Automated Characterization of Heat Capacities and Heats of Gasification of Flammable Materials

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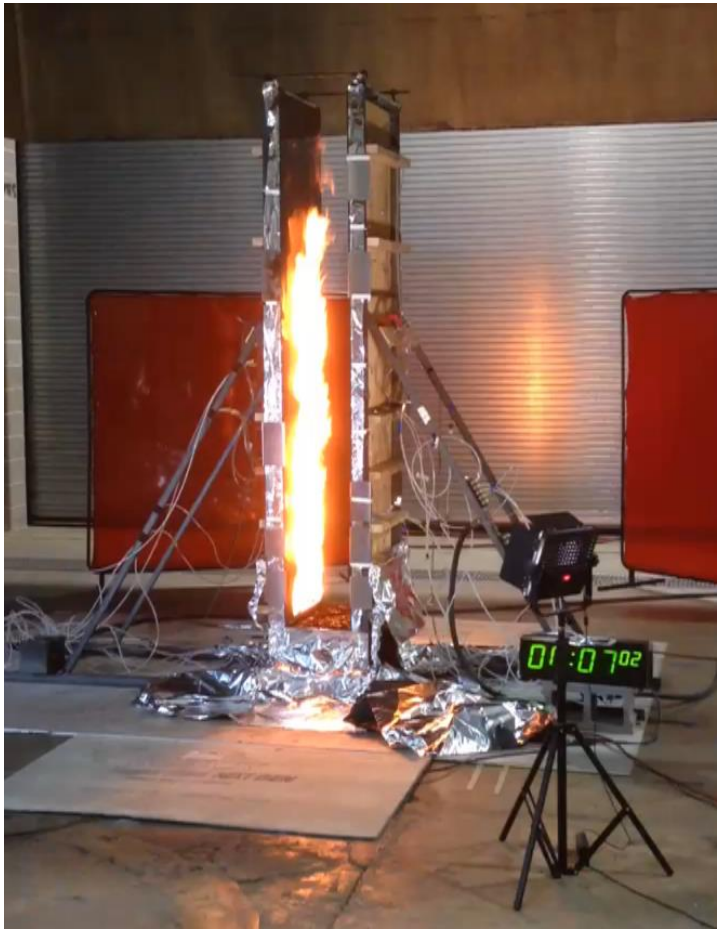
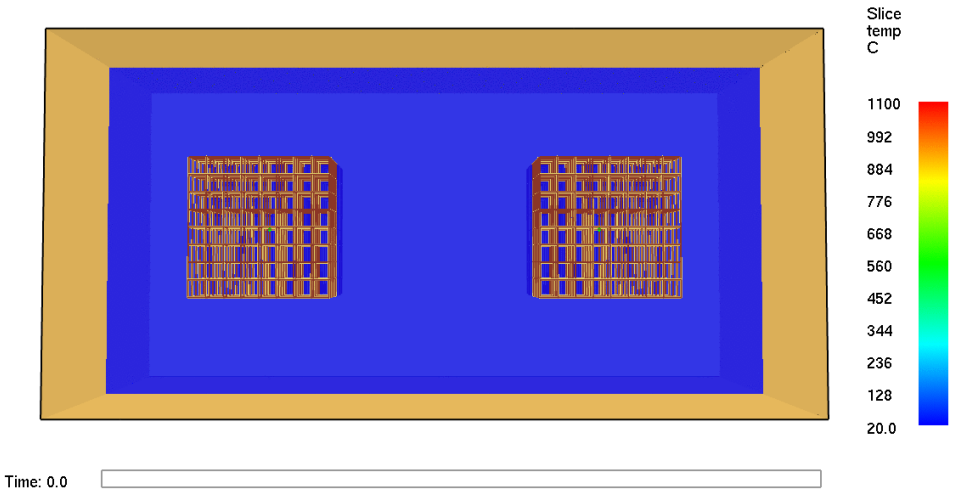
Predicting Fire Growth

- 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

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?

