Automated Fitting of Thermogravimetric Analysis Data

NIST

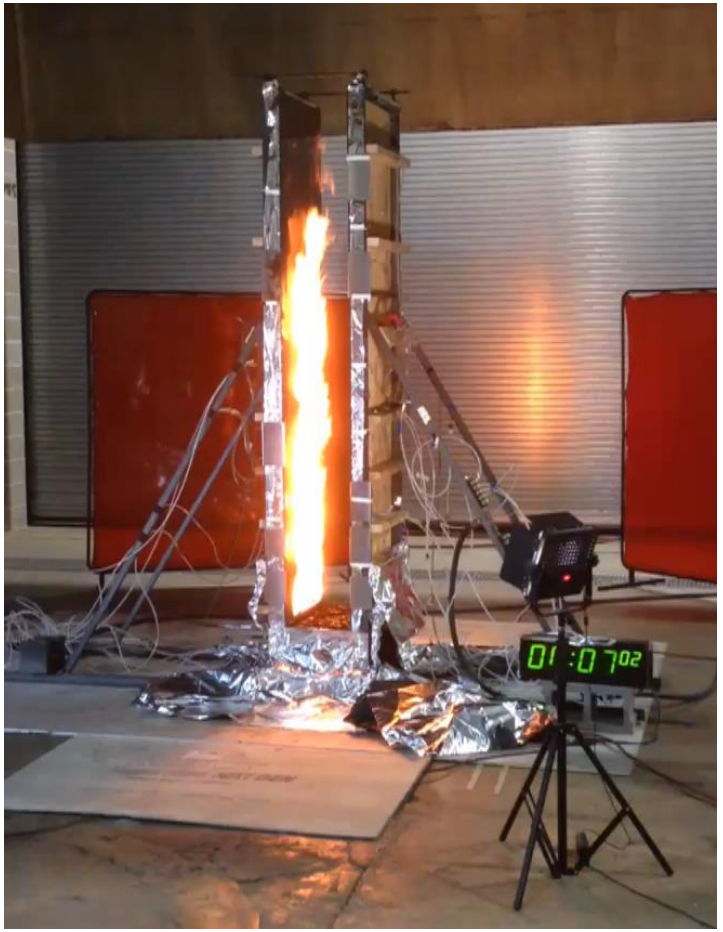
July 2, 2019

Morgan C. Bruns
Virginia Military Institute (USA)

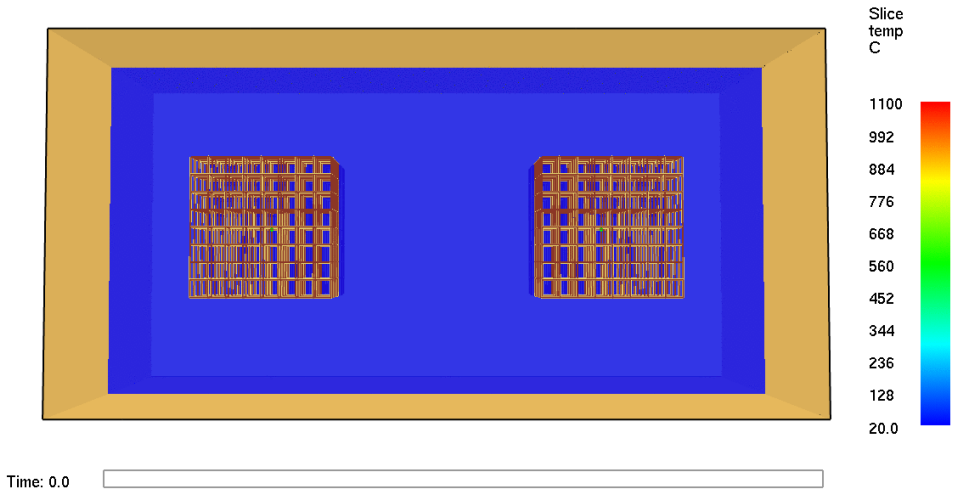
Isaac T. Leventon
National Institute of Standards and Technology (USA)

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

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?

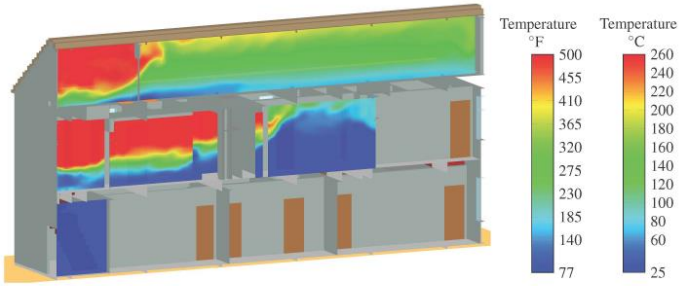
- NFIRS categorizes **38 distinct "types"** of solid materials "First Ignited"
- These "types" are extremely broad categories such as "Plastic", "Rubber", and "Plywood"
- For example, Lyon and Janssens (2005) contains data on **50 common plastics**
- Additional diversity due to processing variability,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

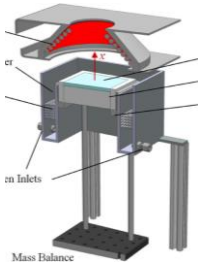
$$A_i, E_i, c_i, k_i, \Delta h_i, \rho_{0,i}$$

