrm{e} m'_{\mathrm{p}} \Delta T$$

Some Details

1. Smoothed data derivatives are found using Savitzky-Golay filter
2. “Small” mass loss rate peaks are neglected
3. Complete algorithm corrects preceding equations for overlapping reactions
4. Reaction mass changes corrected to conserve mass



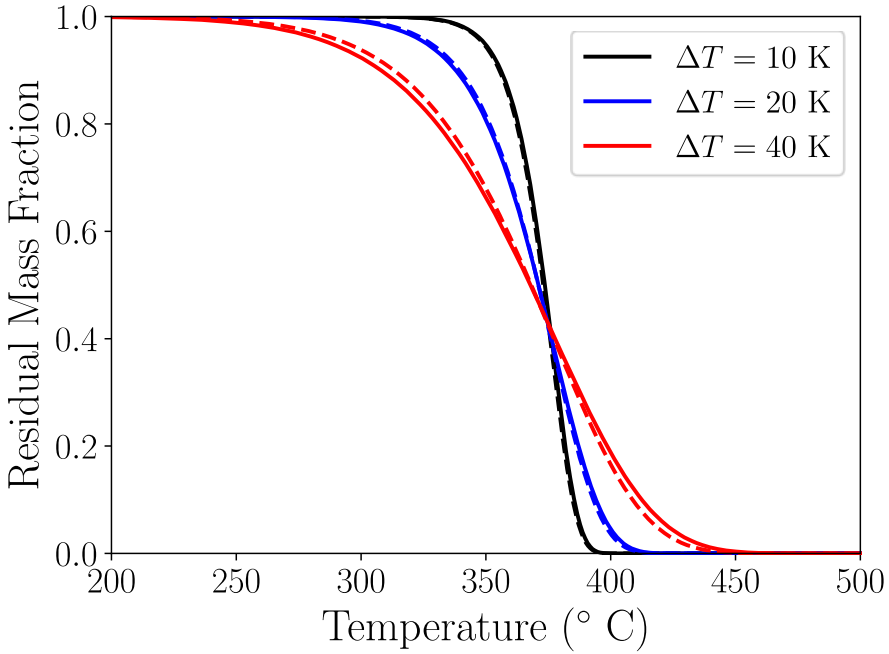
Verification

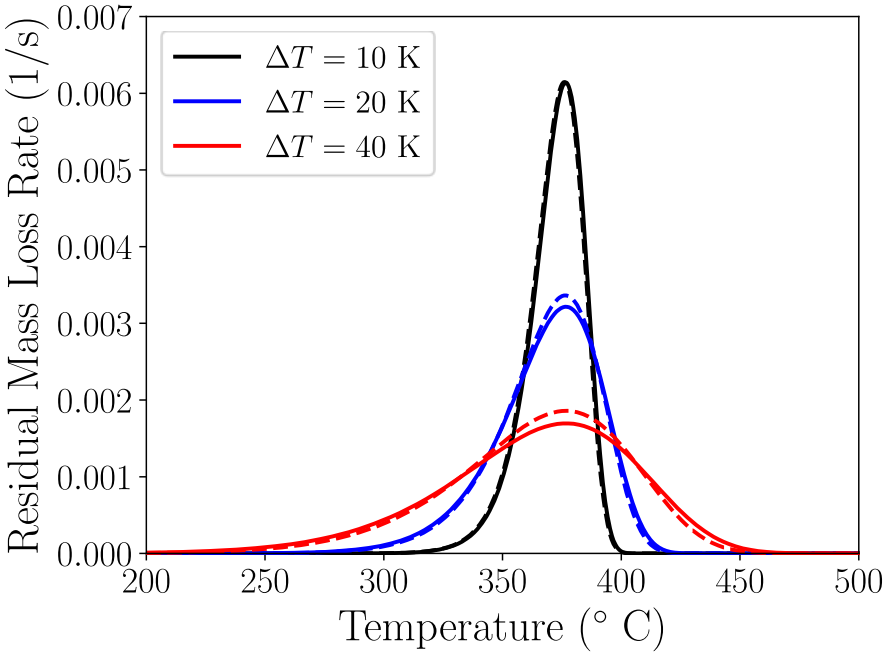
1. Assume kinetic parameters
2. Generate TGA data
3. Use algorithm to find parameters

Purpose:

1. Check implementation
2. Test validity of approximate solution

Single Reaction Verification





Single Reaction Verification

ΔT = 10 K:

Kinetic Parameter	Specified Value	Calibrated Value
T_p (K)	650	649.4
ΔT (K)	10	9.99
ξ	0.01538	0.01539
$\ln[A\ (s^{-1})]$	60.91	60.90
E (kJ/kmol)	351.3×10^3	350×10^3

ΔT = 20 K:

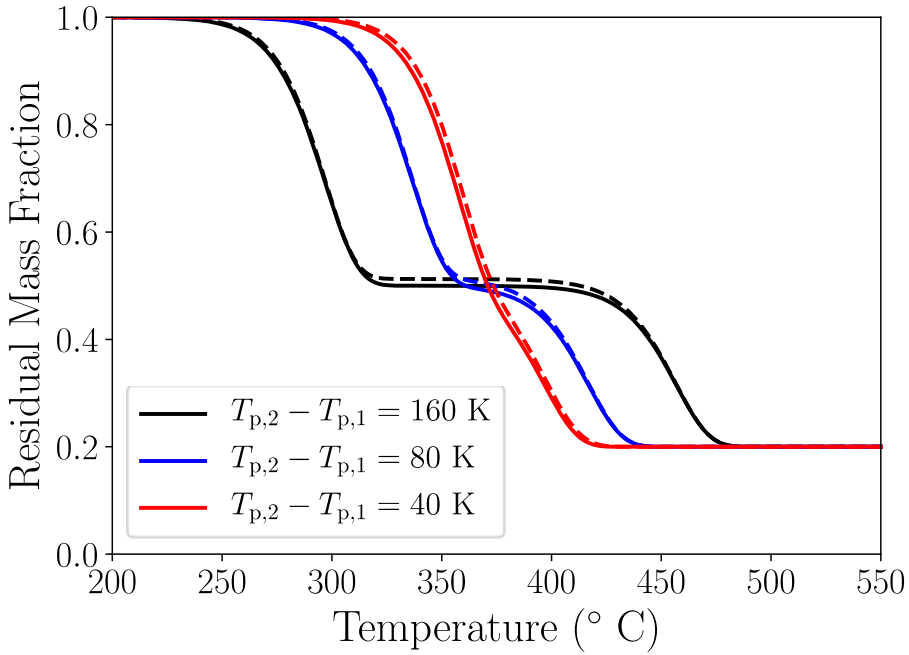
Kinetic Parameter	Specified Value	Calibrated Value
T_p (K)	650	649.4
ΔT (K)	20	19.07
ξ	0.03077	0.02935
$\ln[A\ (s^{-1})]$	27.71	29.34
E (kJ/kmol)	175.6×10^3	184.1×10^3

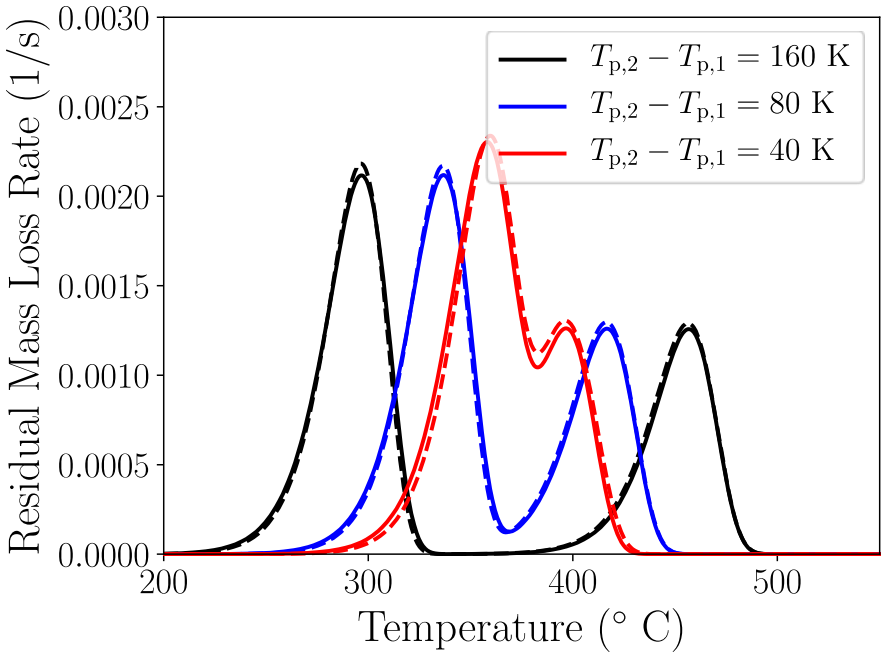
ΔT = 40 K:

