

# Automated Material Characterization for Fire Modeling



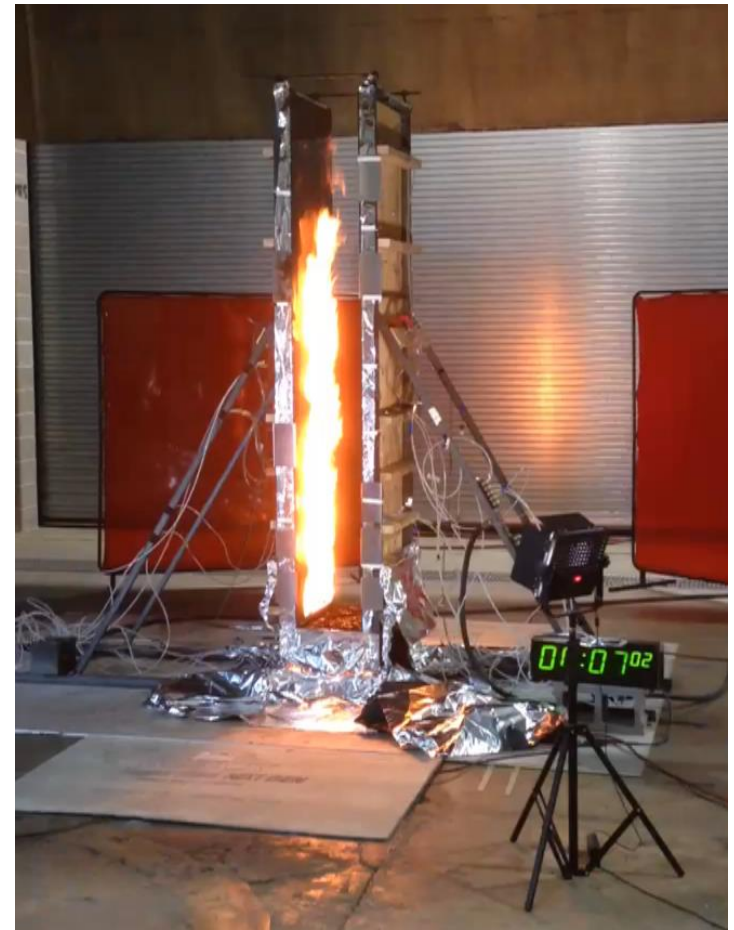
October 29, 2019

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*Virginia Military Institute (USA)*

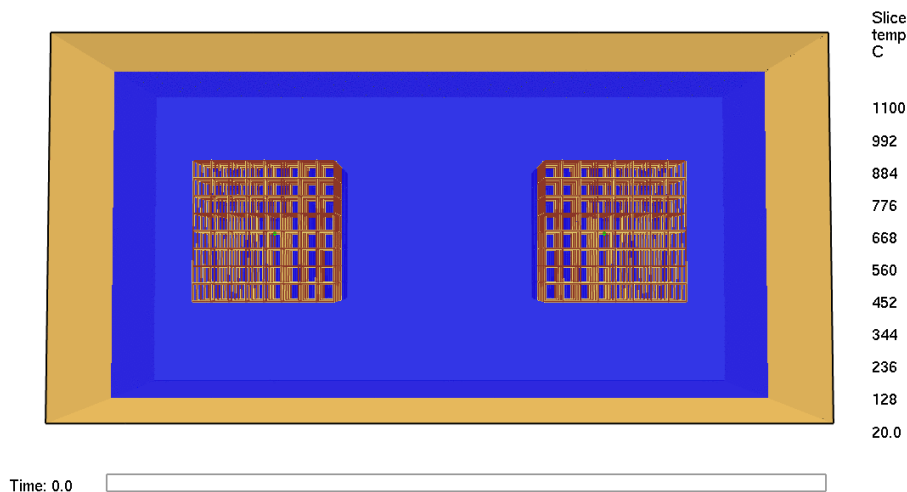
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*National Institute of  
Standards and Technology (USA)*

# Predicting Fire Growth

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

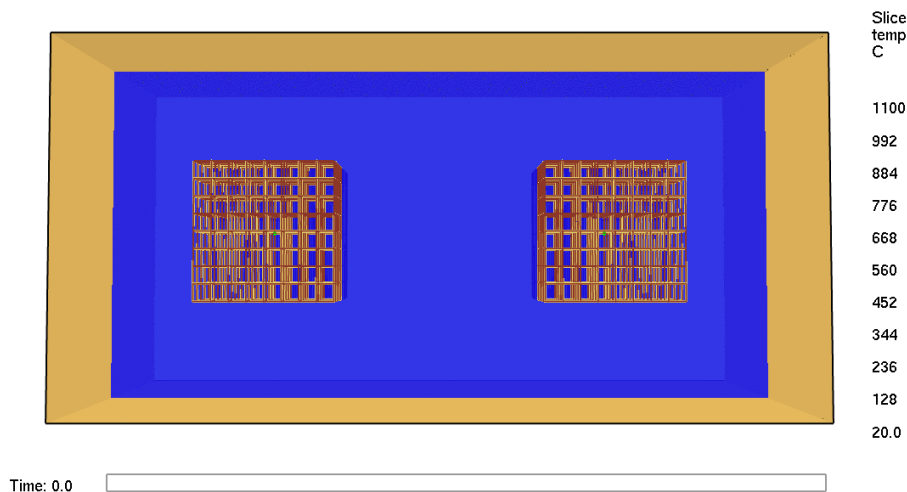


# Condensed Phase Challenges



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

# Condensed Phase Challenges



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

# How Many Parameters?

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

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

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

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

$$k = f(\rho_1, \dots, \rho_N, k_1, \dots, k_N)$$

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

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

Neglecting

- Radiation
- Mass transport
- Charring
- Temperature dependence



At least  $\sim 6N$   
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.

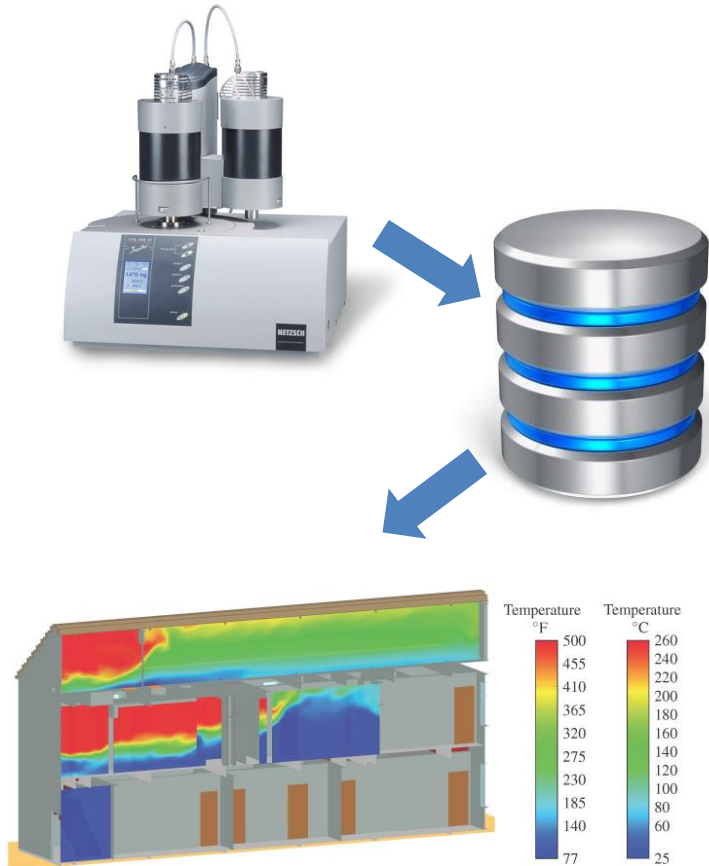
**On the order of  $10^3$  distinct materials relevant to fire growth predictions**

$(10^1 \text{ Parameters}) \times (10^3 \text{ Materials})$   
**=  $10^4$  Properties for reliable fire growth predictions**



**A Material Property Database is needed**

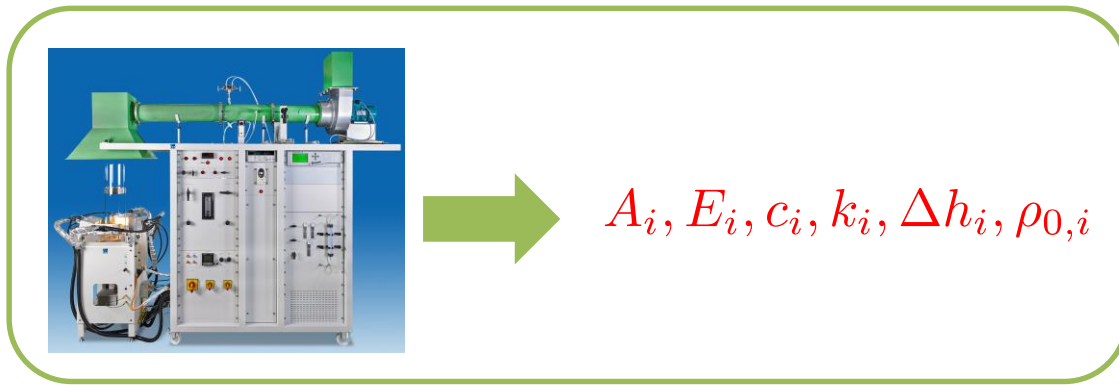
# Material Property Database



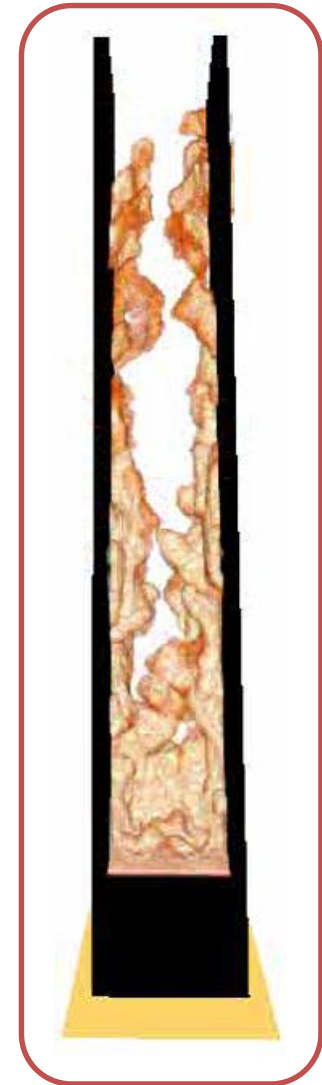
- Being developed at NIST
- Adopting “Hierarchical” approach
- Critical components
  1. Standard formatting
  2. Standard metadata
  - 3. Analysis tools**