Fire Model

Hierarchical Approach

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

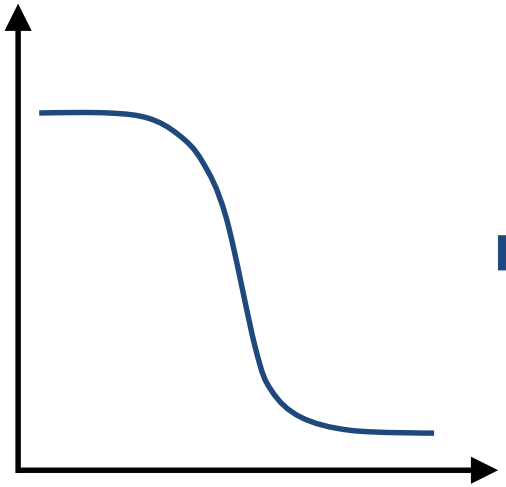
$$c_i, \Delta h_i$$



$$k_i$$

Analysis of TGA Data

How should we estimate pyrolysis kinetic parameters from raw TGA data (Mass vs. Temperature)?

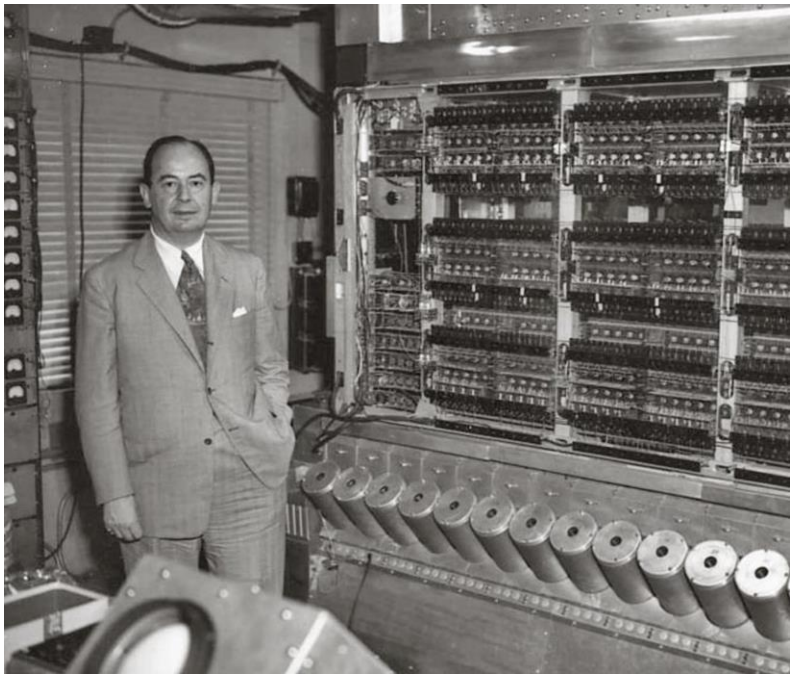


$A_i, E_i, \rho_{0,i}$

Method Requirements

1. Parameters predict data → **Accurate**
2. Many different materials → **Efficient**
3. Many different responses → **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

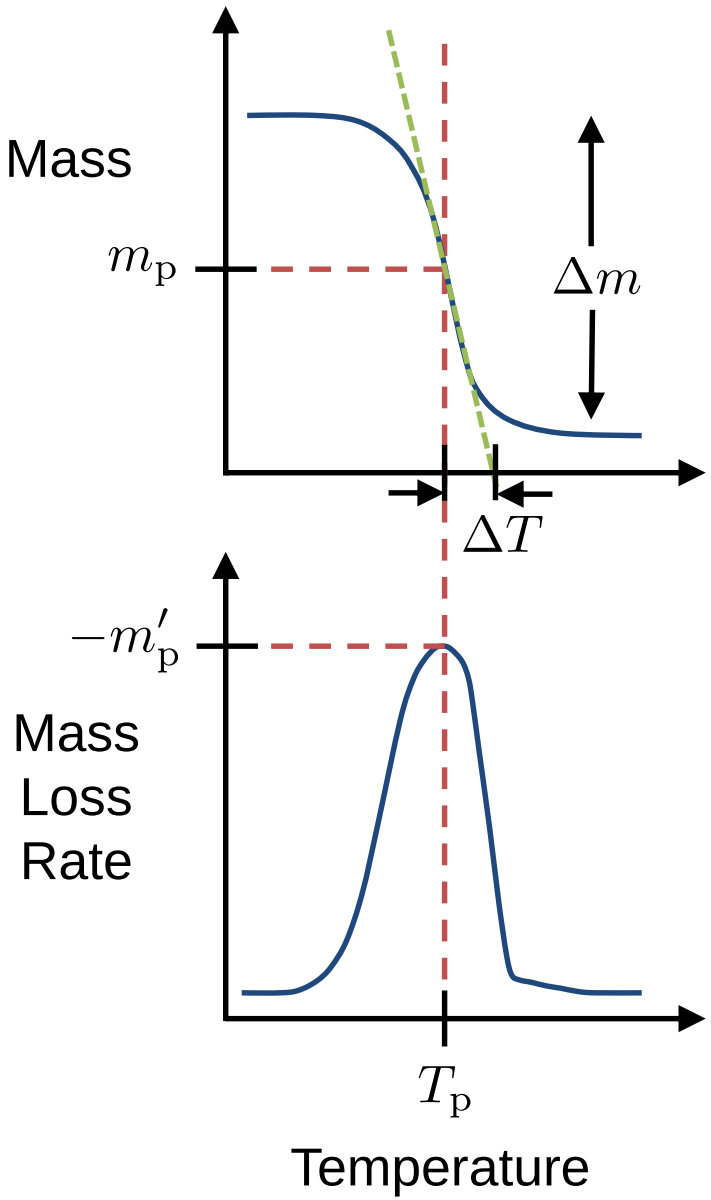
Pyrolysis Model: Independent Unimolecular Reactions