Kinetic Parameter	Specified Value	Calibrated Value
T_p (K)	650	649.4
ΔT (K)	40	36.
ξ	0.06154	0.05563
$\ln[A\ (s^{-1})]$	10.77	12.59
E (kJ/kmol)	87.8×10^3	97.1×10^3

Decreasing ξ
Increasing accuracy

Two Reactions Verification





Closer fit for more separated reactions

Validation

Purpose:

1. Test algorithm with real TGA data

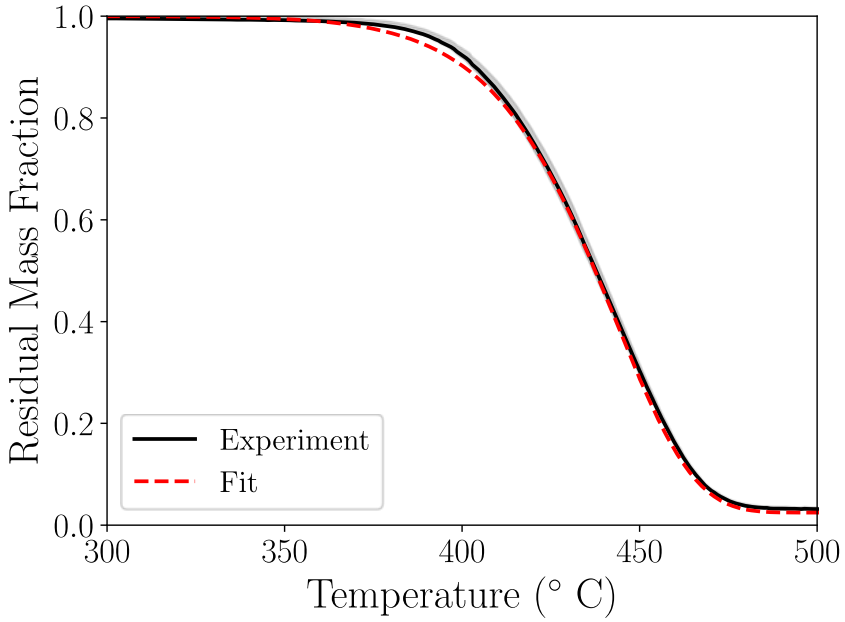
Materials:

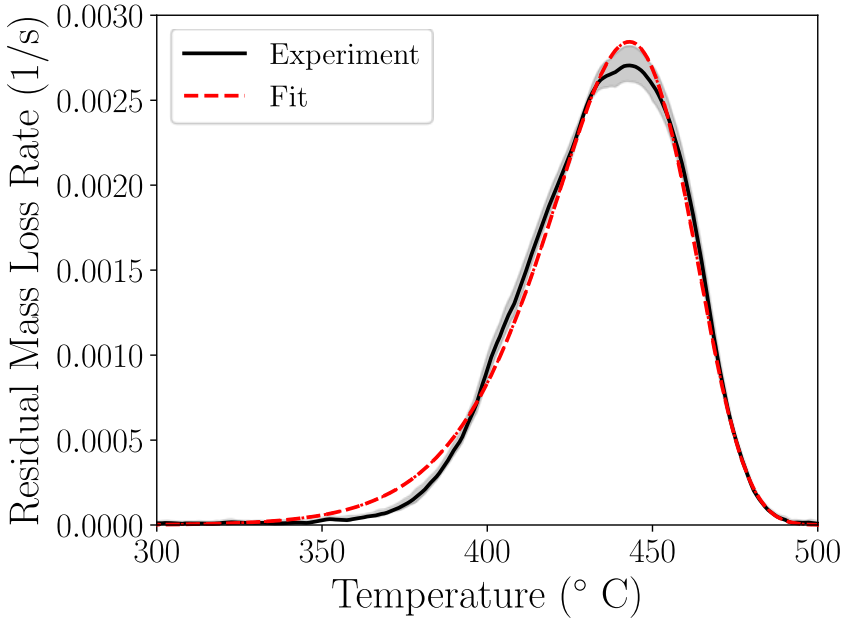
1. Nylon 6,6
2. Flexible polyurethane (PU) foam
3. Polyvinyl Chloride (PVC)

Procedure:

- In nitrogen
- Samples: 3-5.5 mg
- Isothermal heating for 20-30 min
- Dynamic heating at 10 K/min

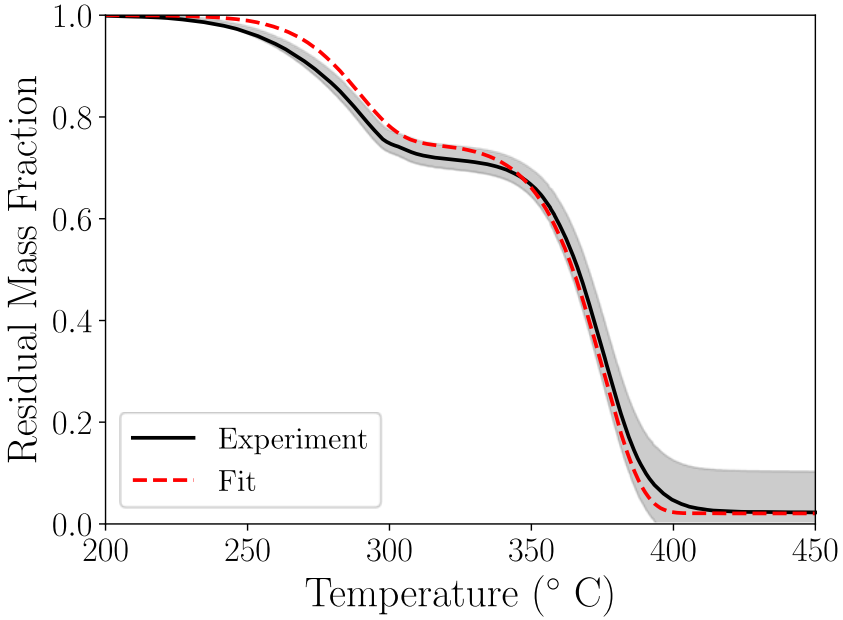
Validation: Nylon 6,6

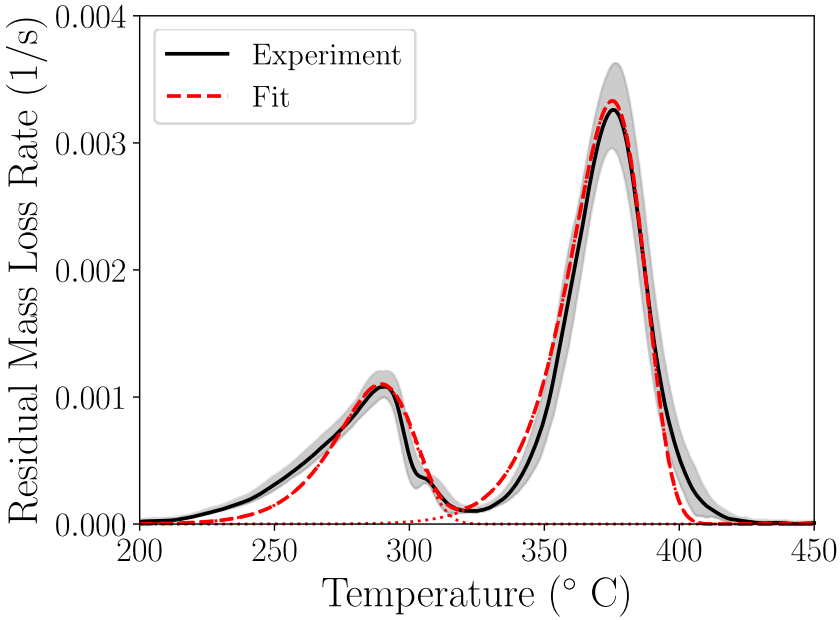




Kinetic Parameter	Reaction 1
T_p (K)	716.3
ΔT (K)	22.11
Δm	0.9754
ξ	0.03087
$\ln[A\ (s^{-1})]$	27.50
E (kJ/kmol)	192.9×10^3