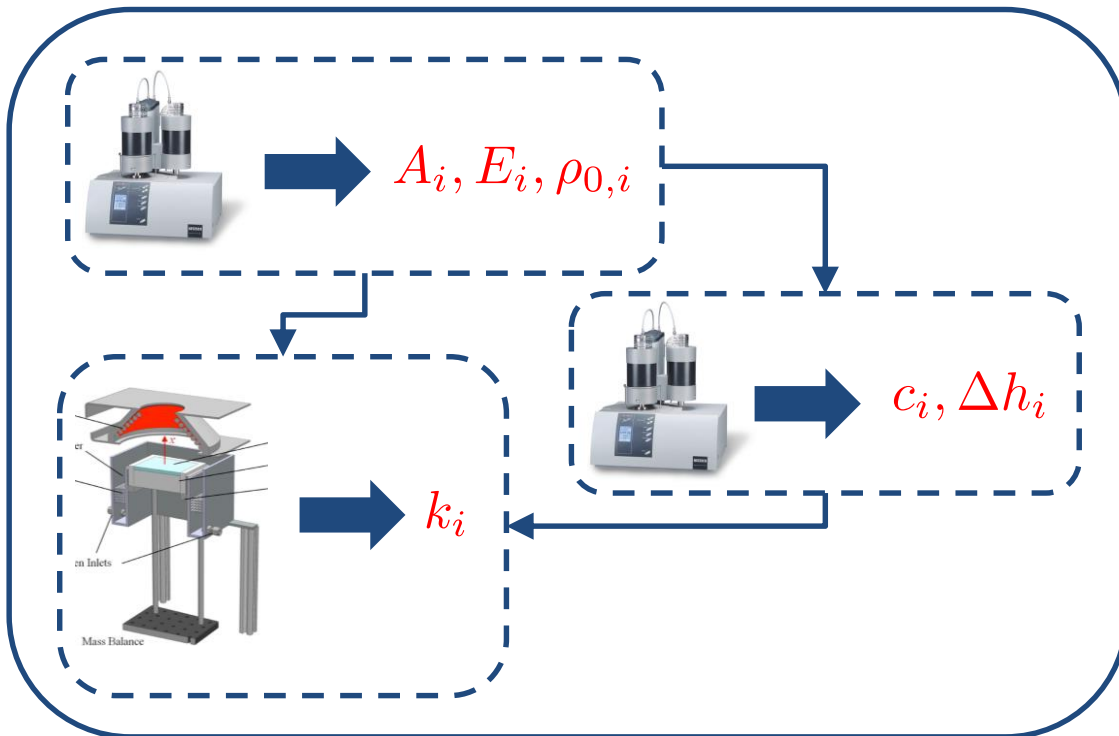
## Global Approach



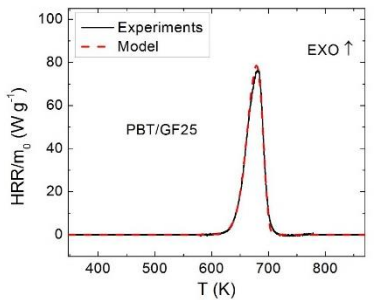
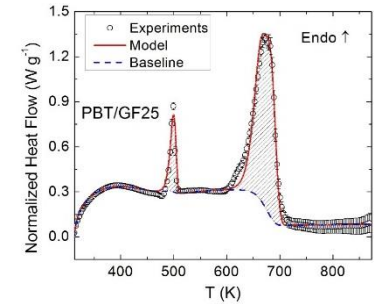
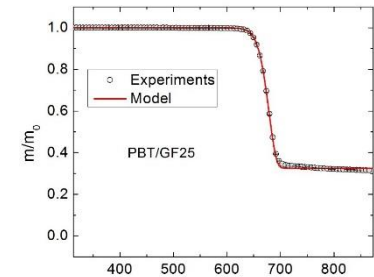
## Fire Model



## Hierarchical Approach



# Model Parameterization: Framework



mg-scale testing

Full scale testing for model validation



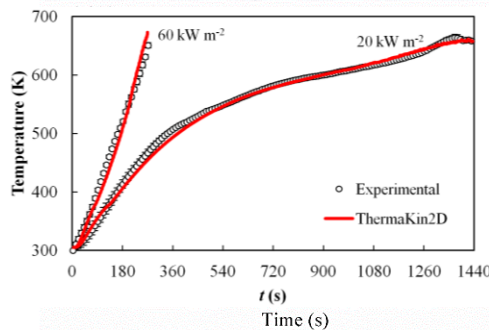
Thermophysical properties

$$\begin{matrix} A & E & \nu \\ c_p & h_i & \Delta H_c \\ k & \rho & \\ \alpha & \varepsilon & \end{matrix}$$

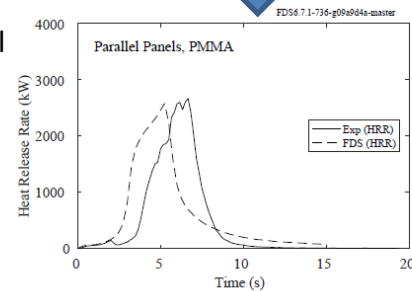
Analysis tools

Computational Model

Computational Model



Bench scale experiments for model calibration



Quantitative prediction of fire growth



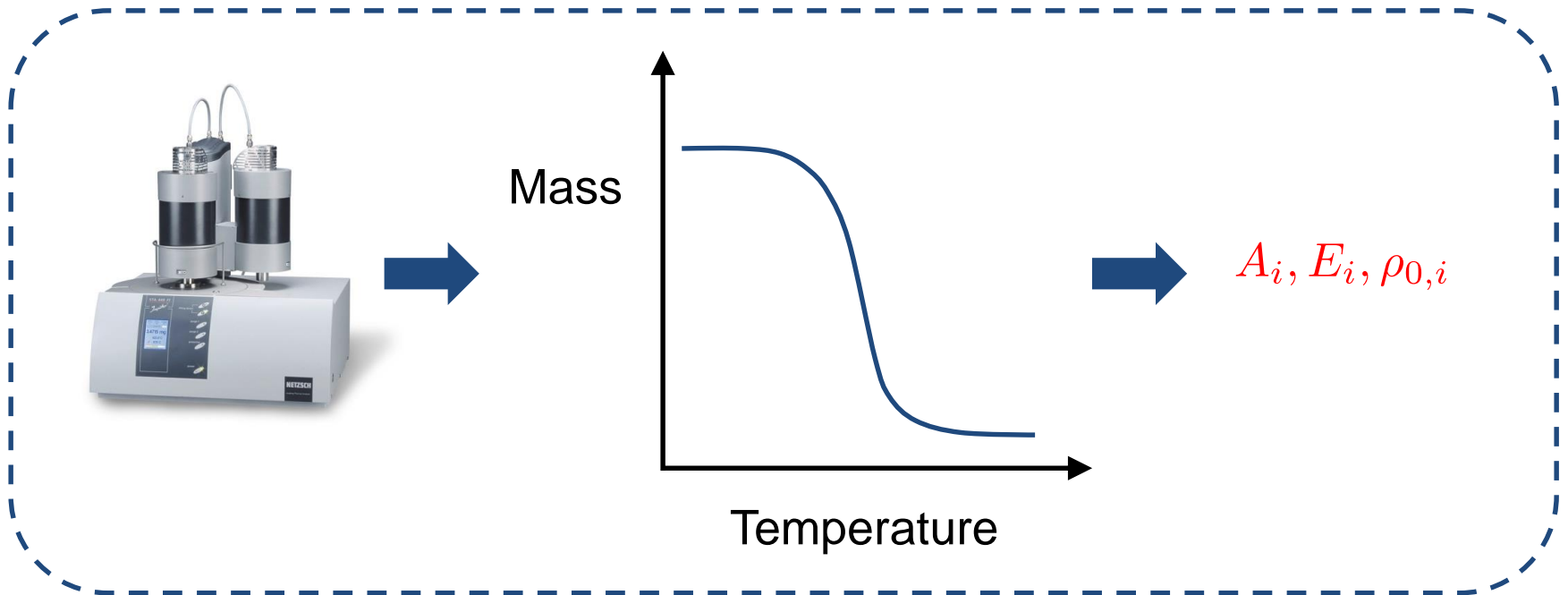
# Model Parameterization

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- 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

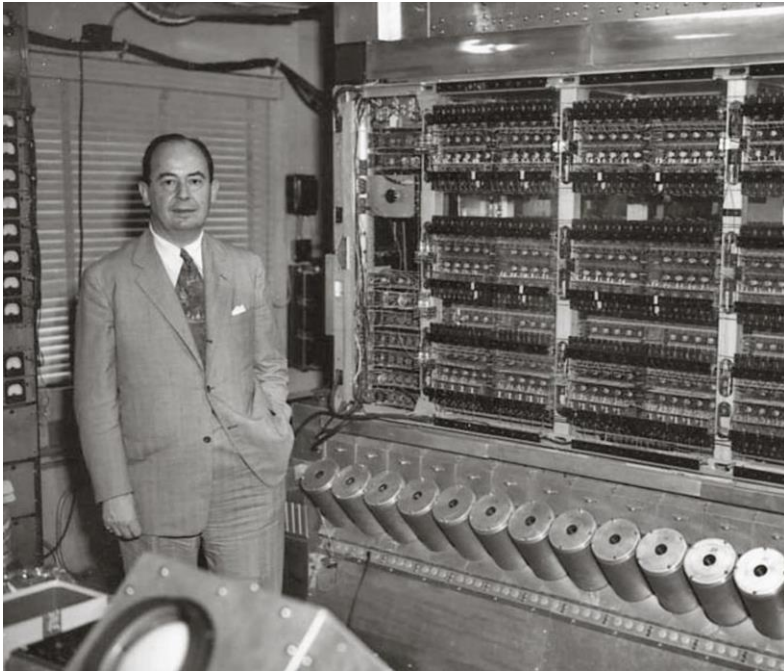
How should we estimate pyrolysis kinetic parameters from raw TGA data?



# 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



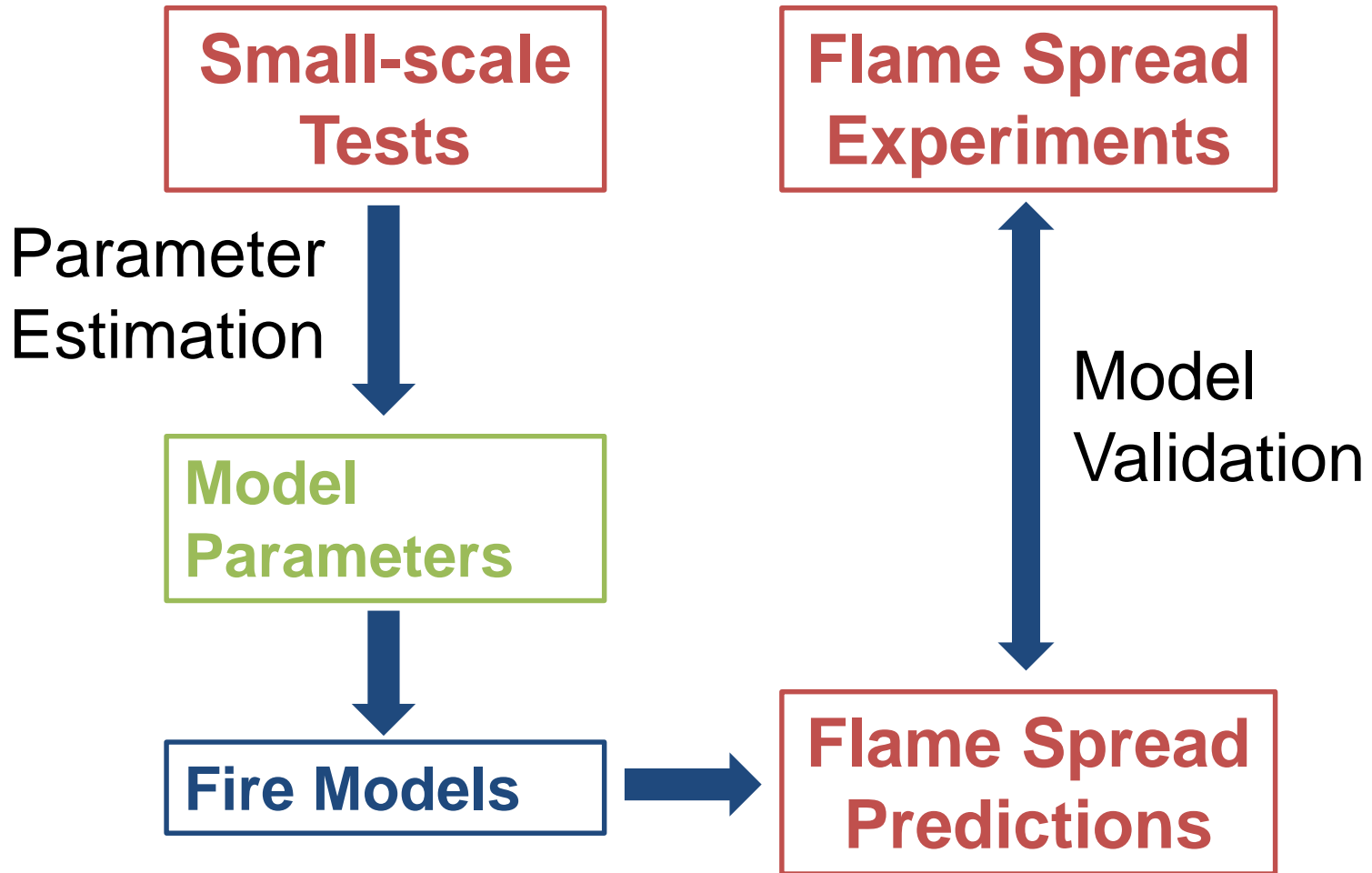
“With four parameters I can fit an elephant, and with five I can make him wiggle his trunk.”