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

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

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

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:

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

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

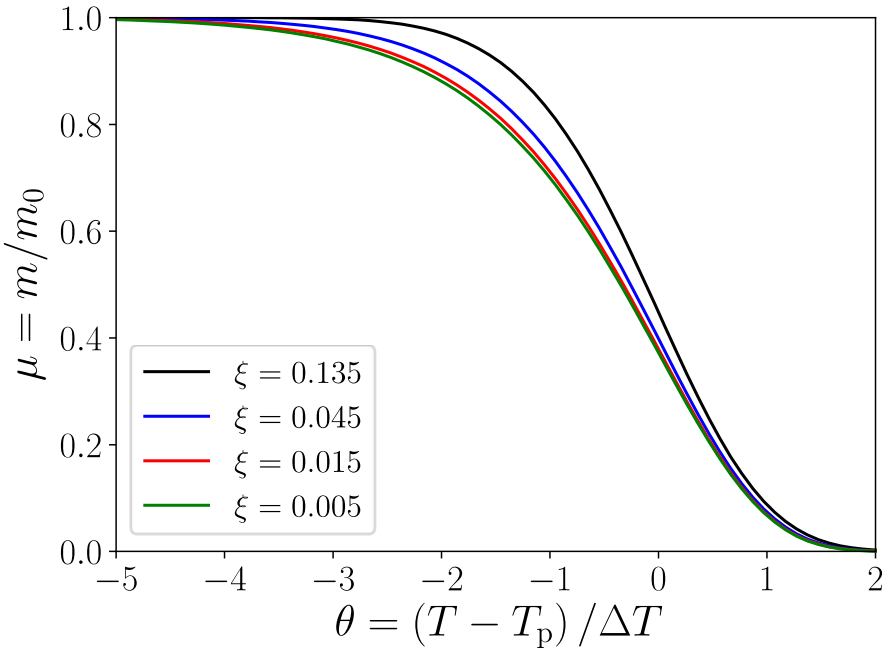
Nondimensional Form

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

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

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

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



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.