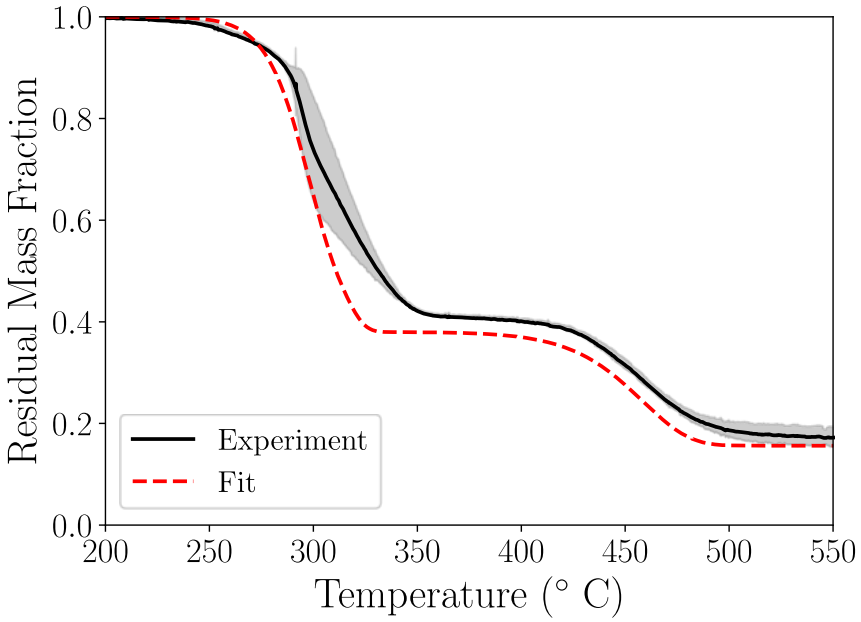
Validation: Polyurethane Foam

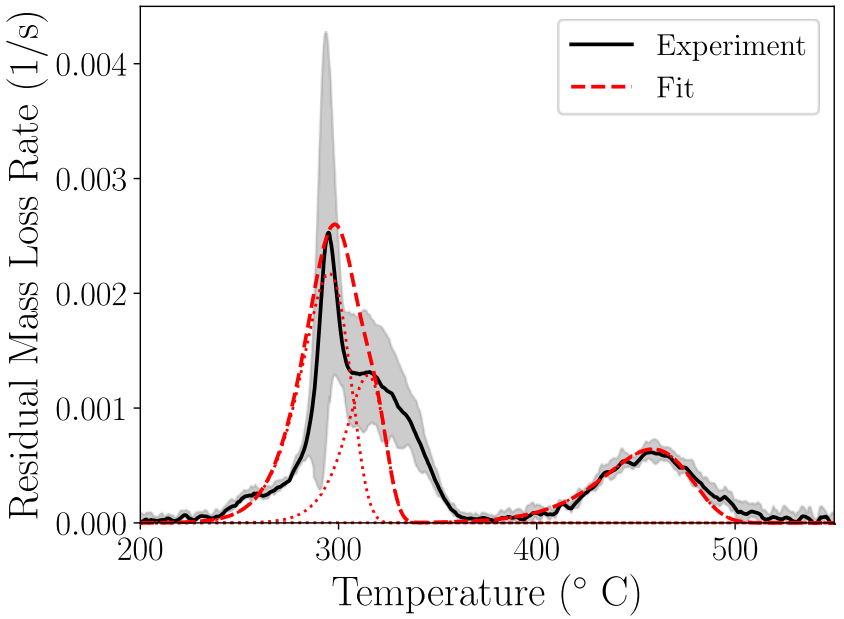




Kinetic Parameter	Reaction 1	Reaction 2
T_p (K)	562.7	648.5
ΔT (K)	14.50	13.69
Δm	0.2511	0.7280
ξ	0.02577	0.02112
$\ln[A\ (s^{-1})]$	34.34	42.95
E (kJ/kmol)	181.5×10^3	255.3×10^3