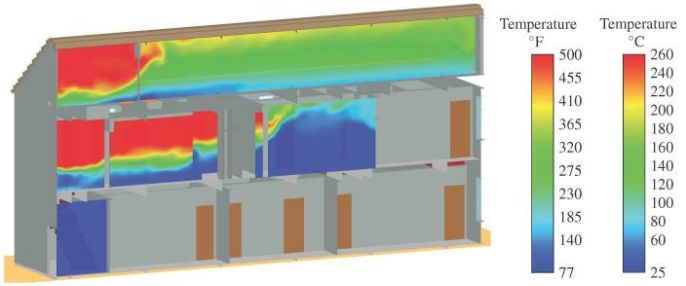
- NFIRS categorizes **38 distinct "types"** of solid materials "First Ignited"
- These "types" are extremely broad categories such as "Plastic", "Rubber", and "Plywood"
- For example, Lyon and Janssens (2005) contains data on **50 common plastics**
- Additional diversity due to processing variability,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

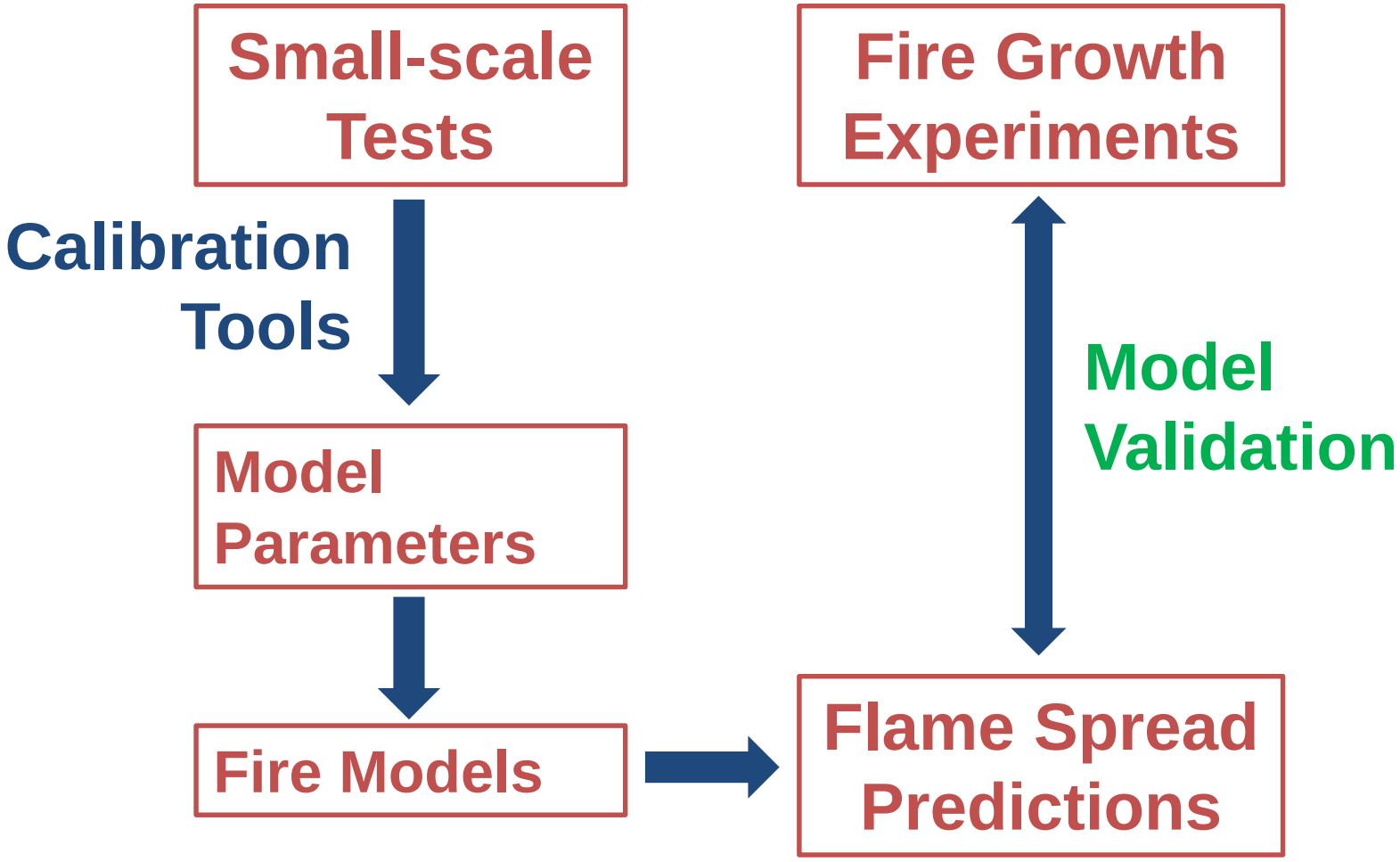
A **Material Property Database** is needed