Estimating Parameters

TGA Data

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

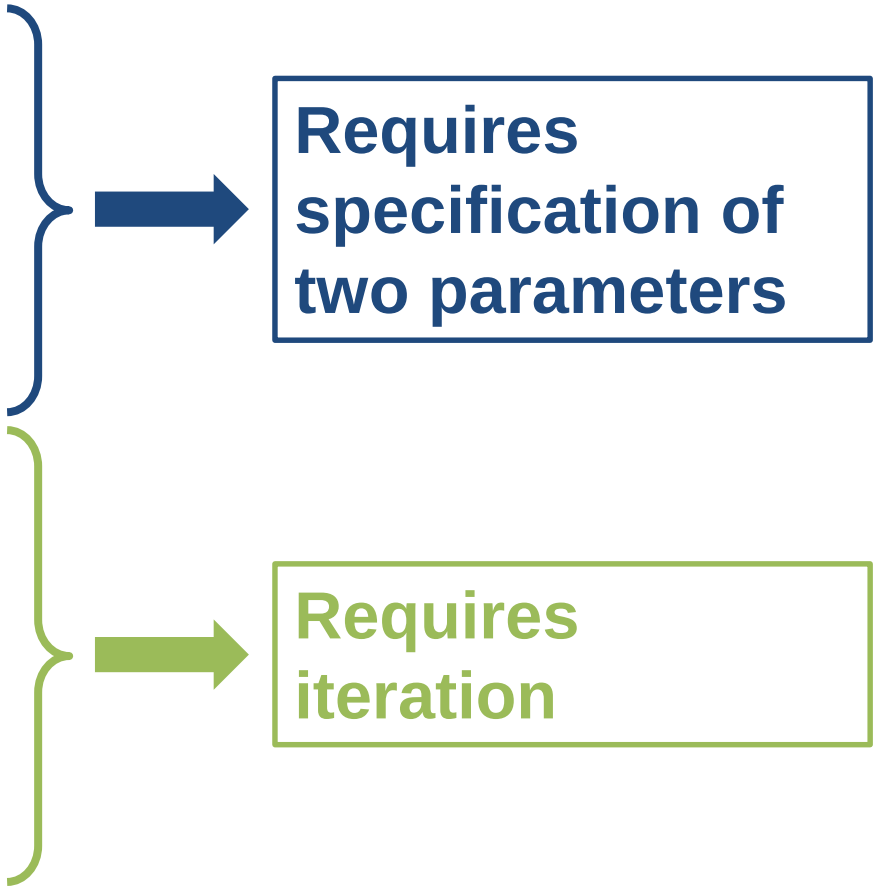
Approximate Solution

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

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

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



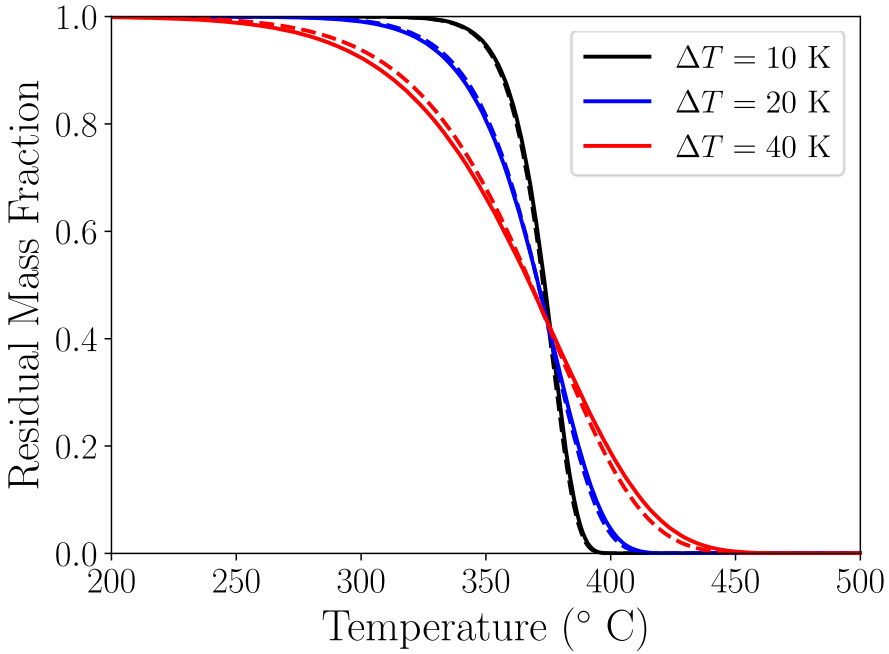
Verification

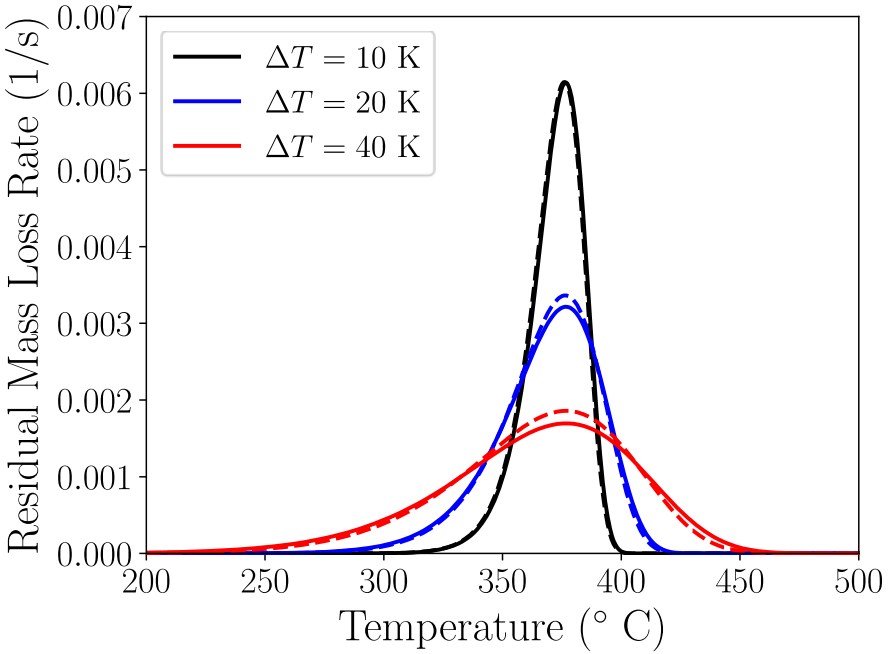
1. Assume kinetic parameters
2. Generate TGA data
3. Use algorithm to find parameters

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:

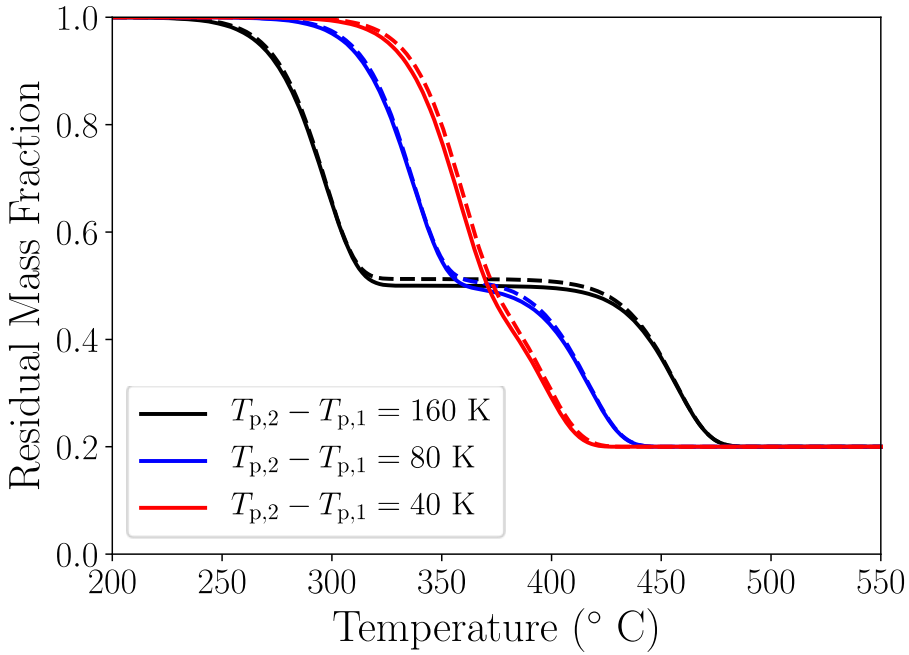
Kinetic Parameter	Specified Value	Calibrated Value
T_p (K)	650	649.4
ΔT (K)	20	19.07
ξ	0.03077	0.02935
$\ln[A\ (s^{-1})]$	27.71	29.34
E (kJ/kmol)	175.6×10^3	184.1×10^3

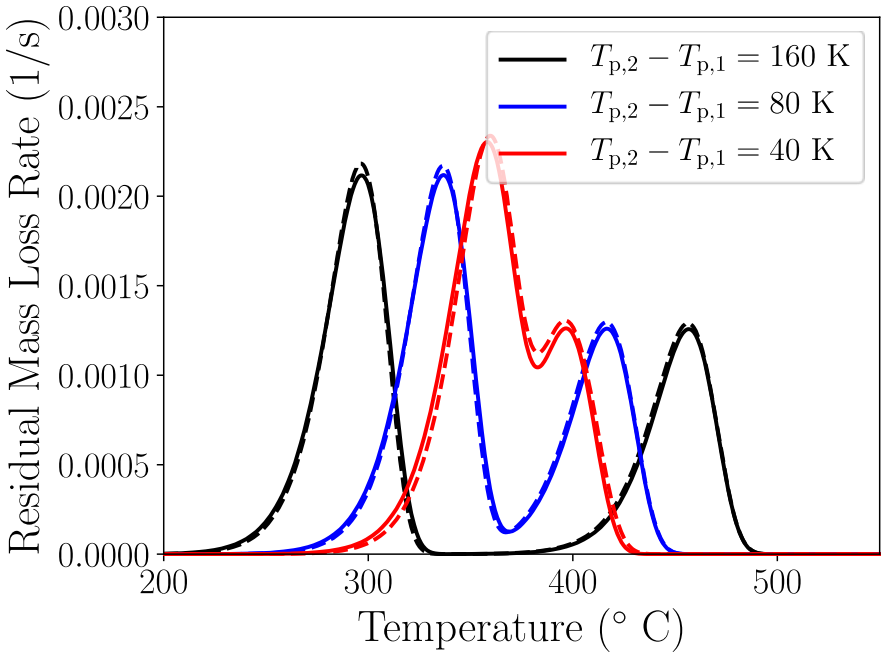
ΔT = 40 K:

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

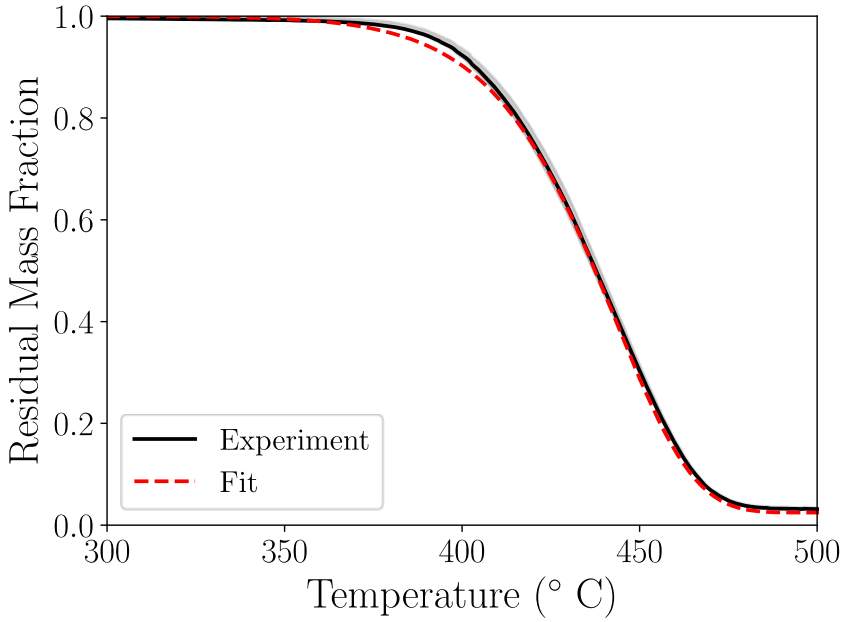
Materials:

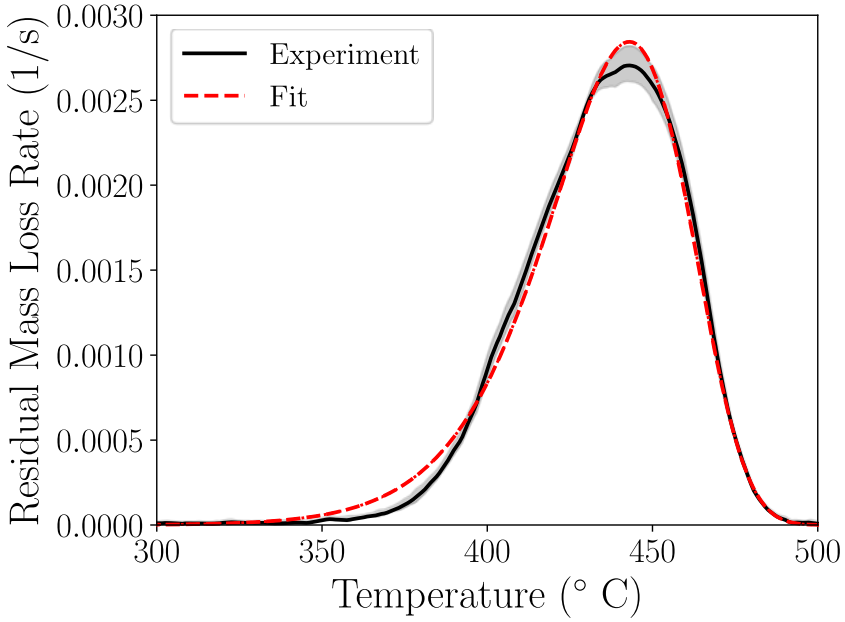
1. Nylon 6,6
2. Flexible polyurethane (PU) foam
3. Polyvinyl Chloride (PVC)

Procedure:

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

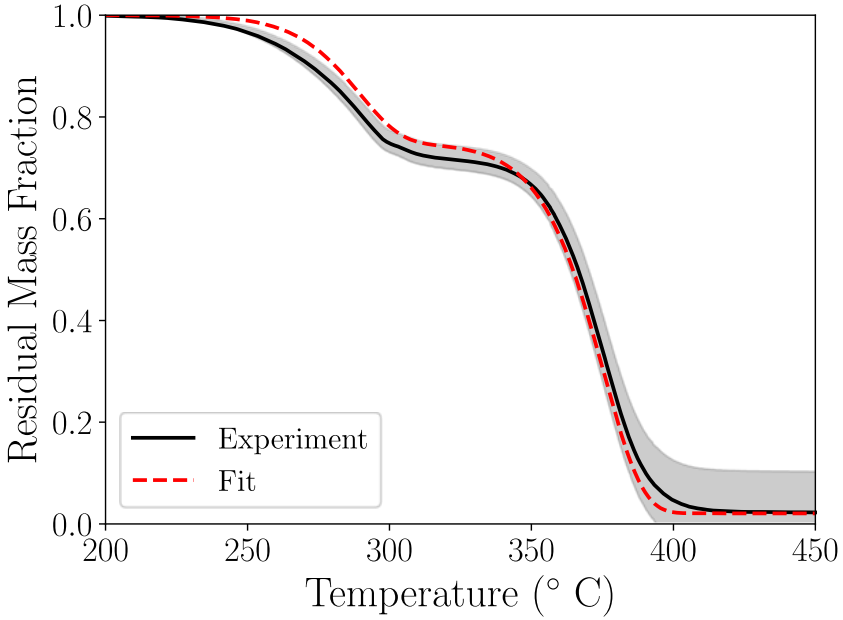
Validation: Nylon 6,6

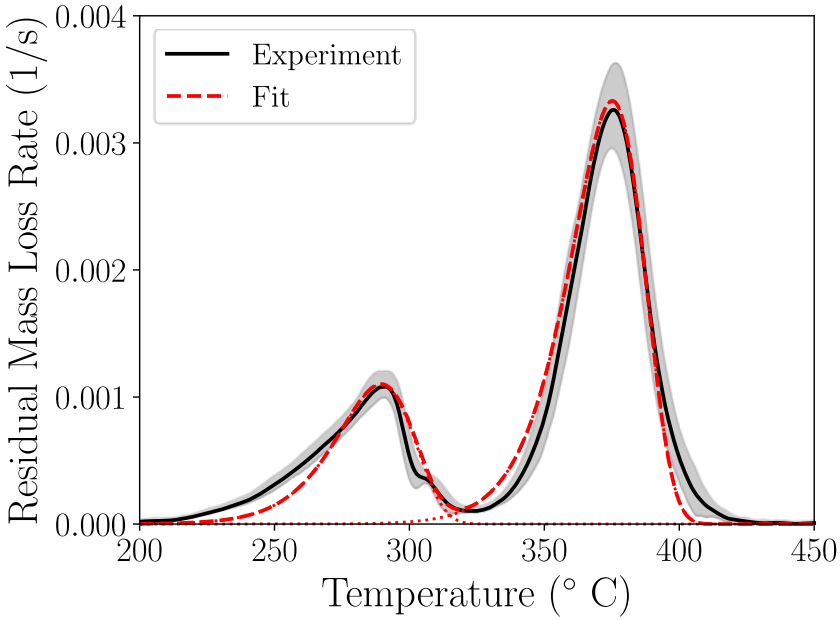




Kinetic Parameter	Reaction 1
T_p (K)	716.3
ΔT (K)	22.11
Δm	0.9754
ξ	0.03087
$\ln[A\ (s^{-1})]$	27.50
E (kJ/kmol)	192.9×10^3