~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

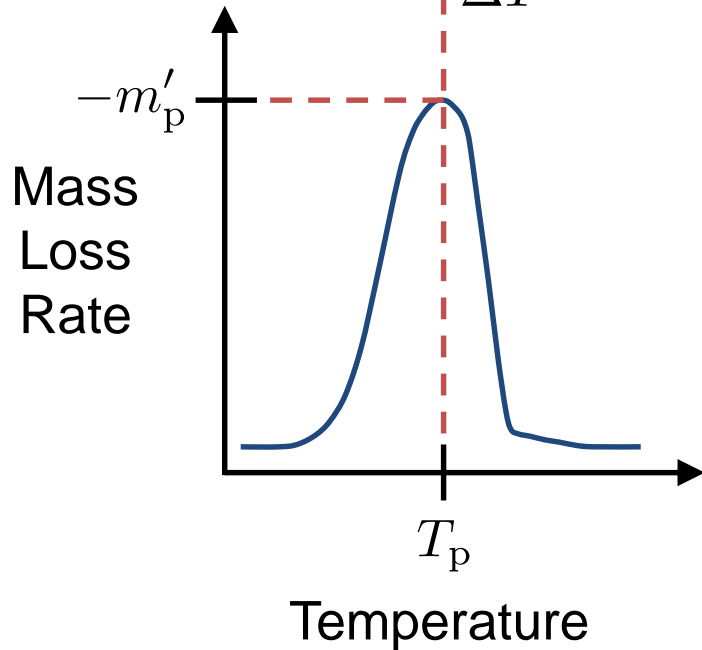
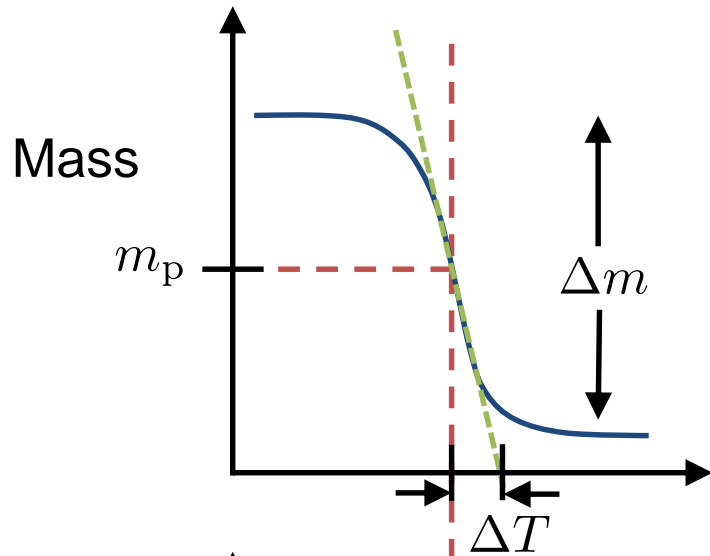


$$k = \left( \frac{A}{\beta} \right) \exp \left( -\frac{E}{RT} \right)$$

$$m' \equiv \frac{dm}{dT} = -(1 - \nu) km, \quad m(T_0) = m_0$$

Appropriateness to be determined by ability to predict fire growth.





Characteristic temperature and mass changes:

$$\Delta T \equiv \frac{m_p}{-m'_p}$$

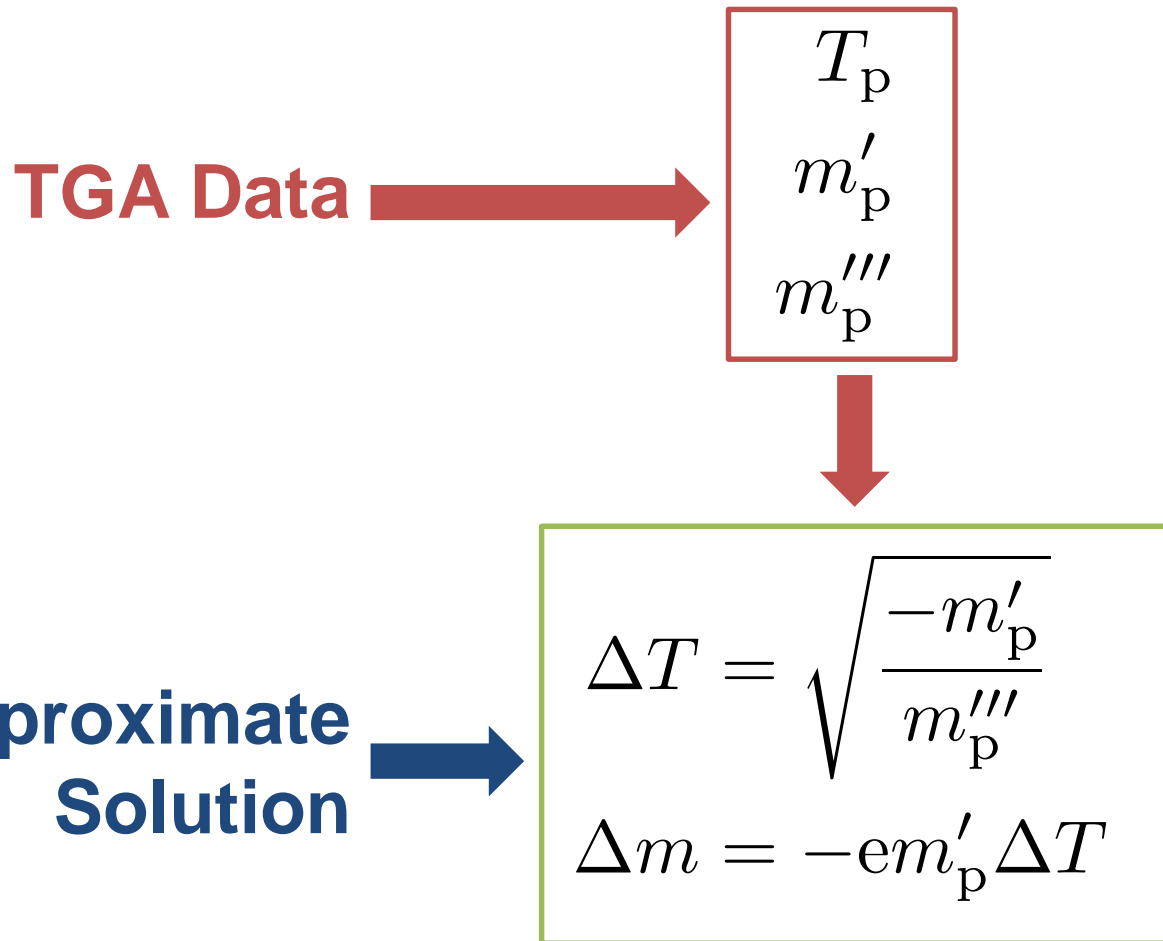
$$\Delta m \equiv m_0 (1 - \nu)$$

Analysis of peak condition yields:

$$E = \frac{RT_p^2}{\Delta T}$$

$$A = \frac{\beta}{\Delta T} \exp\left(\frac{T_p}{\Delta T}\right)$$

# Estimating Parameters



# 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



**Requires  
specification of  
two parameters**



**Requires  
iteration**

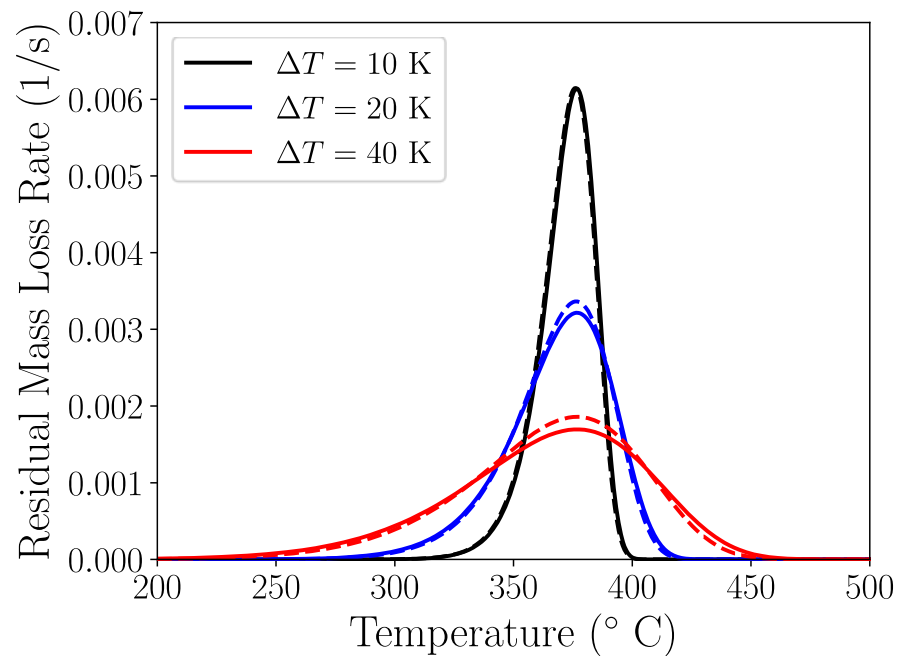
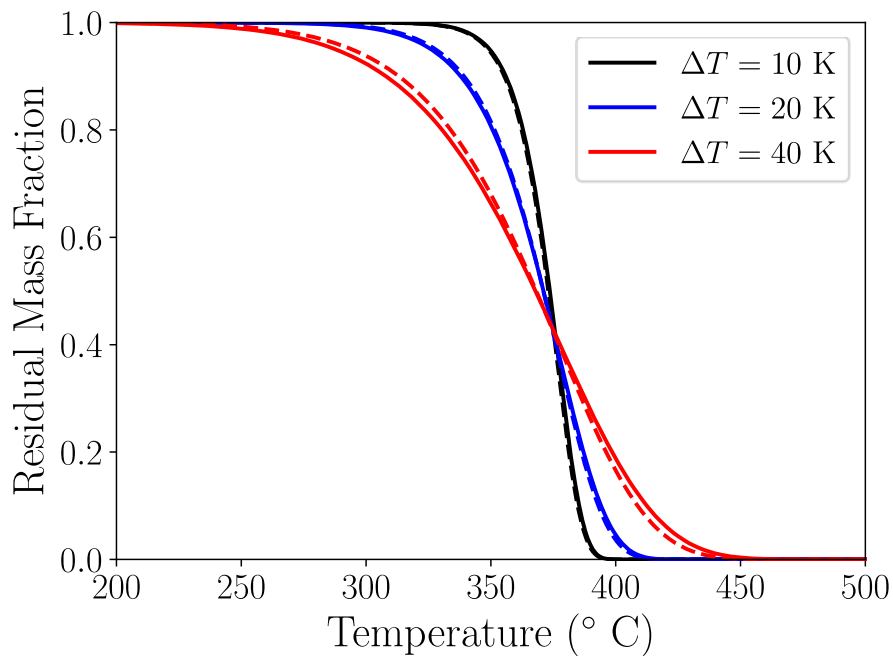
# Verification

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

$\Delta T = 10$  K:

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

$\Delta T = 20$  K:

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

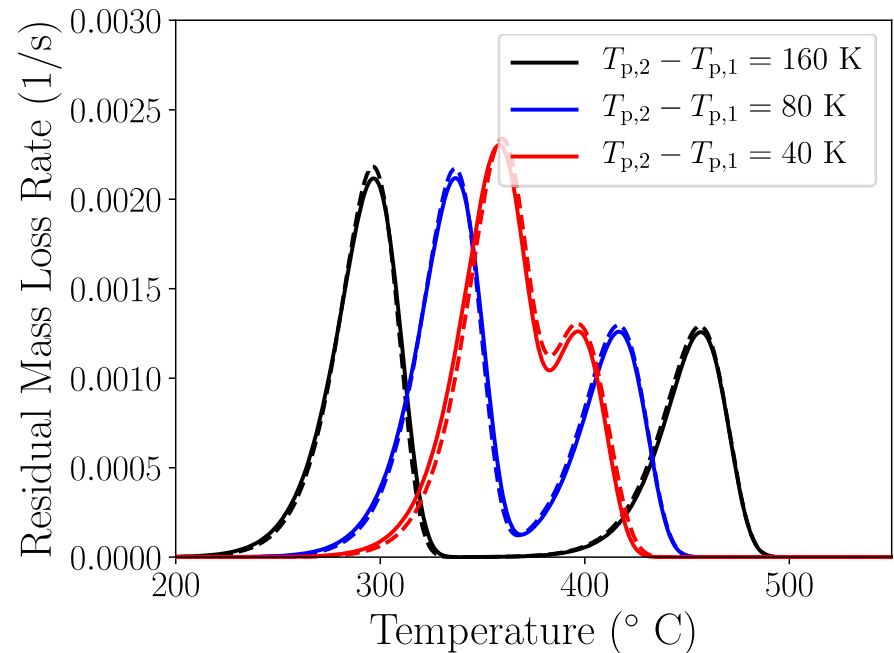
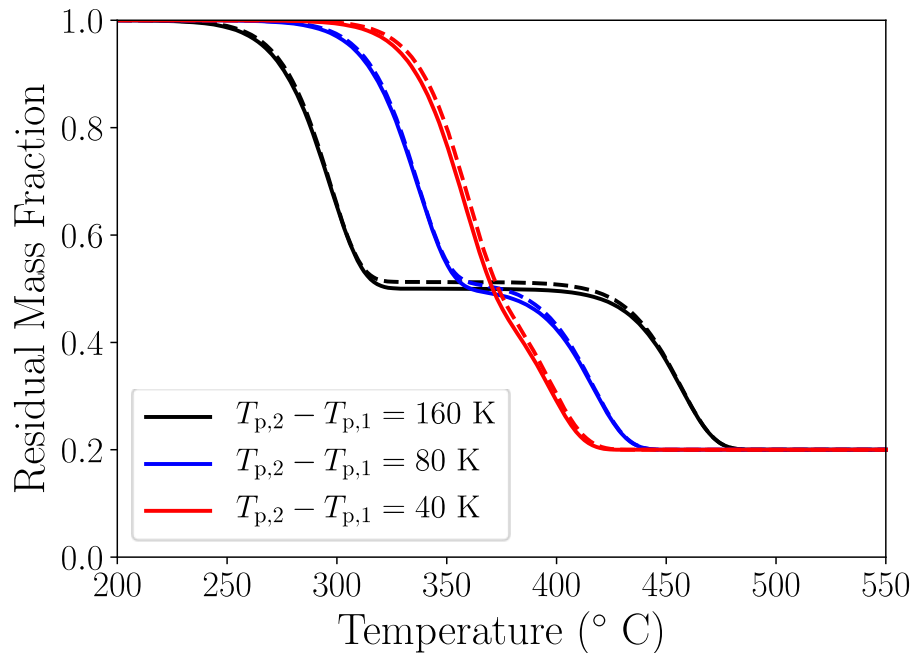
$\Delta T = 40$  K:

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



**Decreasing  $\xi$**   
**Increasing accuracy**

# Two Reactions Verification



**Closer fit for more separated reactions**

# Validation

## **Purpose:**

1. Test algorithm with real TGA data

## **Materials:**

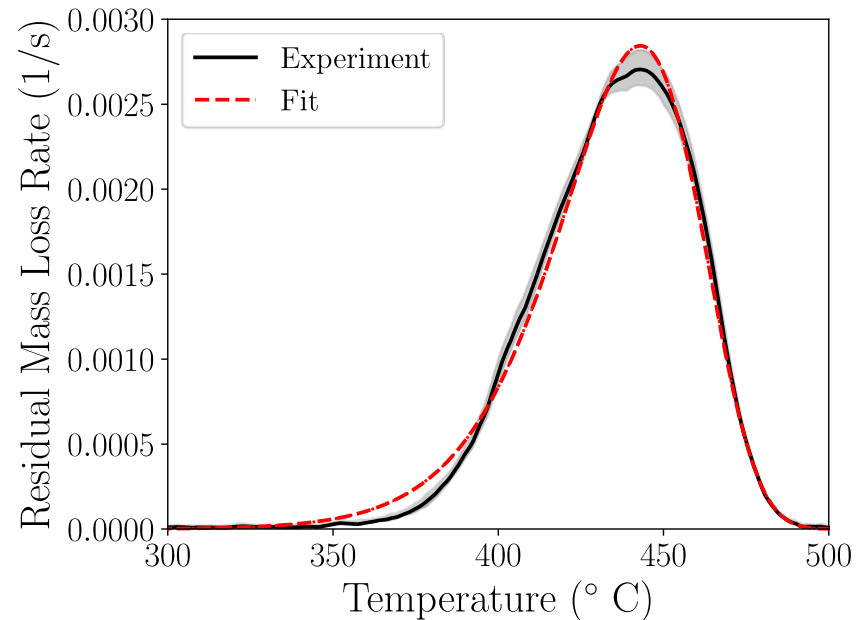
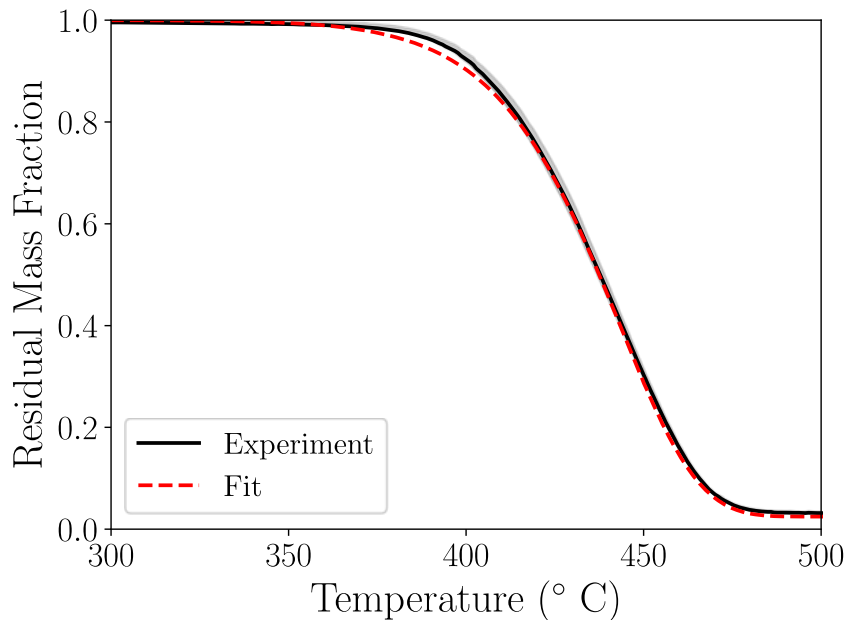
1. Nylon 6,6
2. Flexible polyurethane (PU) foam
3. Polyvinyl Chloride (PVC)

## **Procedure:**

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

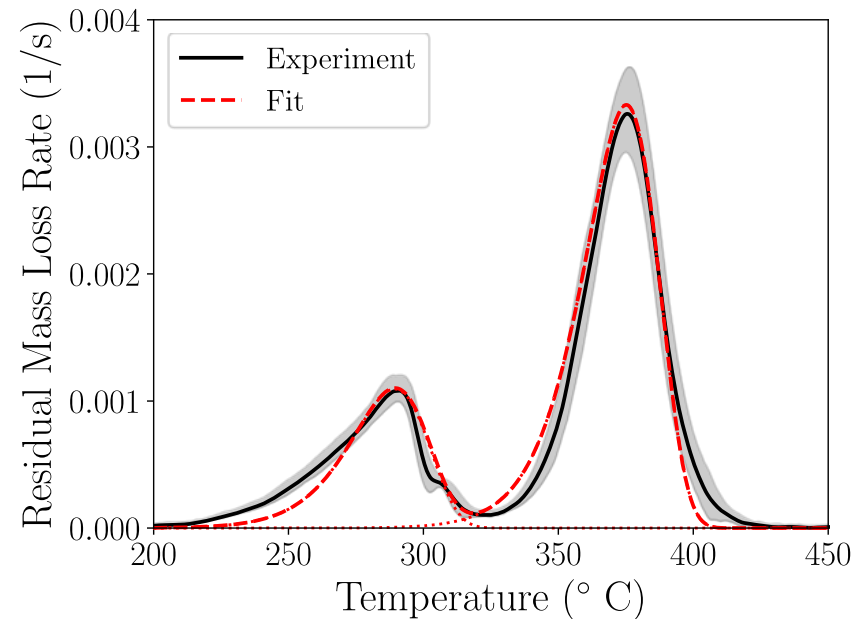
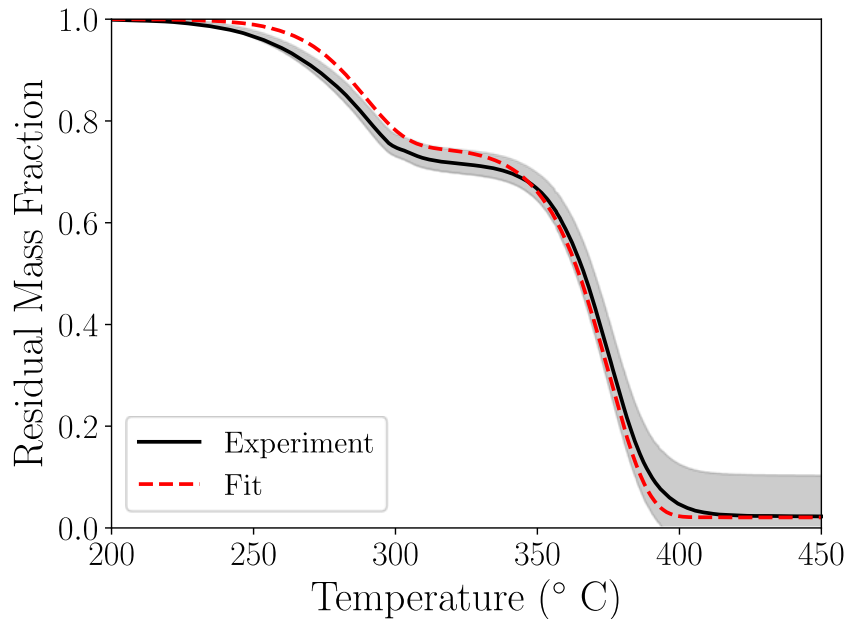