Material Property Database



Critical components

1. Standard data formatting
2. Standard metadata
3. **Calibration tools**
4. Web-based user interface



Quality of **calibration tools** is ultimately determined in **model validation**—*do the parameters predict fire growth?*

Global Approach

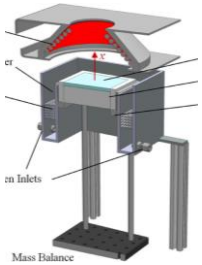
$$A_i, E_i, c_i, k_i, \Delta h_i, \rho_{0,i}$$

Fire Model

Hierarchical Approach

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

$$c_i, \Delta h_i$$



$$k_i$$

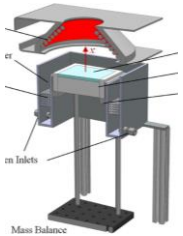
Micro Combustion Calorimeter

$\Delta h_{c,i}$

Thermogravimetric Analysis

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

Controlled Atmosphere Pyrolysis



k_i

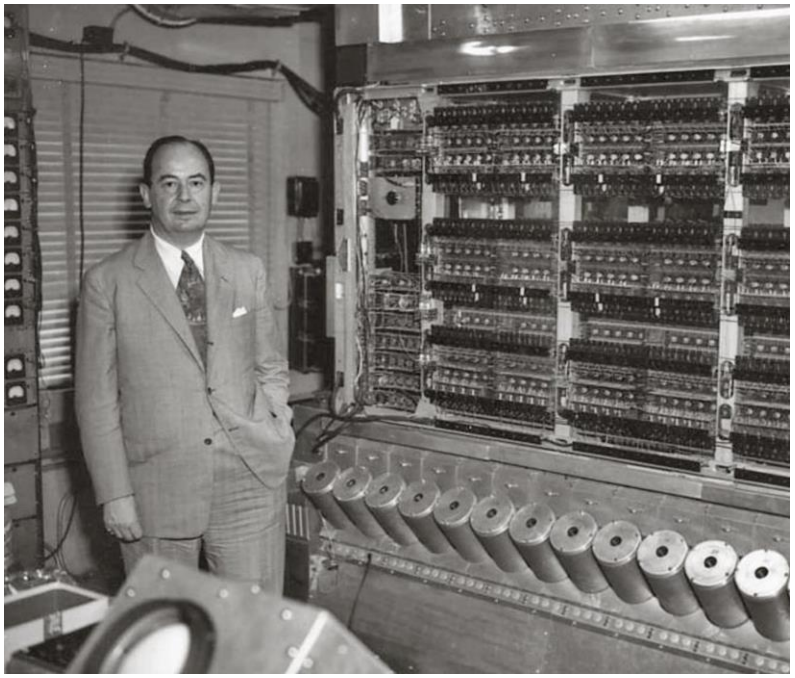
Differential Scanning Calorimetry

$c_i, \Delta h_i$

Calibration Method Requirements

1. Parameters predict data → **Accurate**
2. Values agree with physics → **Realistic**
3. Fast parameter evaluation → **Efficient**
4. Can handle complex behavior → **Robust**
5. Values do not vary → **Stable**