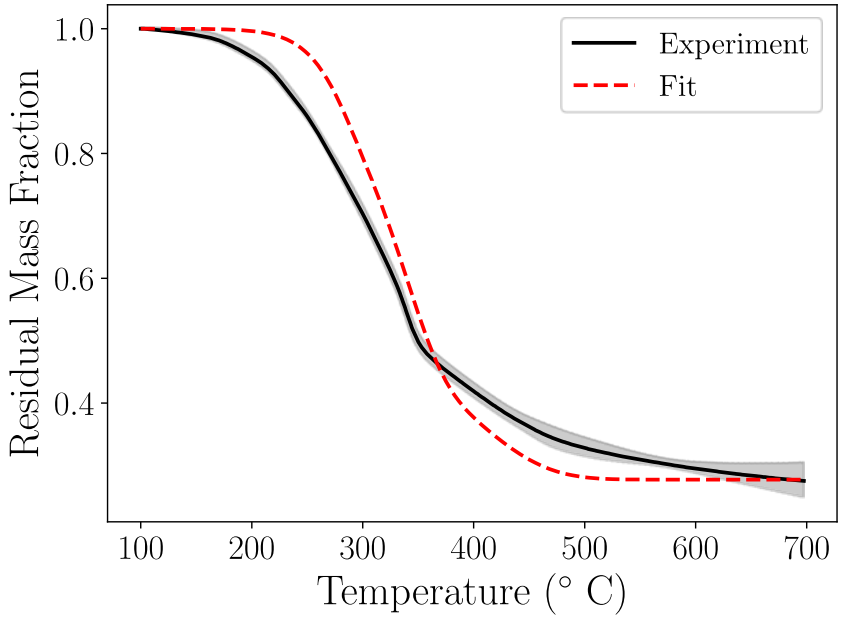
Validation: PVC

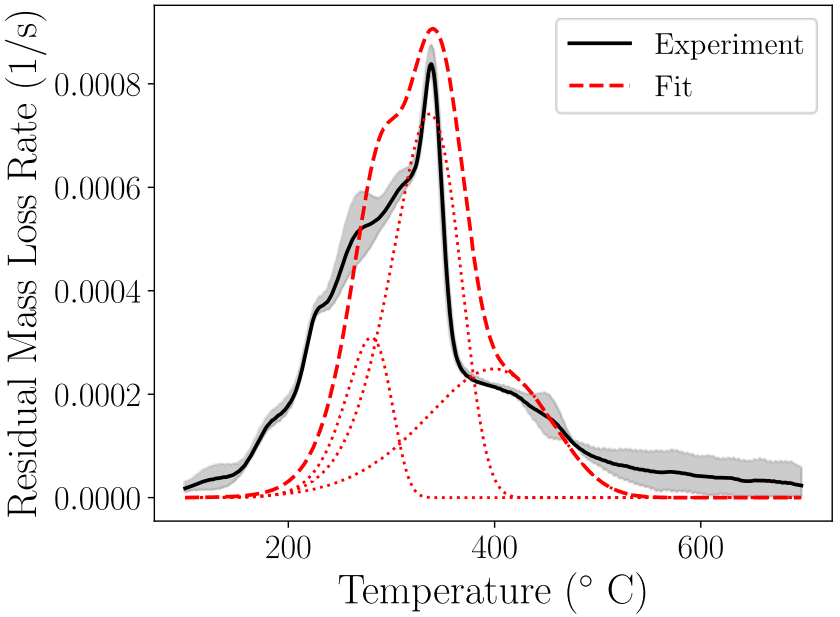




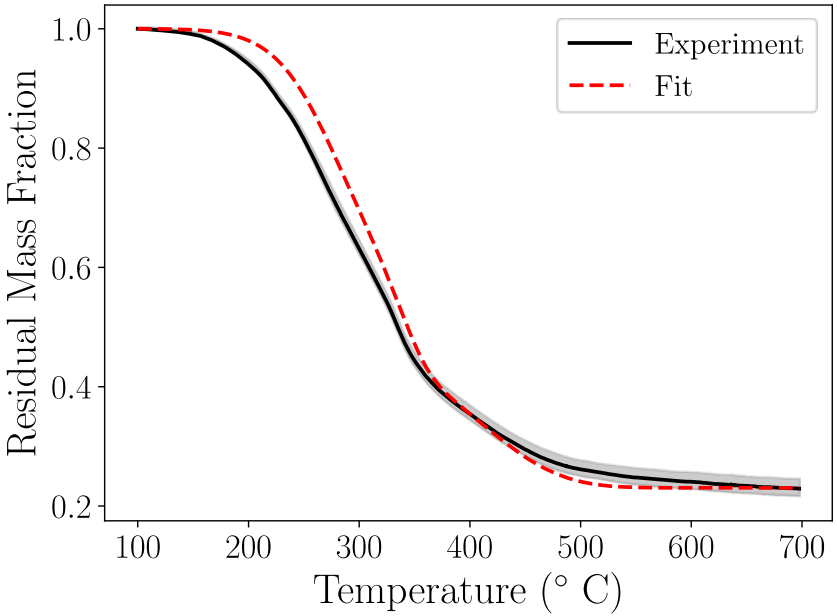
Kinetic Parameter	Reaction 1	Reaction 2	Reaction 3
T_p (K)	568.5	731.7	588.1
ΔT (K)	12.15	22.39	9.62
Δm	0.4200	0.2238	0.1999
ξ	0.02138	0.03060	0.01636
$\ln[A\ (s^{-1})]$	42.49	27.78	57.06
E (kJ/kmol)	221.1×10^3	198.8×10^3	298.8×10^3

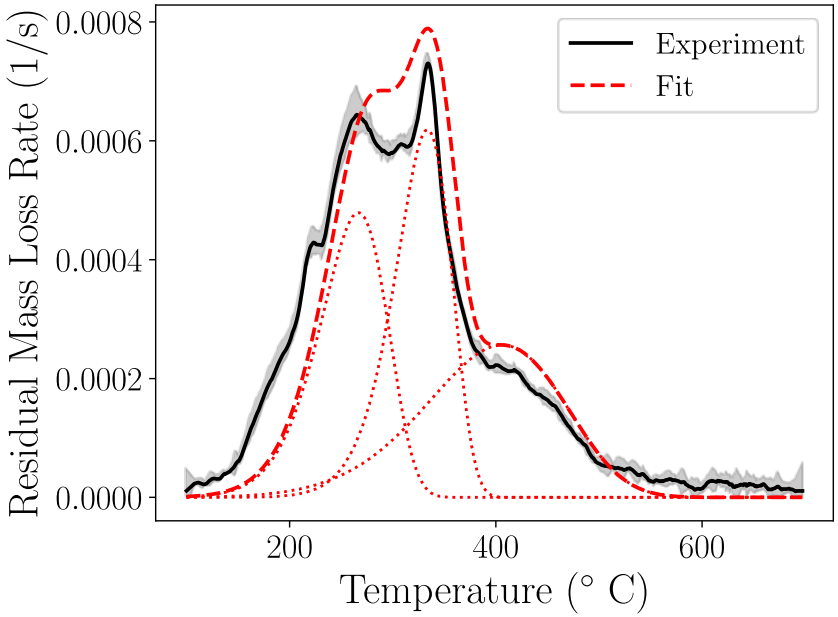
Validation: Lodgepole Pine Leaves





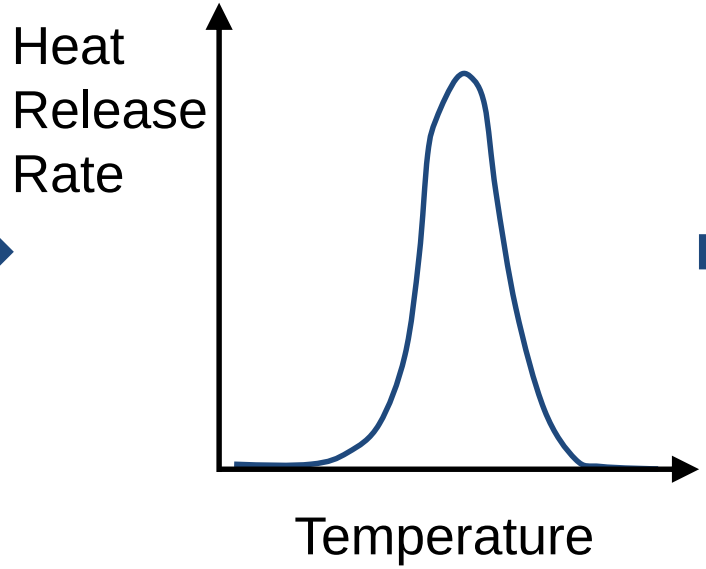
Validation: Douglas Fir Leaves





Analysis of MCC Data

How should we estimate individual reaction heats of combustion ($\Delta h_{c,i}$) from raw MCC data?



$\Delta h_{c,i}$

Single Reaction

$$\dot{Q}(T) = \dot{m}(T)\,\Delta h$$

1) Value at Peak Temperature: T_p

$$\Delta h = \frac{\dot{Q}(T_\mathrm{p})}{\dot{m}(T_\mathrm{p})}$$

2) Simple Average: N_d data points

$$\Delta h = \frac{1}{N_\mathrm{d}} \sum_{k=1}^{N_\mathrm{d}} \frac{\dot{Q}(T_k)}{\dot{m}(T_k)}$$

Multiple Reactions

$$\dot{Q}(T) = \sum_{i=1}^{N_\mathrm{r}} \dot{m}_i(T)\,\Delta h_i$$

1) Linear System: N_r equations, N_r unknowns

$$\sum_{i=1}^{N_\mathrm{r}} \dot{m}_i(T_{\mathrm{p},j})\,\Delta h_i = \dot{Q}(T_{\mathrm{p},j}),\ j = 1,\ldots,N_\mathrm{r}$$

2) Multiple Linear Regression: N_d data points

$$\sum_{i=1}^{N_\mathrm{r}} \dot{m}_i(T_k)\,\Delta h_i = \dot{Q}(T_k),\ k = 1,\ldots,N_\mathrm{d} > N_\mathrm{r}$$