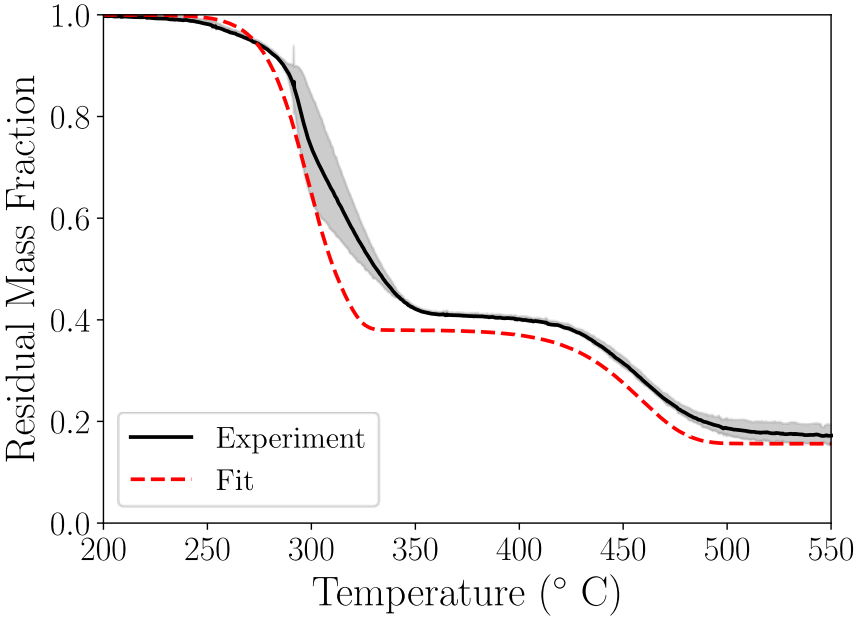
Validation: Polyurethane Foam

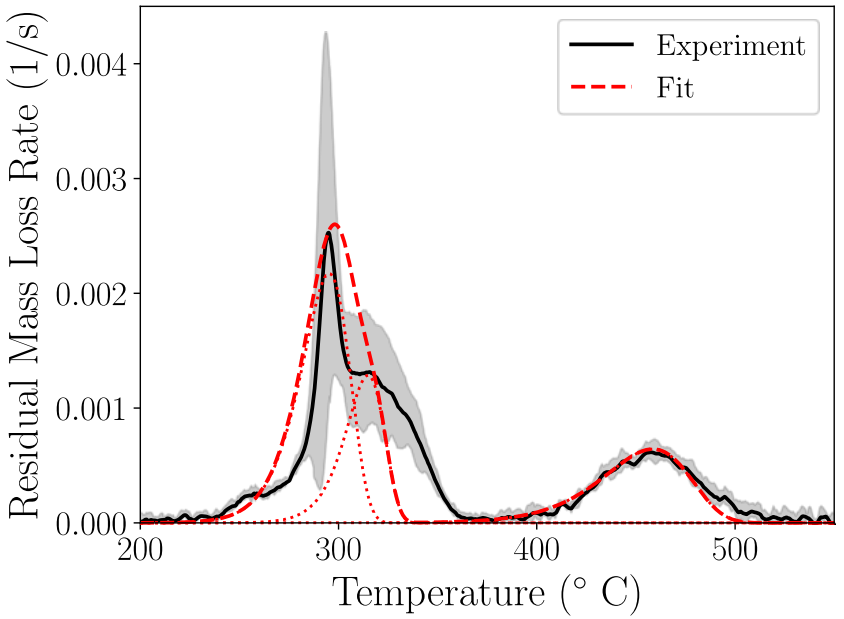




Kinetic Parameter	Reaction 1	Reaction 2
T_p (K)	562.7	648.5
ΔT (K)	14.50	13.69
Δm	0.2511	0.7280
ξ	0.02577	0.02112
$\ln[A\ (s^{-1})]$	34.34	42.95
E (kJ/kmol)	181.5×10^3	255.3×10^3