# Validation: Nylon 6,6



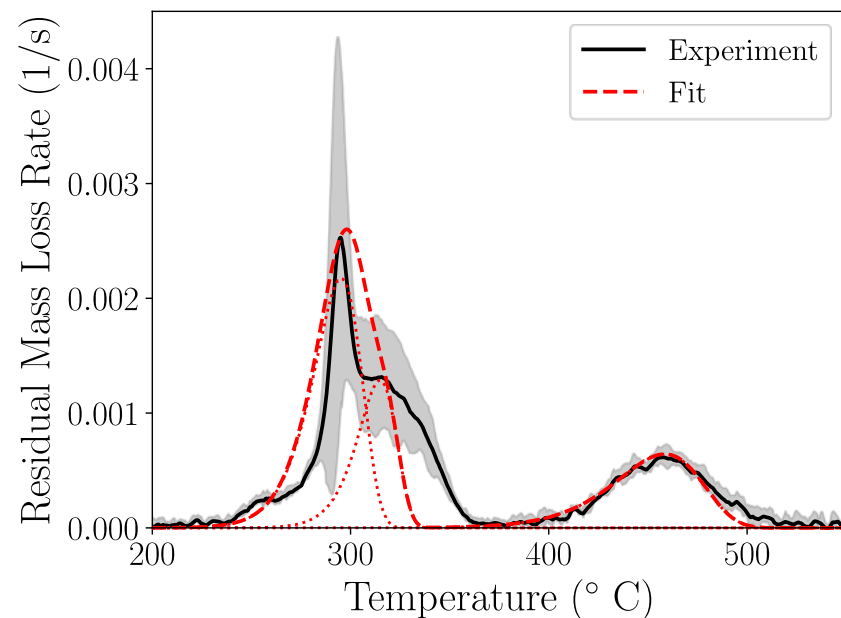
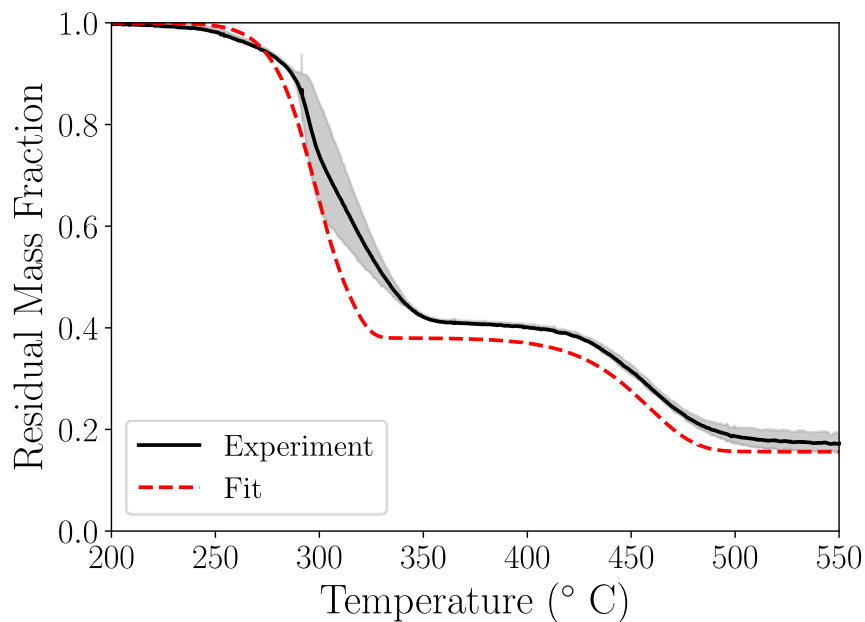
Kinetic Parameter	Reaction 1
$T_p$ (K)	716.3
$\Delta T$ (K)	22.11
$\Delta m$	0.9754
$\xi$	0.03087
$\ln[A \text{ (s}^{-1}\text{)}]$	27.50
$E$ (kJ/kmol)	$192.9 \times 10^3$

# Validation: Polyurethane Foam



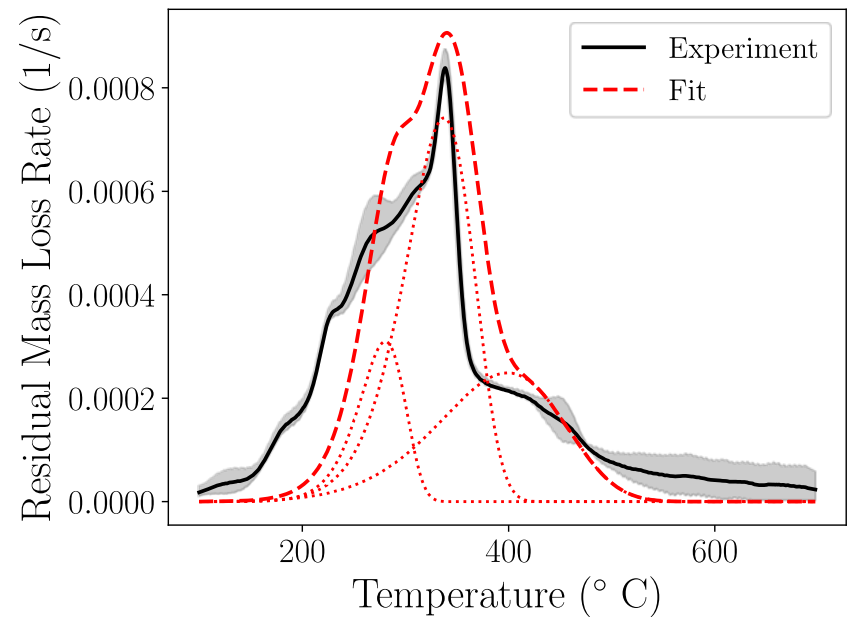
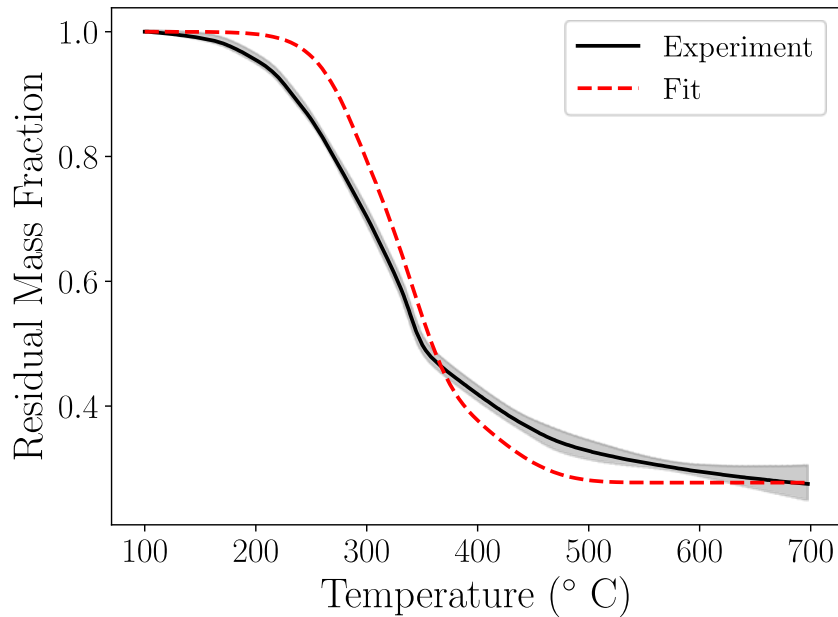
Kinetic Parameter	Reaction 1	Reaction 2
$T_p$ (K)	562.7	648.5
$\Delta T$ (K)	14.50	13.69
$\Delta m$	0.2511	0.7280
$\xi$	0.02577	0.02112
$\ln[A (s^{-1})]$	34.34	42.95
$E$ (kJ/kmol)	$181.5 \times 10^3$	$255.3 \times 10^3$

# Validation: PVC

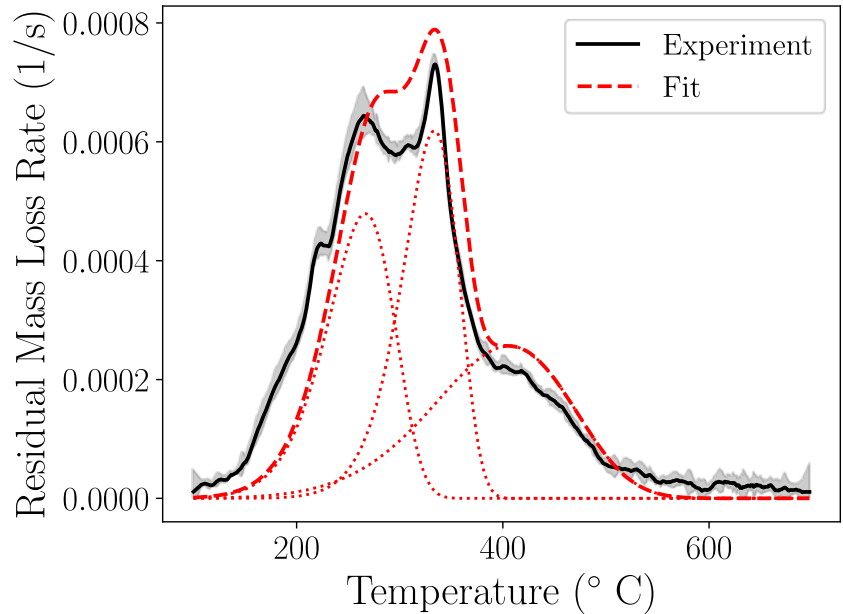
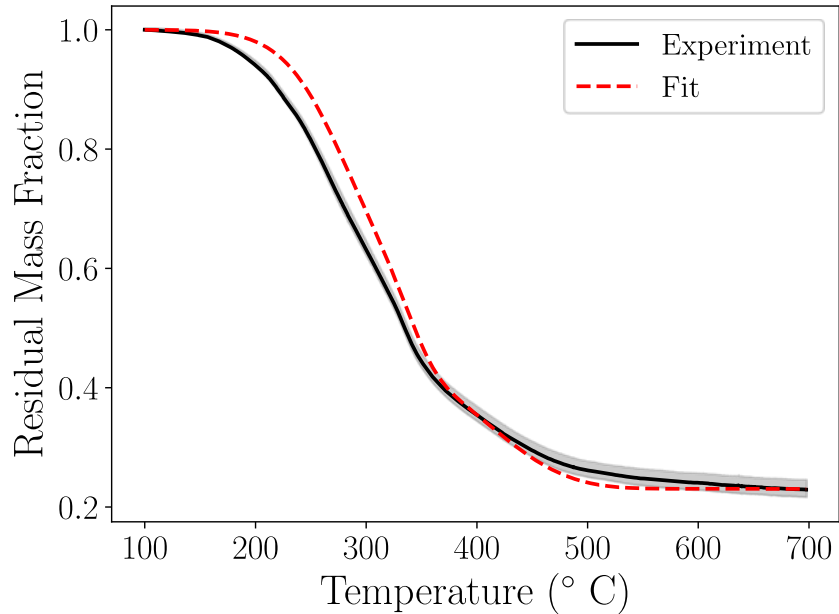


Kinetic Parameter	Reaction 1	Reaction 2	Reaction 3
$T_p$ (K)	568.5	731.7	588.1
$\Delta T$ (K)	12.15	22.39	9.62
$\Delta m$	0.4200	0.2238	0.1999
$\xi$	0.02138	0.03060	0.01636
$\ln[A (s^{-1})]$	42.49	27.78	57.06
$E$ (kJ/kmol)	$221.1 \times 10^3$	$198.8 \times 10^3$	$298.8 \times 10^3$

# Validation: Lodgepole Pine Leaves

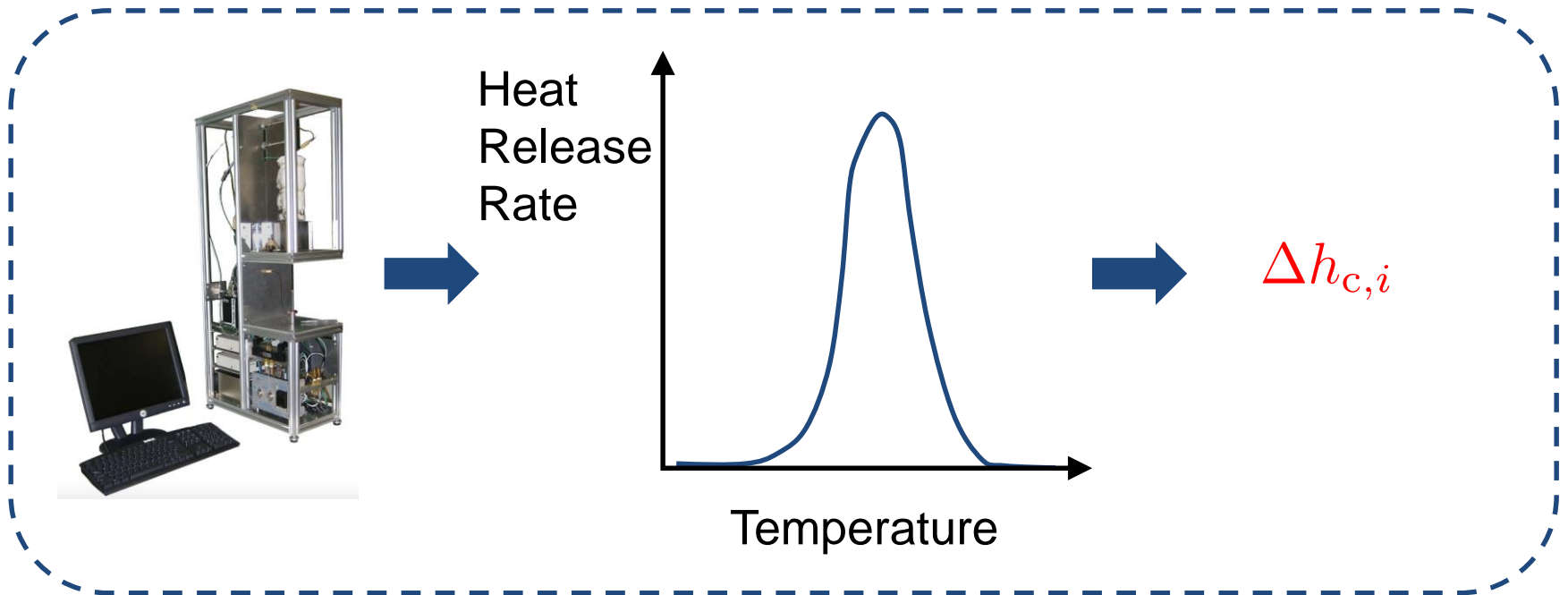


# Validation: Douglas Fir Leaves



# Analysis of MCC Data

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



# Single Reaction

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

1) Value at Peak Temperature:  $T_p$

$$\Delta h = \frac{\dot{Q}(T_p)}{\dot{m}(T_p)}$$

2) Simple Average:  $N_d$  data points

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

# Multiple Reactions

$$\dot{Q}(T) = \sum_{i=1}^{N_r} \dot{m}_i(T) \Delta h_i$$

1) Linear System:  $N_r$  equations,  $N_r$  unknowns

$$\sum_{i=1}^{N_r} \dot{m}_i(T_{p,j}) \Delta h_i = \dot{Q}(T_{p,j}), \quad j = 1, \dots, N_r$$