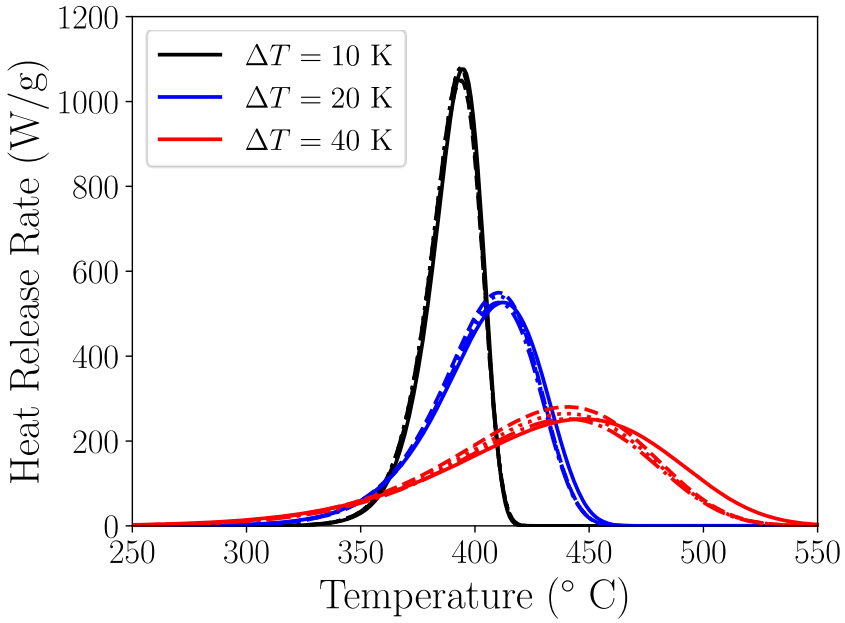
Verification

1. Assume **kinetic parameters** and **heats of combustion**
2. Generate TGA data
3. Use TGA fit algorithm to find kinetic parameters
4. Use TGA predictions and MCC data to find heats of combustion

Purpose:

1. Check implementation
2. Test validity of approximate solution

MCC: Single Reaction Verification



- TGA Data
  - 10 K/min
  - T_{p} = 650 K
- MCC Data
  - 60 K/min
  - Δh = 30 kJ/g

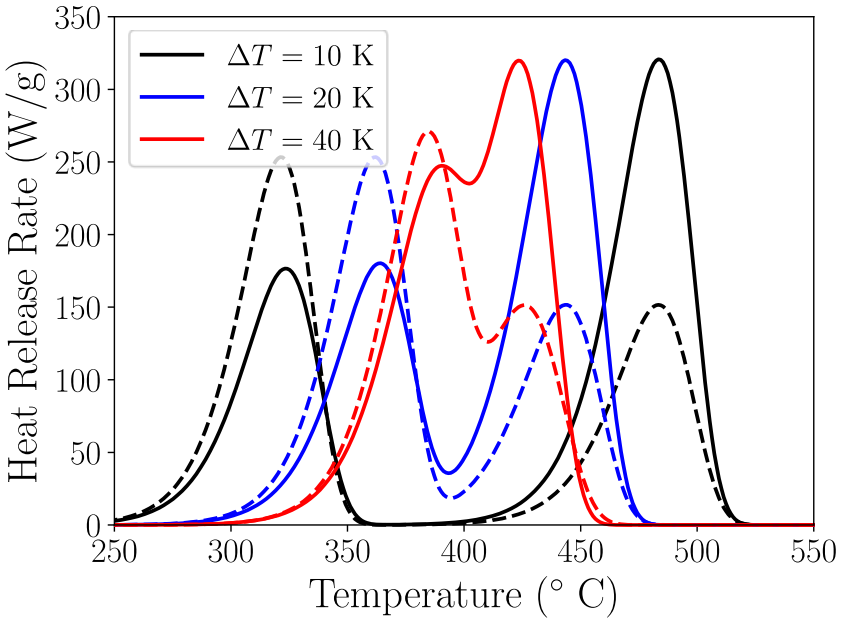
Solid: Simulated Data
Dash: Total HRR/mass
Dash-Dot: Peak Match
Dot: Simple Average

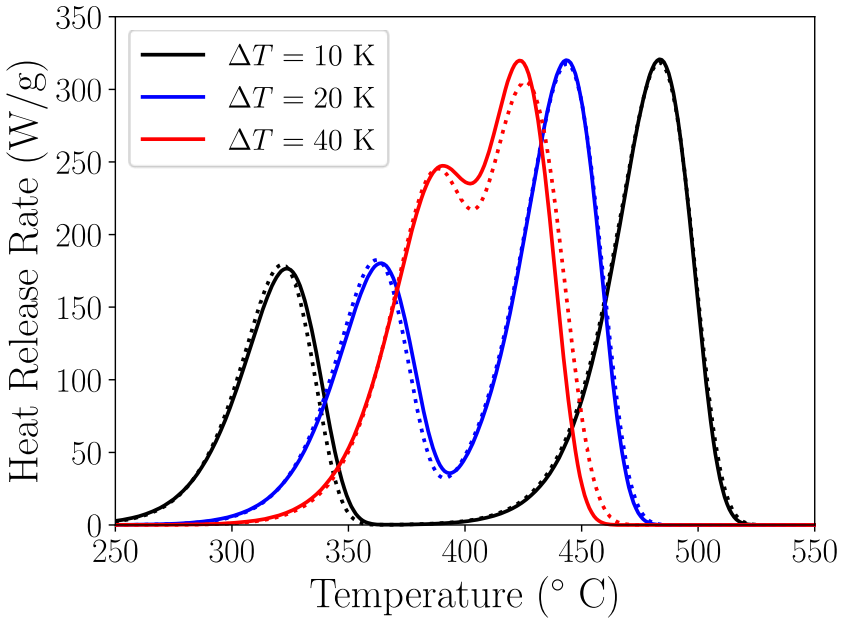
MCC: Single Reaction Verification

Scenario	Δh (kJ/g) (Total HR/mass)	Method 1: Peak Ratio Δh (kJ/g)	Method 2: Simple Average Δh (kJ/g)
ΔT = 10 K/min	30.026	30.792	30.849
ΔT = 20 K/min	29.997	28.731	29.556
ΔT = 40 K/min	29.997	26.949	28.291

- Total HR/mass not applicable to multiple reaction
- Method 2 performs better than Method 1