How to be **Realistic**



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

~John von Neumann

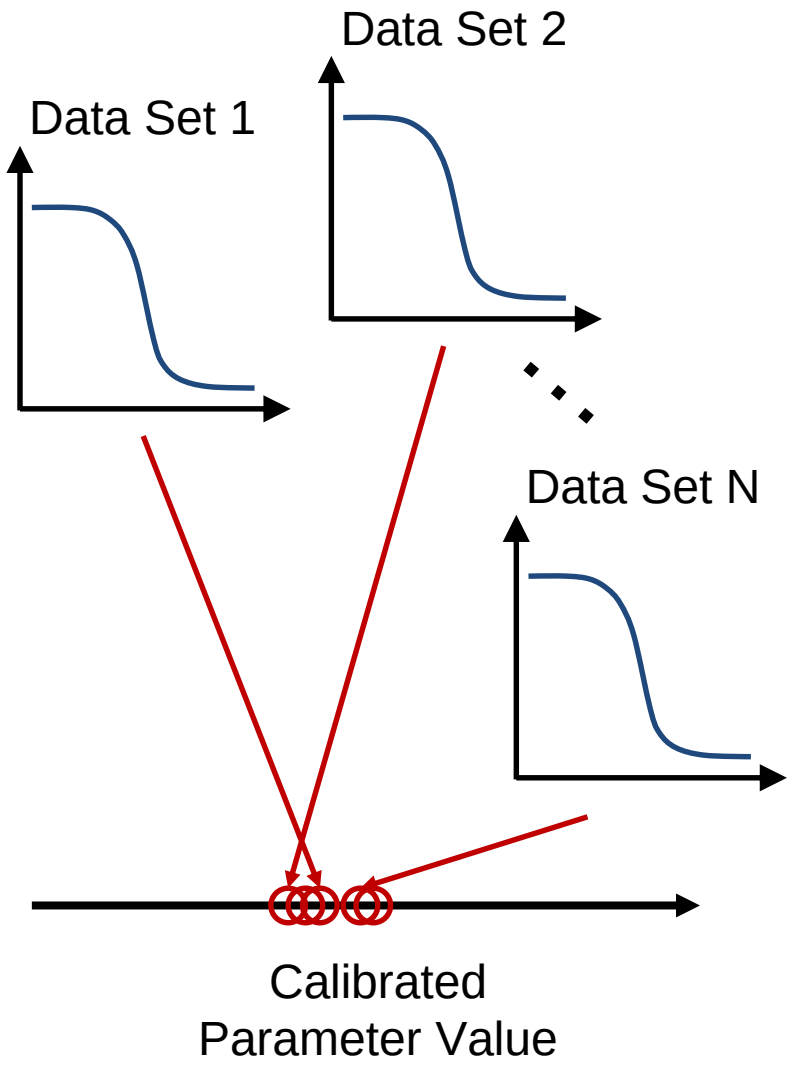
- Appropriate physical models
- Experiments that isolate physical
- Update models and data as necessary!

Why be **realistic**? Confidence in vastly different scenarios

How to be **Consistent**

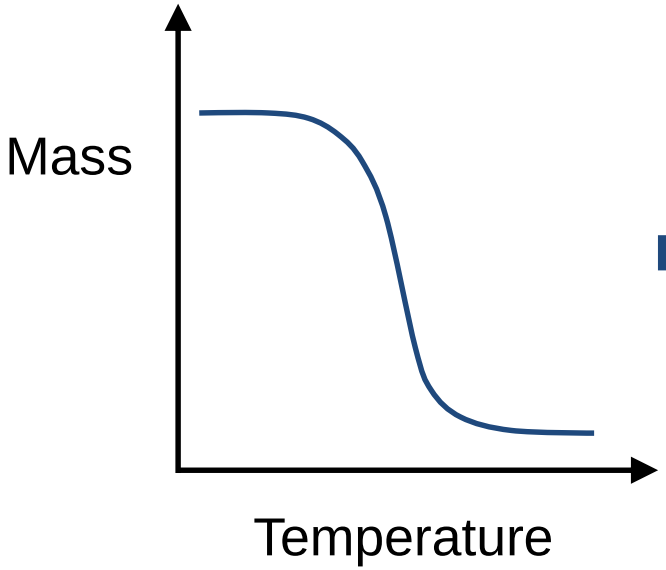
For a given material, the method should always produce the similar parameters

- Solve well-posed problems
- Avoid free parameters
- Don not use random numbers



Analysis of TGA Data

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



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

Pyrolysis Model: Independent First-Order Reactions

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

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

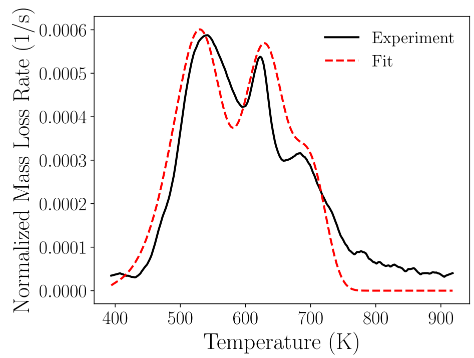
$$m' \equiv \frac{\mathrm{d}m}{\mathrm{d}T} = -(1-\nu)\,km, \quad m(T_0) = m_0$$