2) Multiple Linear Regression:  $N_d$  data points

$$\sum_{i=1}^{N_r} \dot{m}_i(T_k) \Delta h_i = \dot{Q}(T_k), \quad k = 1, \dots, N_d > N_r$$



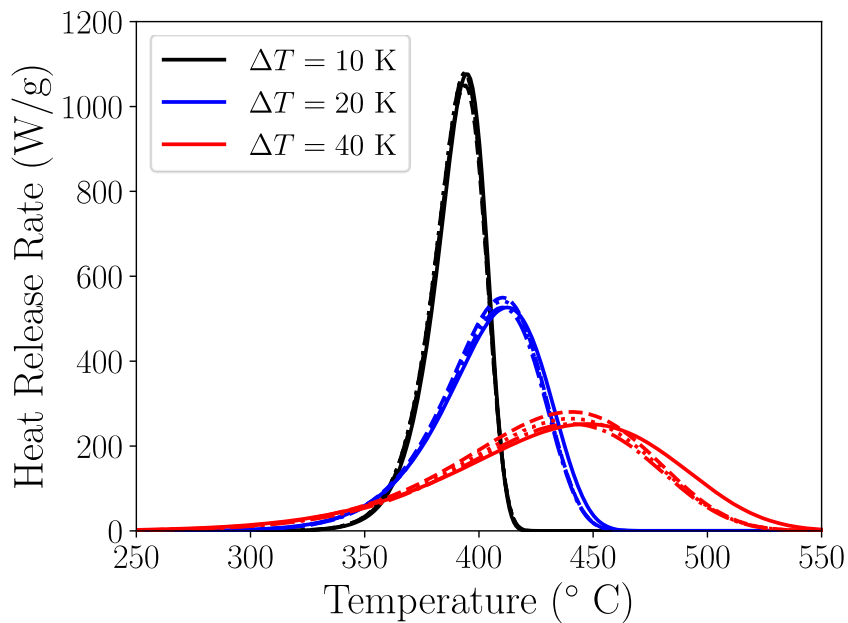
# Verification

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
  - $\Delta h = 30$  kJ/g

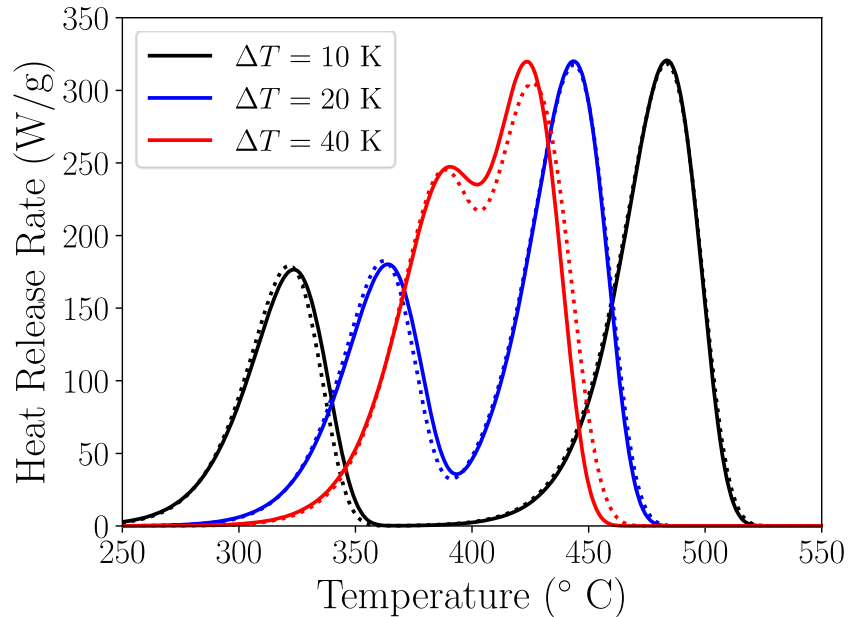
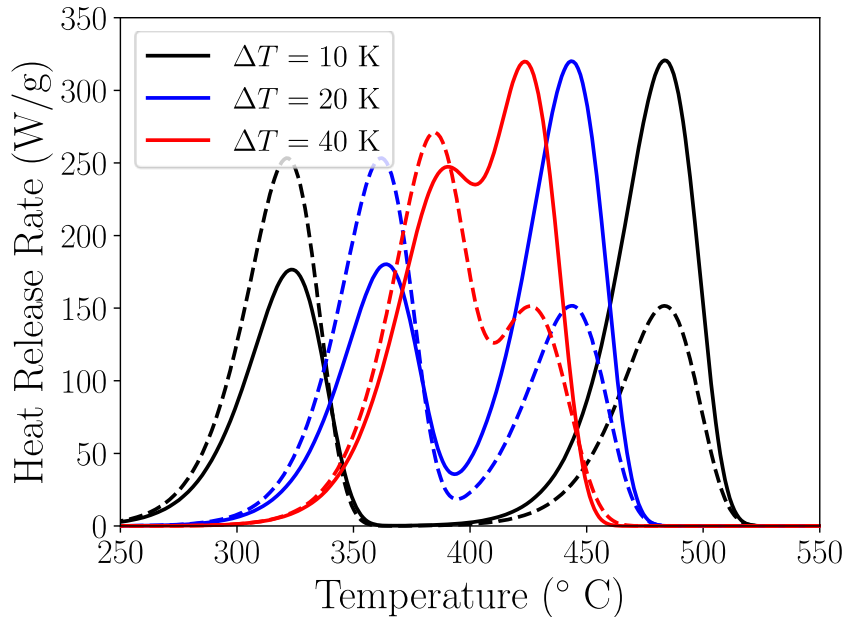
**Solid:** Simulated Data  
**Dash:** Total HRR/mass  
**Dash-Dot:** Peak Match  
**Dot:** Simple Average

# MCC: Single Reaction Verification

Scenario	$\Delta h$ (kJ/g) (Total HR/mass)	Method 1: Peak Ratio $\Delta h$ (kJ/g)	Method 2: Simple Average $\Delta h$ (kJ/g)
$\Delta T = 10$ K/min	30.026	30.792	30.849
$\Delta T = 20$ K/min	29.997	28.731	29.556
$\Delta T = 40$ 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

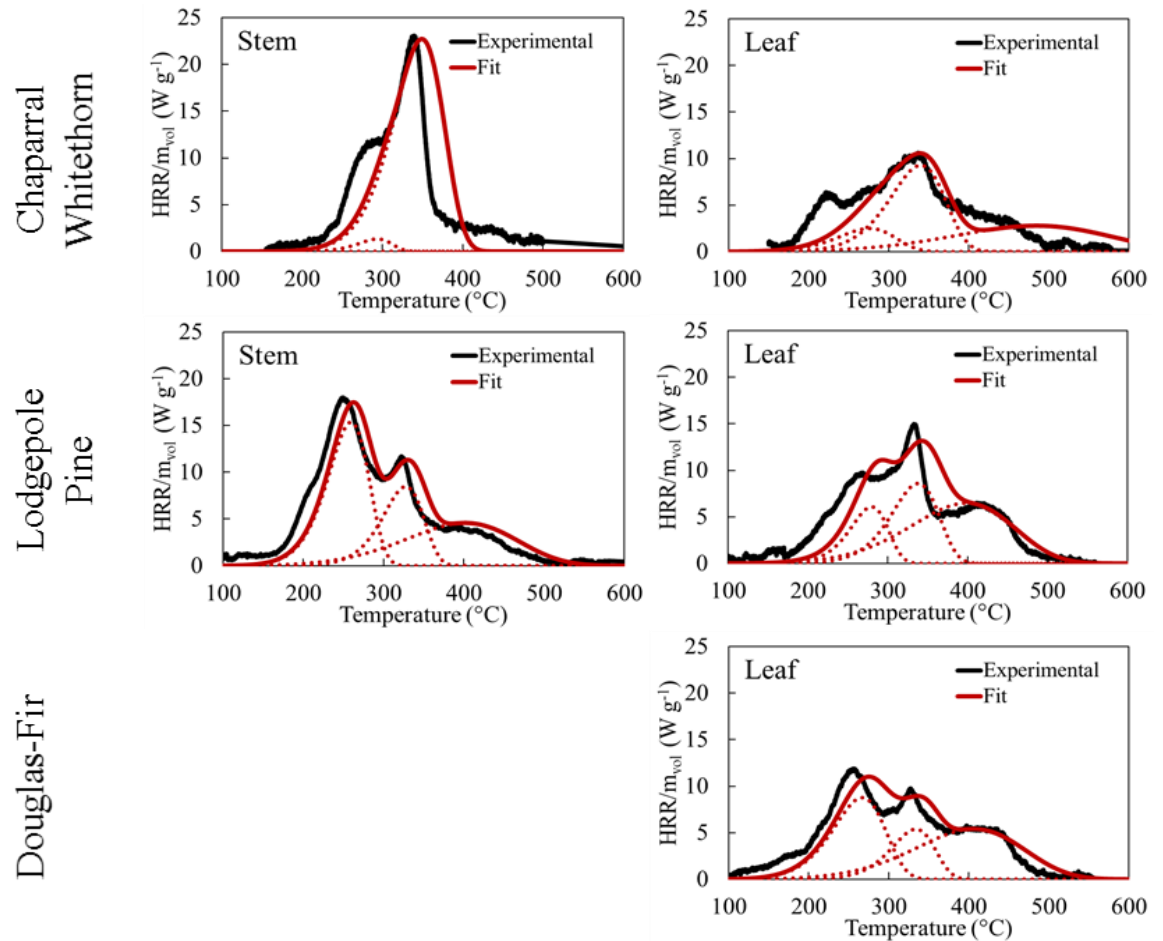
Method 2: Multiple linear regression

# MCC: Two Reactions Verification

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

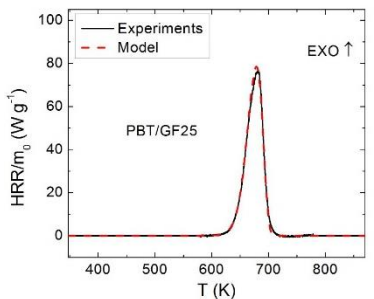
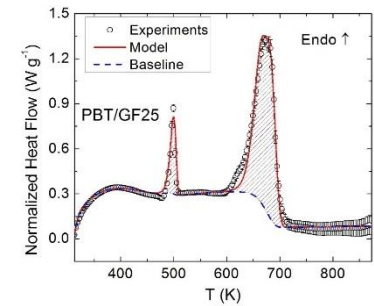
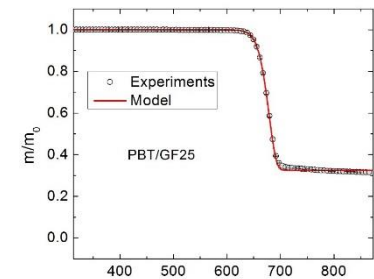
Sample Name	$\Delta H_{c,1}$ (kJ g <sup>-1</sup> )	$\Delta H_{c,2}$ (kJ g <sup>-1</sup> )	$\Delta H_{c,3}$ (kJ g <sup>-1</sup> )	$\Delta H_{c,total}$ (kJ g <sup>-1</sup> )	$\mu_{char}$ (-)
Leaves					
Chamise	17.3±2.6	12.9±1.9	22.9±3.4	11.7±1.2	0.25±0.04
Bigberry Manzanita	15.4±2.3	14.9±2.2	21.8±3.3	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