MCC: Two Reactions Verification





Evenly distributed heat release

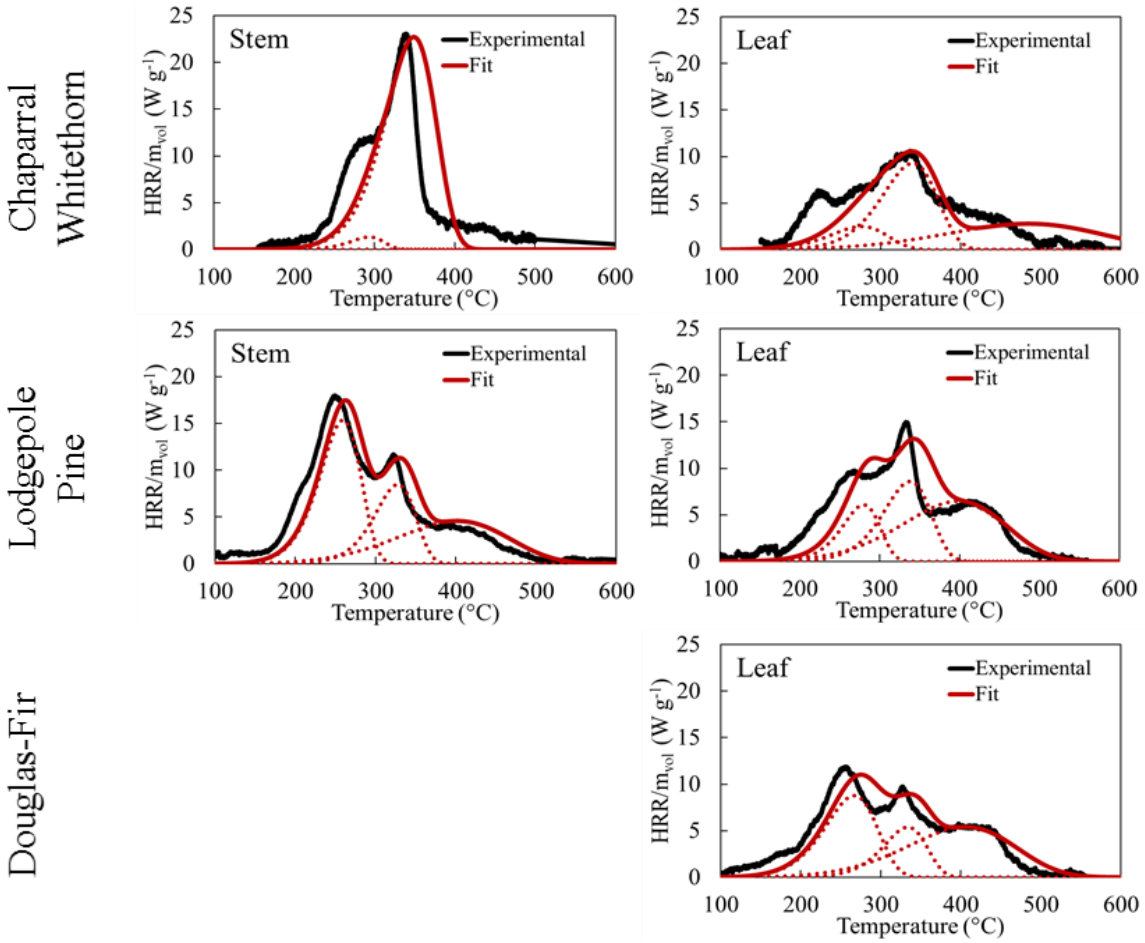
Method 2: Multiple linear regression

MCC: Two Reactions Verification

		$-\Delta h_1$ (kJ/g)	$-\Delta h_2$ (kJ/g)	$-\Delta h_{total}$ (kJ/g)
Specified Value		15	45	21
ΔT = 10 K/min	Simple Integration	--	--	20.998
	Linear Regression	14.854	44.085	21.021
ΔT = 20 K/min	Simple Integration	--	--	20.998
	Linear Regression	14.953	43.973	21.061
ΔT = 40 K/min	Simple Integration	--	--	20.998
	Linear Regression	15.415	42.304	21.501

- Accuracy decreases with longer reactions
- Future work: correct individual reaction values to force match of total value

MCC: Vegetative Fuels Validation



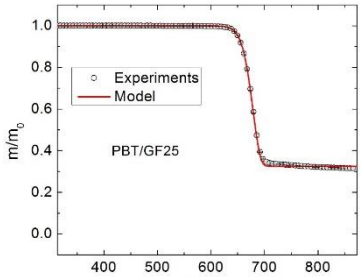
MCC: Vegetative Fuel Heats of Combustion

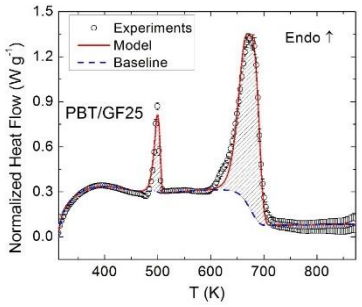
Sample Name	$\Delta H_{c,1}$ (kJ g^{-1})	$\Delta H_{c,2}$ (kJ g^{-1})	$\Delta H_{c,3}$ (kJ g^{-1})	$\Delta H_{c,total}$ (kJ g^{-1})	μ_{char} (-)
		Leaves			
Chamise	17.3±2.6	12.9±1.9	22.9±3.4	11.7±1.2	0.25±0.04
Bigberry Manzanita	15.4±2.3	14.9±2.2	21.8±3.3	12.4±0.9	0.22±0.06
Desert Ceanothus	17.1±2.6	30.7±4.6	47.4±7.1	12.3±1.1	0.32±0.03
Chaparral Whitethorn	7.9±1.2	20.7±3.1	19.0±2.8	10.4±1.8	0.33±0.04
Lodgepole Pine	10.8±1.6	16.1±2.4	23.6±3.5	12.6±0.6	0.24±0.04
Douglas-Fir	18.3±2.7	8.7±1.3	21.1±3.2	12.2±0.6	0.25±0.04
Average Leaf *	-	-	-	11.9±0.8	0.27±0.05
		Stems			
Chamise	17.5±2.6	7.3±1.1	5.5±0.8	8.9±0.6	0.27±0.04
Bigberry Manzanita	9.0±1.4	12.9±1.9	21.9±3.3	8.9±0.9	0.37±0.06
Desert Ceanothus	13.2±2.0	11.7±1.8		9.1±0.5	0.25±0.06
Chaparral Whitethorn	6.1±0.9	16.1±2.4		11.5±2.6	0.23±0.05
Lodgepole Pine	20.8±3.1	15.4±2.3	18.6±2.8	14.4±2.0	0.22±0.04
Average Stem*	-	-	-	10.9±2.3	0.27±0.05

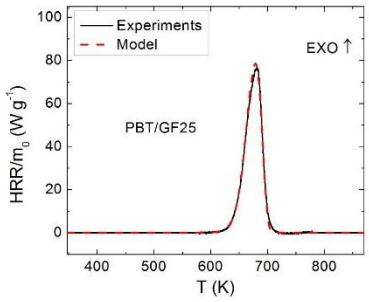
Summary

- Fire models need material property parameters to **predict** fire growth
- Obtaining material properties requires
  - Small-scale tests
  - **Parameter estimation algorithms**
- Parameter estimation algorithms are presented for obtaining
  - pyrolysis kinetic models from TGA data
  - individual reaction heats of combustions from MCC data
- The algorithms performs well for
  - Manufactured solution verification cases
  - Multiple reaction materials with well-separated reaction peaks
- More work is needed for
  - Multiple reaction materials with overlapping reaction peaks

Model Parameterization: Framework







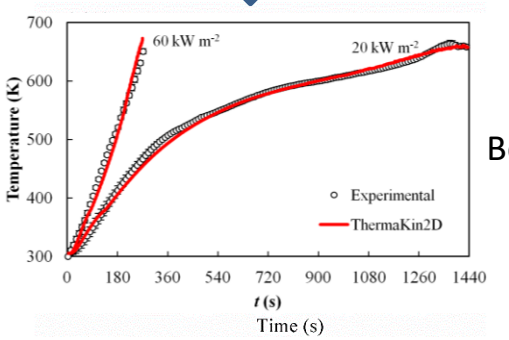
mg-scale testing

Analysis tools

Thermophysical properties

$$A \quad E \quad \nu$$
$$c_p \quad h_i \quad \Delta H_c$$

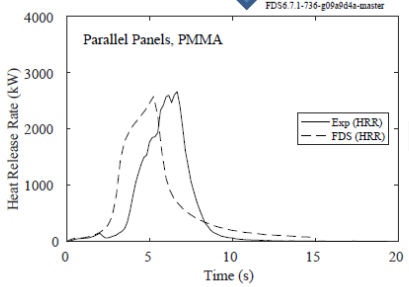
Computational Model



Computational Model

Bench scale experiments for model calibration

Full scale testing for model validation



Quantitative prediction of fire growth

Users

- FPEs
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- Materials Companies
- Investigators
- Product Designers

Extras…

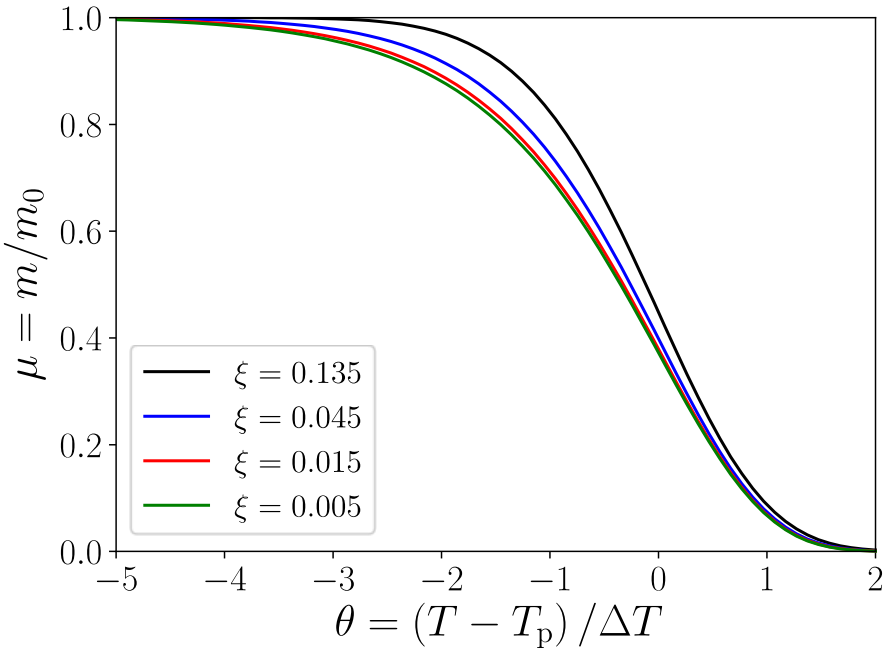
Nondimensional Form

$$\frac{\mathrm{d}\mu}{\mathrm{d}\theta} = -\mu \exp\left(\frac{\theta}{\xi\theta + 1}\right), \quad \mu\left(\theta \to -\infty\right) = 1$$