Validation: PVC

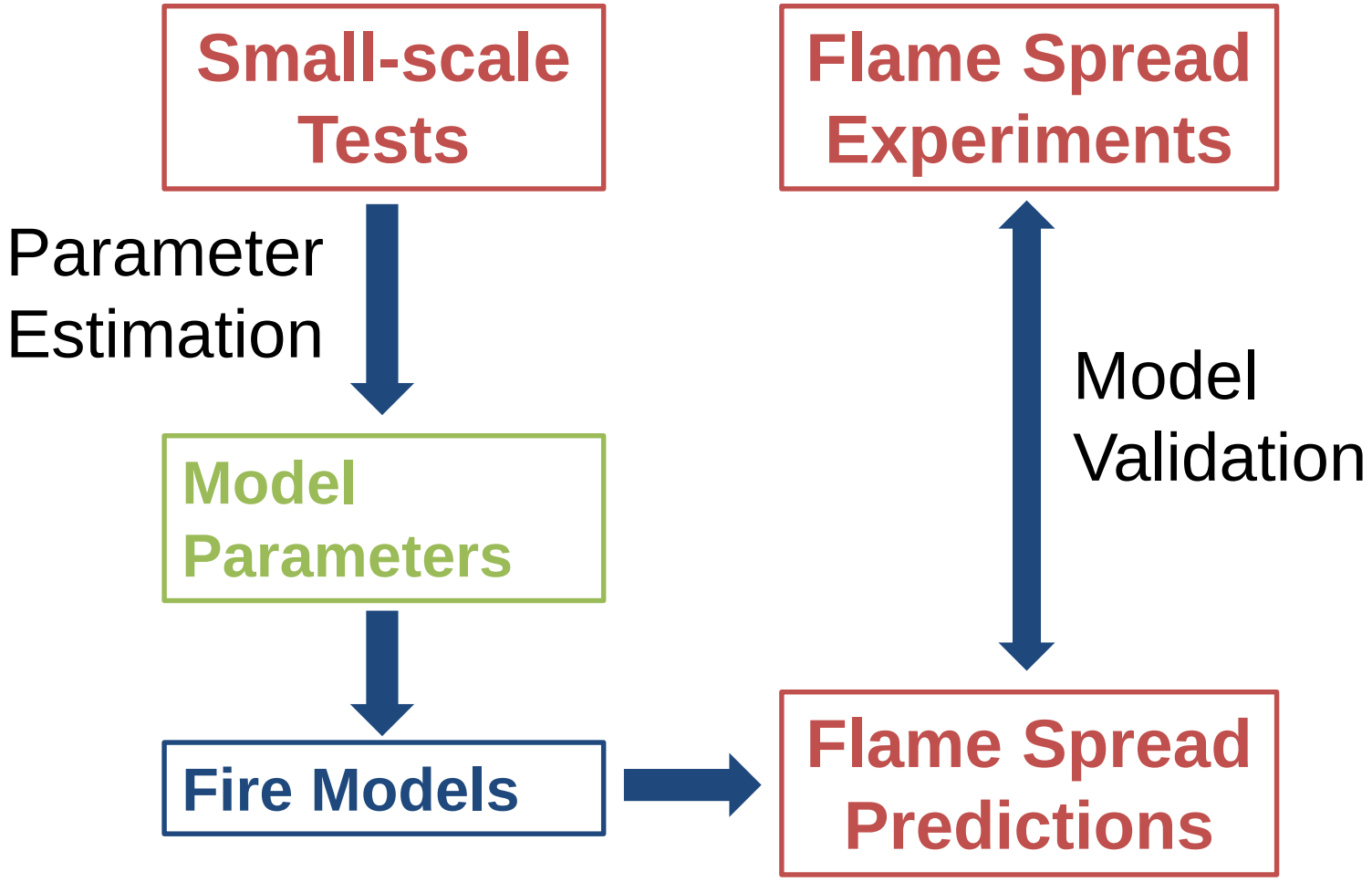




Kinetic Parameter	Reaction 1	Reaction 2	Reaction 3
T_p (K)	568.5	731.7	588.1
ΔT (K)	12.15	22.39	9.62
Δm	0.4200	0.2238	0.1999
ξ	0.02138	0.03060	0.01636
$\ln[A\ (s^{-1})]$	42.49	27.78	57.06
E (kJ/kmol)	221.1×10^3	198.8×10^3	298.8×10^3

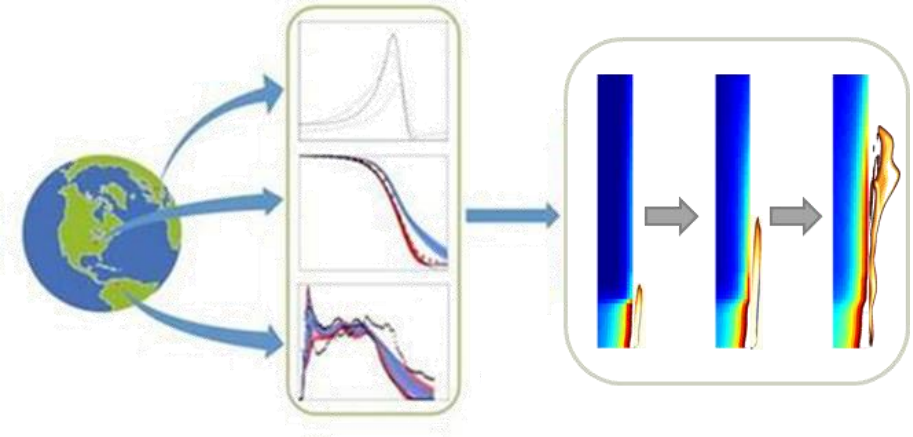
Summary

- Fire models need material property parameters to **predict** fire growth
- Obtaining material properties requires
  - Small-scale tests
  - **Parameter estimation algorithms**
- A parameter estimation algorithm is presented for obtaining pyrolysis kinetic models from TGA data
- The algorithm 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



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

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



April 26, 2020

Waterloo, Canada

https://iafss.org/macfp/