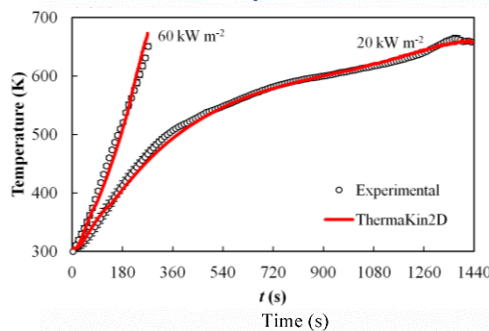
Thermophysical properties

$$\begin{matrix} A & E & \nu \\ c_p & h_i & \Delta H_c \end{matrix}$$

Computational Model

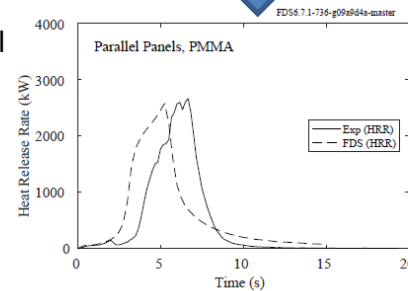


Computational Model



Bench scale experiments for model calibration

Full scale testing for model validation



Quantitative prediction of fire growth

Users

FPEs

Researchers

Materials Companies

Investigators

Product Designers

# Extras...

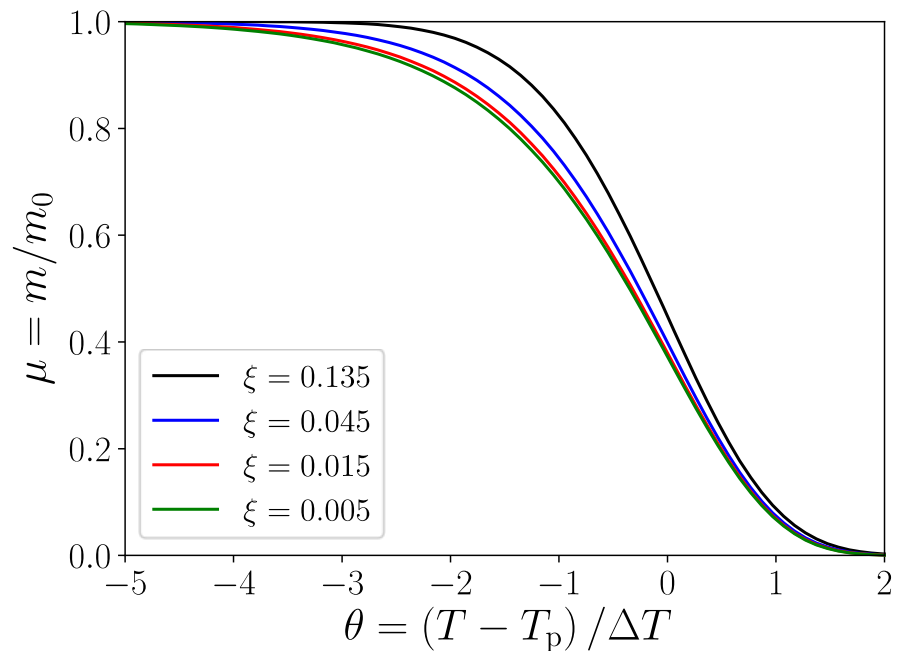
# Nondimensional Form

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

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

$$\theta \equiv \frac{T - T_p}{\Delta T}$$

$$\xi \equiv \frac{\Delta T}{T_p}$$



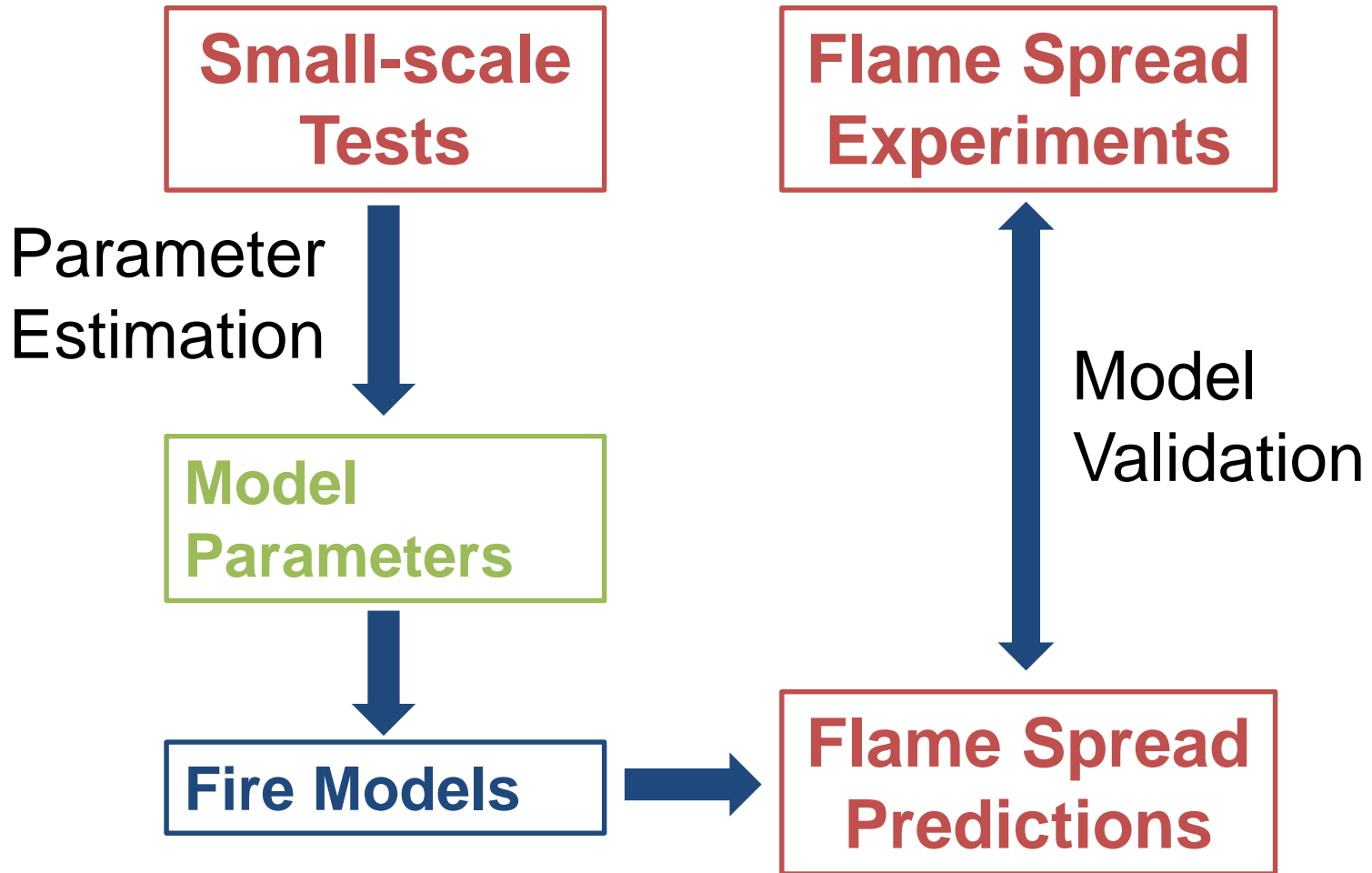
# Approximate Solution

$$\xi \rightarrow 0 \quad (T_p \gg E/R) \implies \frac{d\mu}{d\theta} = -\mu \exp \theta$$



$$\mu = \exp [-\exp (\theta)]$$
$$m = m_0 \exp \left[ -\exp \left( \frac{T - T_p}{\Delta T} \right) \right]$$

Also applies for multiple, independent reactions.



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

# Gasification Apparatus

## Introduction

The Fire Problem  
Controlling Mechanisms  
of Fire Growth  
Methodology

## Experimental Apparatus

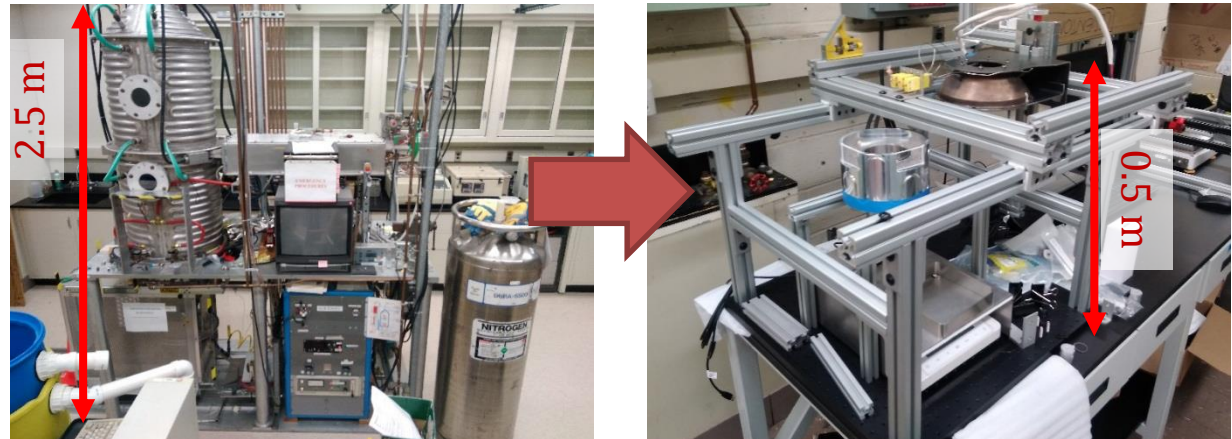
Milligram scale  
**Bench scale**  
Full Scale

## Modelling

Analytical Tools  
Model Validation

## Applications and Future Work

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



# Flame Spread Apparatus

(intermediate scale)

## Introduction

The Fire Problem  
Controlling Mechanisms  
of Fire Growth  
Methodology

## Experimental Apparatus

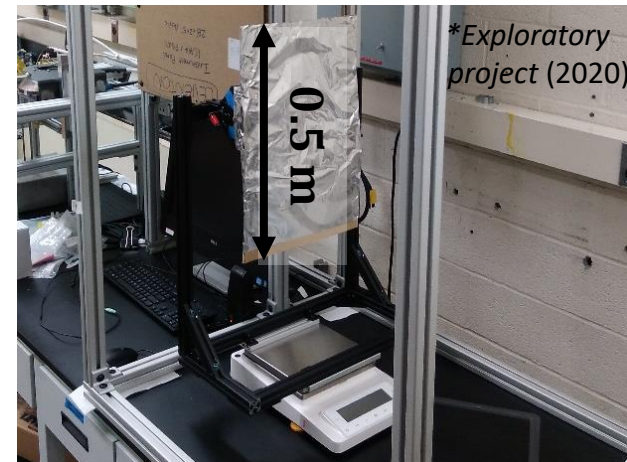
Milligram scale  
**Bench scale**  
Full Scale

## Modelling

Analytical Tools  
Model Validation

## Applications and Future Work

- 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



# Parallel Panel Apparatus

(full scale)