$$\mu \equiv \frac{m}{m_0}$$

$$\theta \equiv \frac{T - T_\mathrm{p}}{\Delta T}$$

$$\xi \equiv \frac{\Delta T}{T_\mathrm{p}}$$



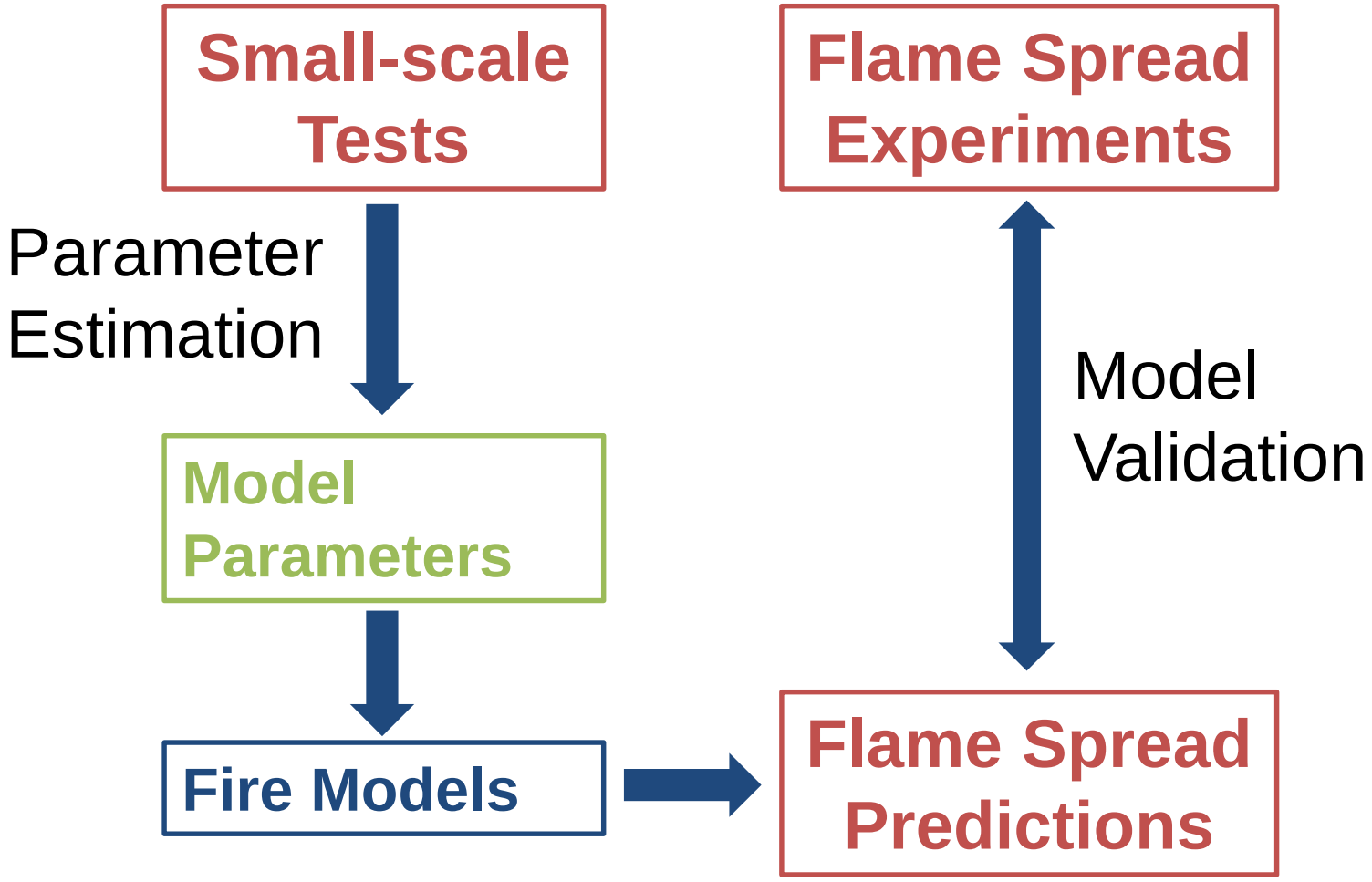
Approximate Solution

$$\xi \to 0 \quad (T_\mathrm{p} \gg E/R) \implies \frac{\mathrm{d}\mu}{\mathrm{d}\theta} = -\mu \exp\theta$$

$$\mu = \exp\left[-\exp\left(\theta\right)\right]$$

$$m = m_0 \exp\left[-\exp\left(\frac{T - T_\mathrm{p}}{\Delta T}\right)\right]$$

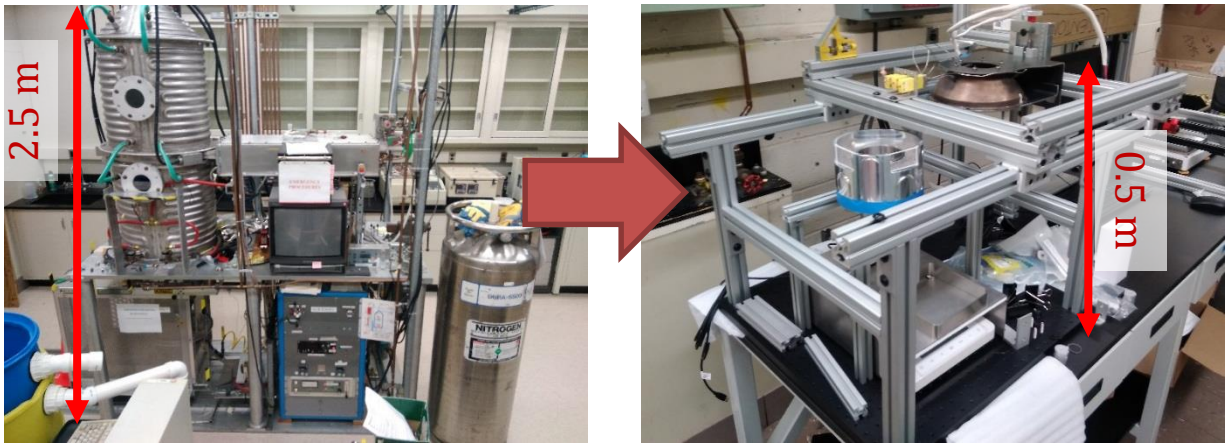
Also applies for multiple, independent reactions.