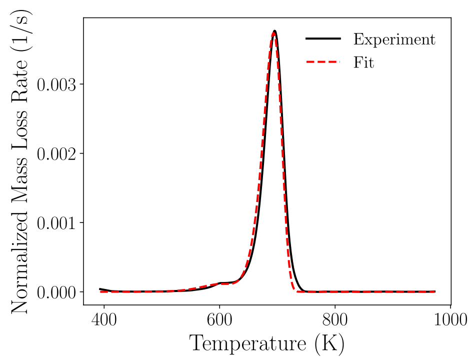
Appropriateness to be determined by ability to predict fire growth.

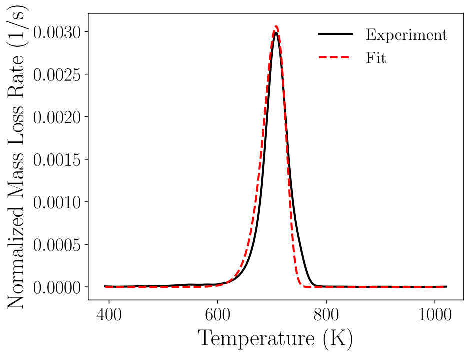
TGA Validation Summary

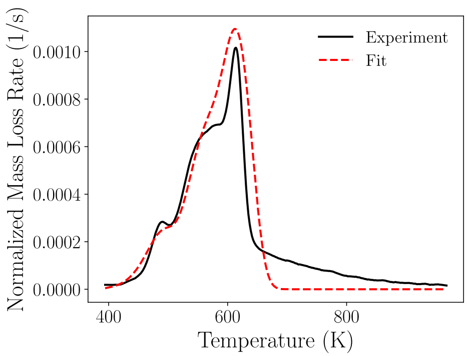
25 materials:

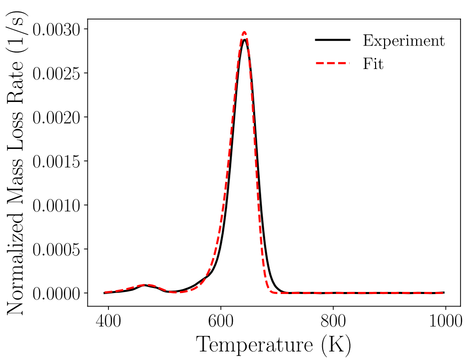
```
# list of all current TGA test series
tga_tests = [
    'ABS_Expt_TGA_N2_10K',
    'BigBerry-Leaf_Expt_TGA_N2_10K',
    'BigBerry-Stem_Expt_TGA_N2_10K',
    'Chamise-Leaf_Expt_TGA_N2_10K',
    'Chamise-Stem_Expt_TGA_N2_10K',
    'Chaparral-Leaf_Expt_TGA_N2_10K',
    'Chaparral-Stem_Expt_TGA_N2_10K',
    'DesertCeanothus-Leaf_Expt_TGA_N2_10K',
    'DesertCeanothus-Stem_Expt_TGA_N2_10K',
    'DouglasFir-Leaf_Expt_TGA_N2_10K',
    'HDPE_Expt_TGA_N2_10K',
    'HIPS_Expt_TGA_N2_10K',
    'Kydex_Expt_TGA_N2_10K',
    'LodgepolePine-Leaf_Expt_TGA_N2_10K',
    'LodgepolePine-Stem_Expt_TGA_N2_10K',
    'MaCFP_PMMA_Expt_TGA_N2_10K',
    'PolyIso1_Expt_TGA_N2_10K',
    'PolyIso2_Expt_TGA_N2_10K',
    'PolyIso05_Expt_TGA_N2_10K',
    'POMGF_Expt_TGA_N2_10K',
    'XPSgreen_Expt_TGA_N2_10K',
    'XPSpink_Expt_TGA_N2_10K'
]
```