## Introduction

The Fire Problem  
Controlling Mechanisms  
of Fire Growth  
Methodology

## Experimental Apparatus

Milligram scale  
Bench scale  
**Full Scale**

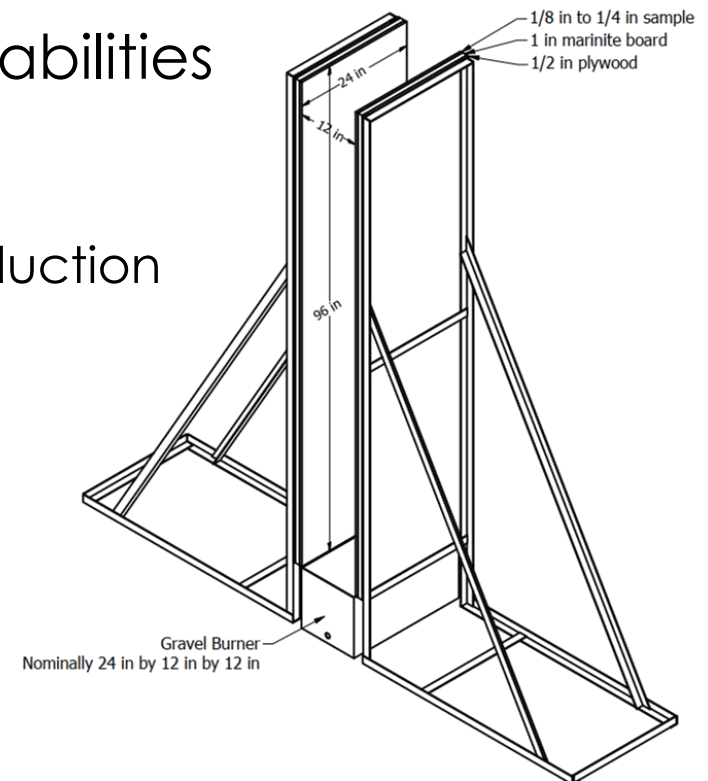
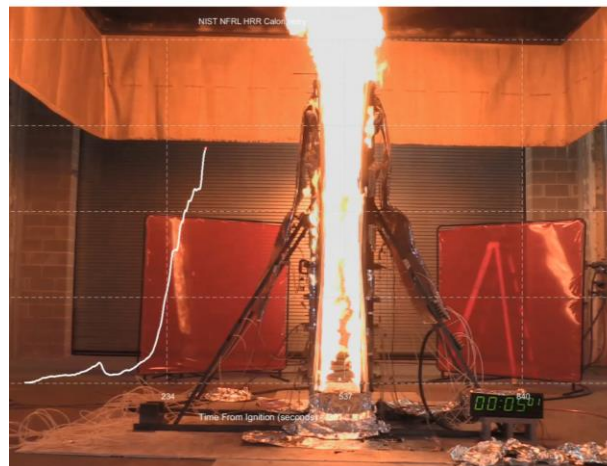
## Modelling

Analytical Tools  
Model Validation

## Applications and Future Work

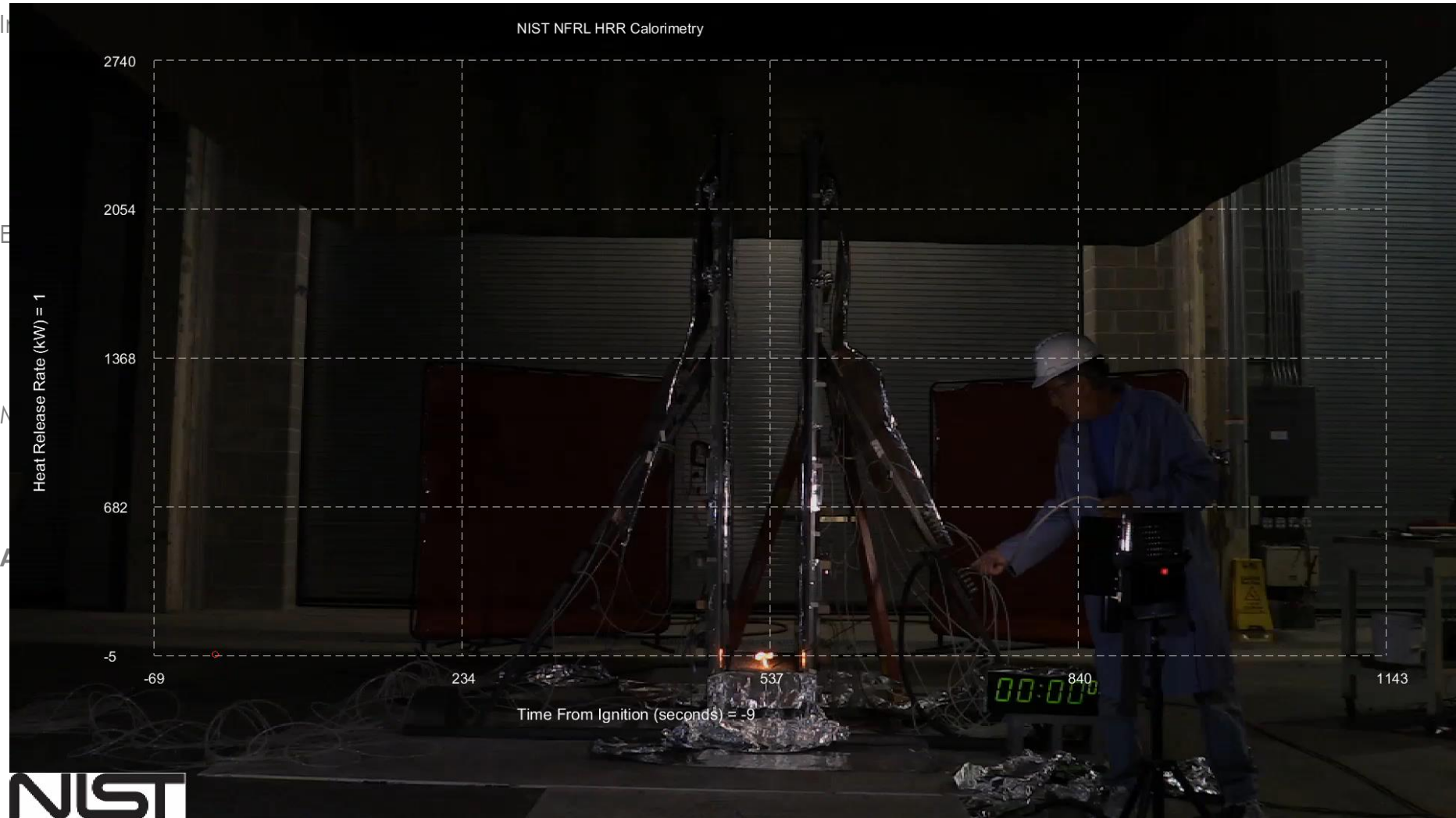
- Ignitability and flame spread
  - Sample size: **2.45 m tall, 0.6 m wide**

- Measurement capabilities
  - Heat release rate
  - Flame heat flux
  - CO<sub>2</sub>, CO, soot production

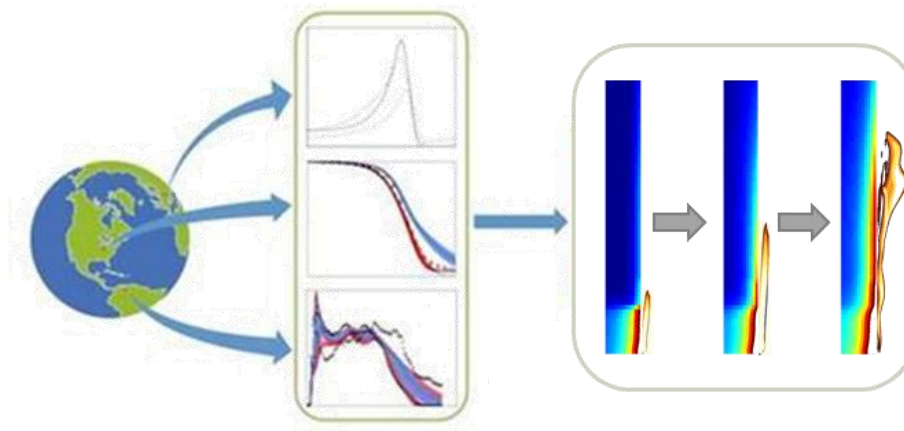




# Full Scale Fire Behavior Parallel Panel Apparatus



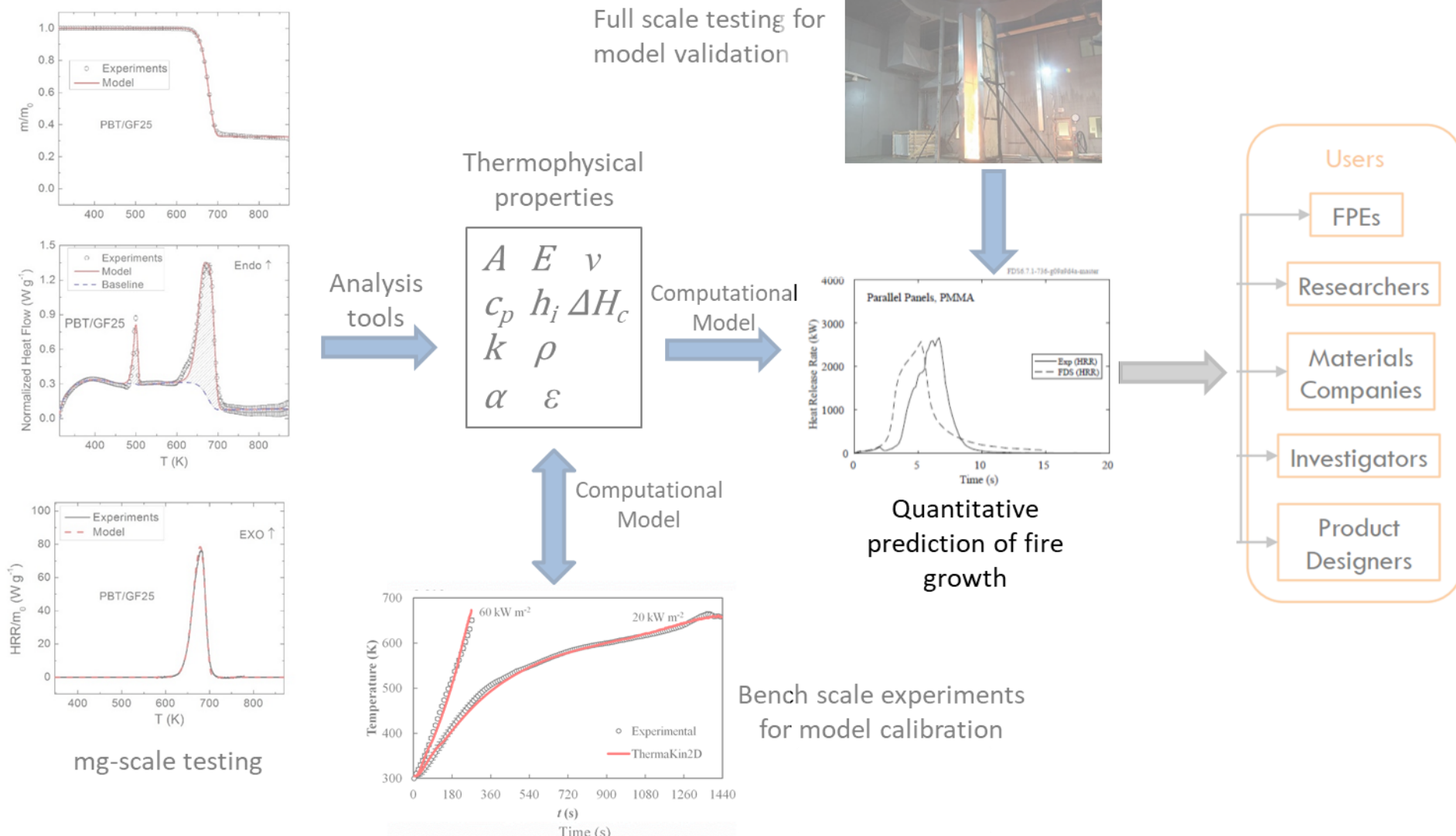
# IAFSS Measurement and Computation of Fire Phenomena (MaCFP)—Condensed Phase Workshop



April 26, 2020

Waterloo, Canada

<https://iafss.org/macfp/>



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