The quality of any **parameter estimation** algorithm is ultimately determined in **model validation**

Gasification Apparatus

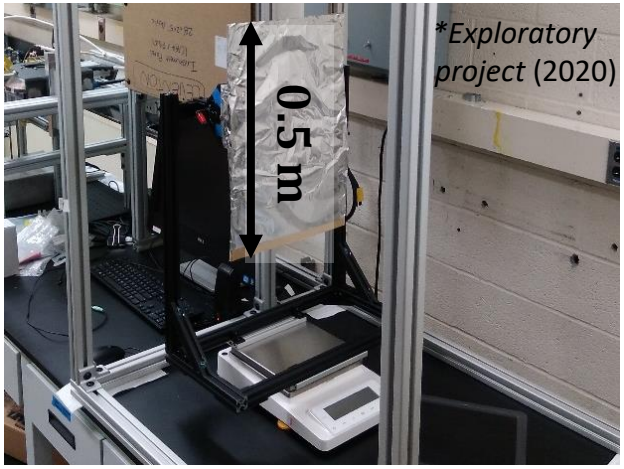
- Carefully characterized boundary conditions
  - 1D heating environment $0 \leq \dot{q}''_{ext} \leq 75\ kW\ m^{-2}$
  - O_2 concentration: $0.01 \leq X_{O_2} \leq 0.21$
- Measurement capabilities
  - Mass loss rate
  - Temperatures
  - Structural deformation



Flame Spread Apparatus

(intermediate scale)

- Steady burning, flame spread
  - Sample size: up to **0.5 m tall, 0.2 m wide**
  - Variable configuration (orientation, aspect ratio)
- Measurement capabilities
  - Mass loss rate
  - Flame heat flux
  - Temperatures
  - Heat Release Rate*
  - Temperature & species profiles across flame sheet*
- Applications
  - Model validation
  - Flammability behavior

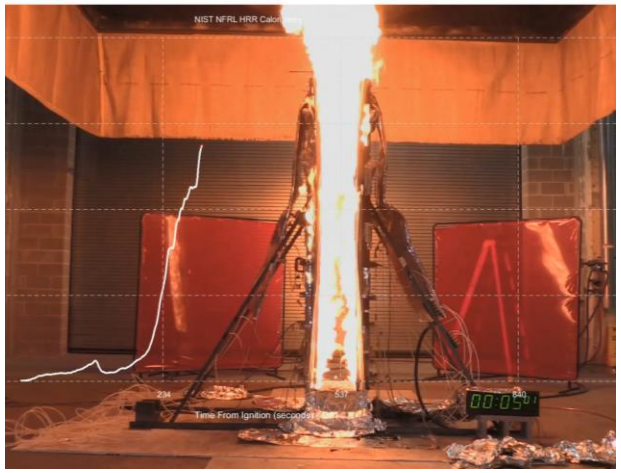


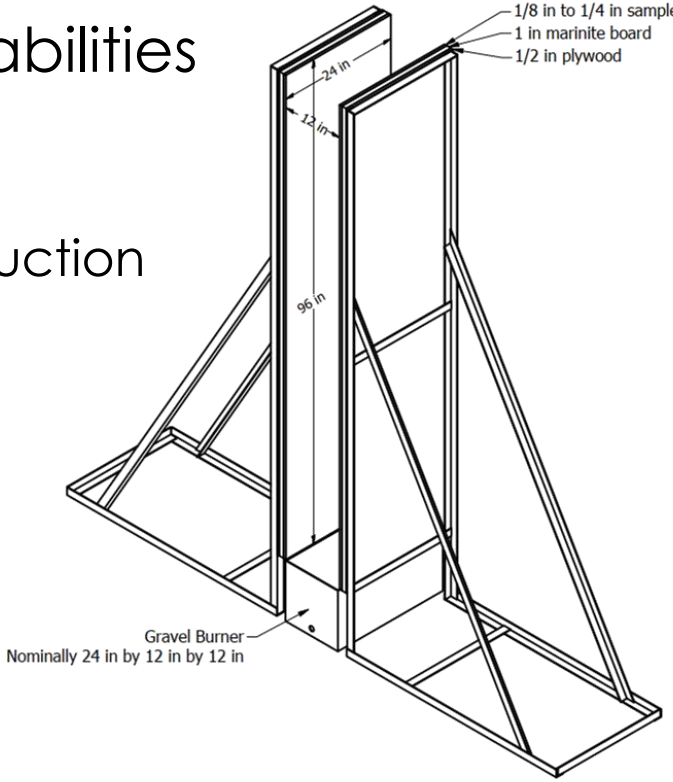
**Exploratory project* (2020)

Parallel Panel Apparatus

(full scale)

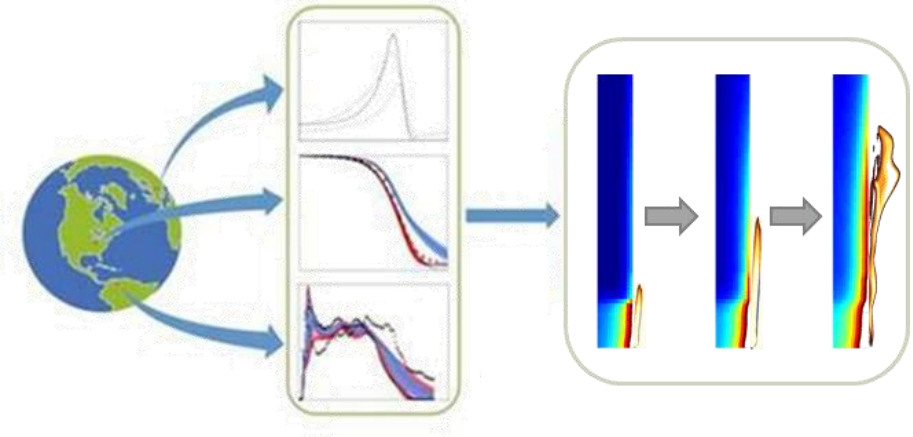
- Ignitability and flame spread
  - Sample size: **2.45 m tall, 0.6 m wide**
- Measurement capabilities
  - Heat release rate
  - Flame heat flux
  - CO_2, CO, soot production





Full Scale Fire Behavior Parallel Panel Apparatus

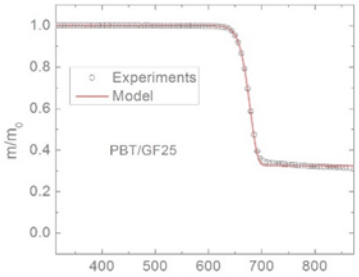
IAFSS Measurement and Computation of Fire Phenomenona (MaCFP)—Condensed Phase Workshop

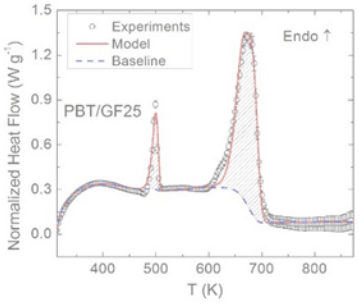


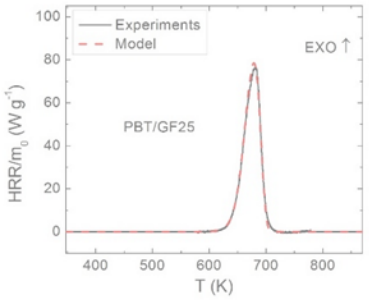
April 26, 2020

Waterloo, Canada

https://iafss.org/macfp/







mg-scale testing

Analysis tools

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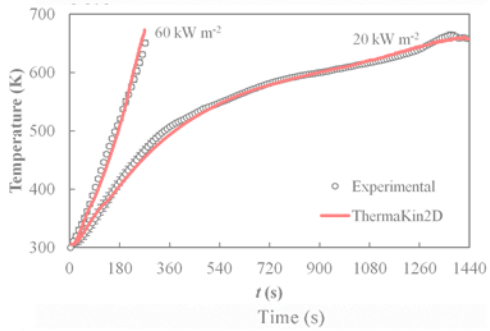
$$A \quad E \quad \nu$$
$$c_p \quad h_i \quad \Delta H_c$$
$$k \quad \rho$$
$$\alpha \quad \varepsilon$$

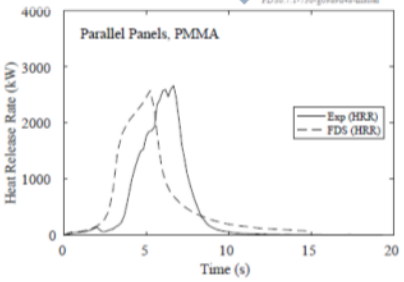
Computational Model

Computational Model



Bench scale experiments for model calibration

Full scale testing for model validation



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