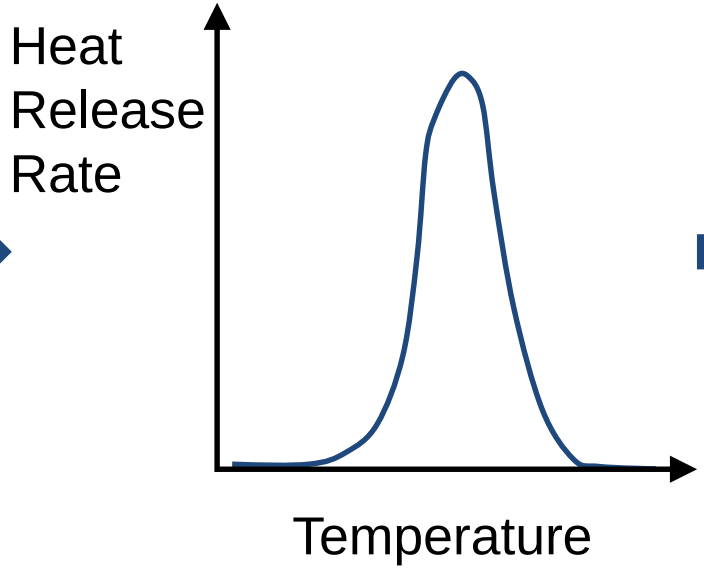






Analysis of MCC Data

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

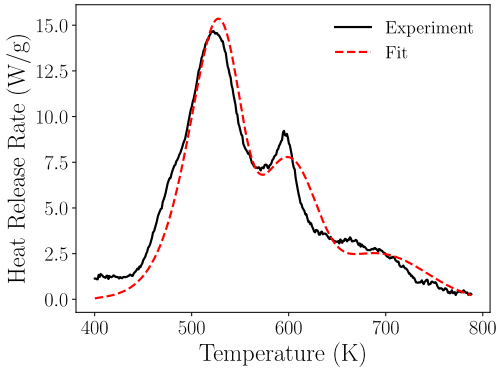


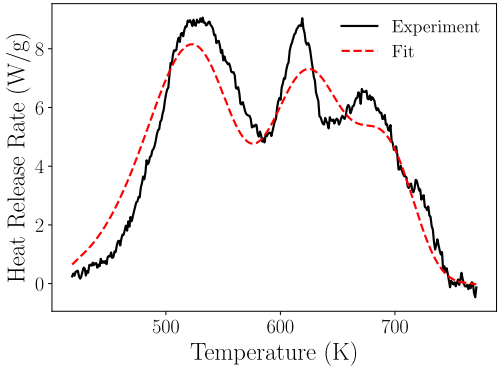
$\Delta h_{c,i}$

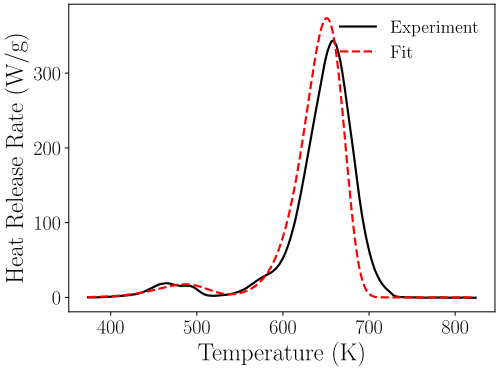
MCC Validation

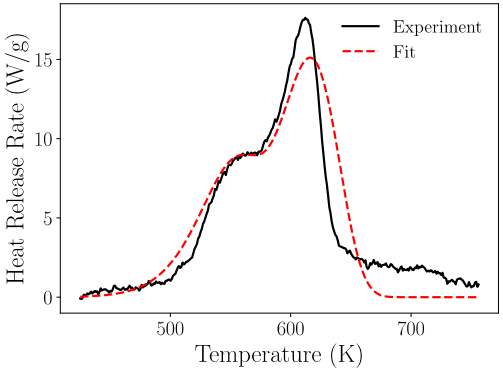
12 materials:

```
# list of all current MCC test series
mcc_tests = [
    'BigBerry-Leaf_Expt_MCC_N2_10K',
    'BigBerry-Stem_Expt_MCC_N2_10K',
    'Chamise-Leaf_Expt_MCC_N2_10K',
    'Chamise-Stem_Expt_MCC_N2_10K',
    'Chaparral-Leaf_Expt_MCC_N2_10K',
    'Chaparral-Stem_Expt_MCC_N2_10K',
    'DesertCeanothus-Leaf_Expt_MCC_N2_10K',
    'DesertCeanothus-Stem_Expt_MCC_N2_10K',
    'DouglasFir-Leaf_Expt_MCC_N2_10K',
    'LodgepolePine-Leaf_Expt_MCC_N2_10K',
    'LodgepolePine-Stem_Expt_MCC_N2_10K',
    'MaCFP_PMMA_Expt_MCC_N2_60K',
]
```

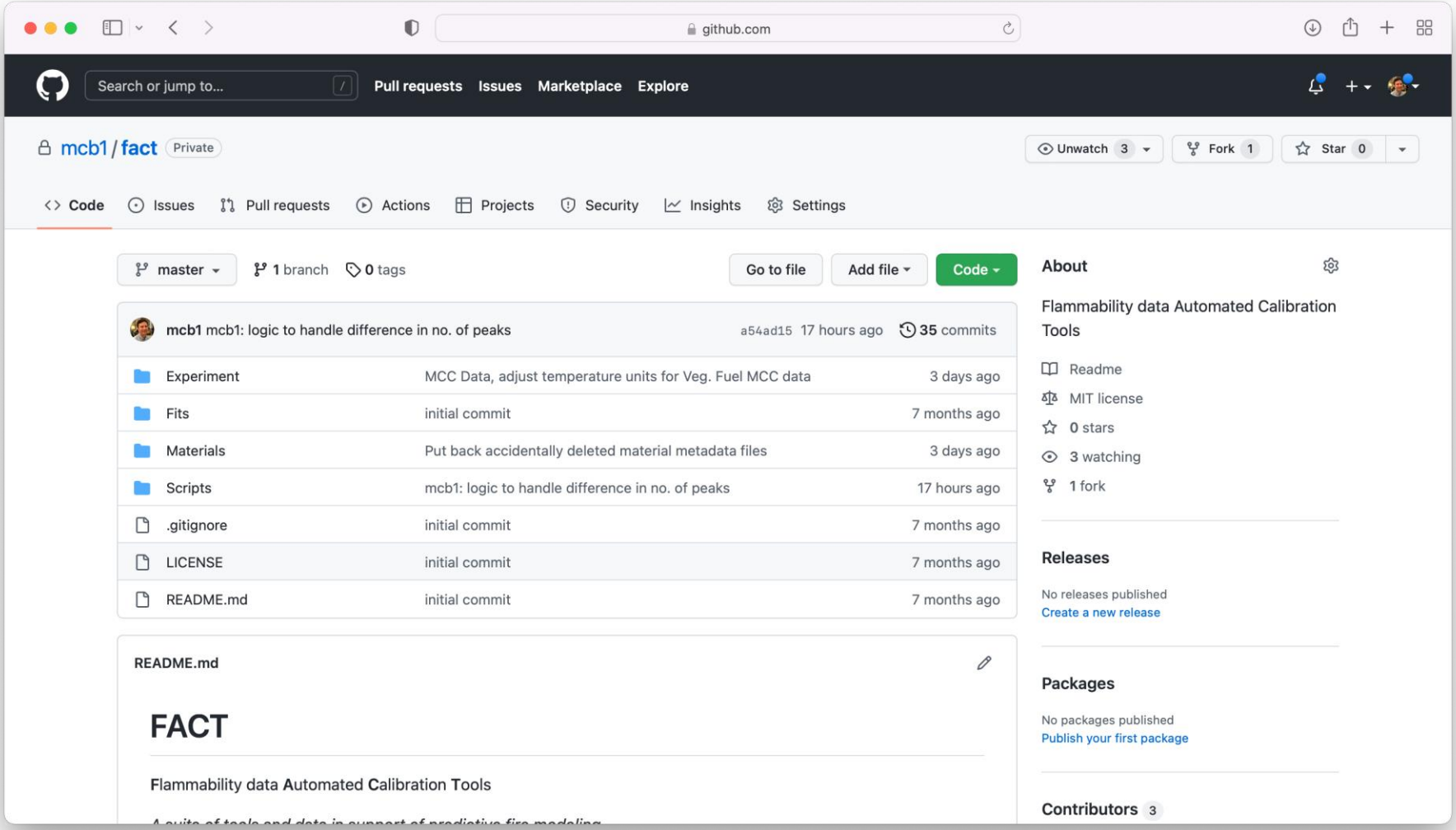




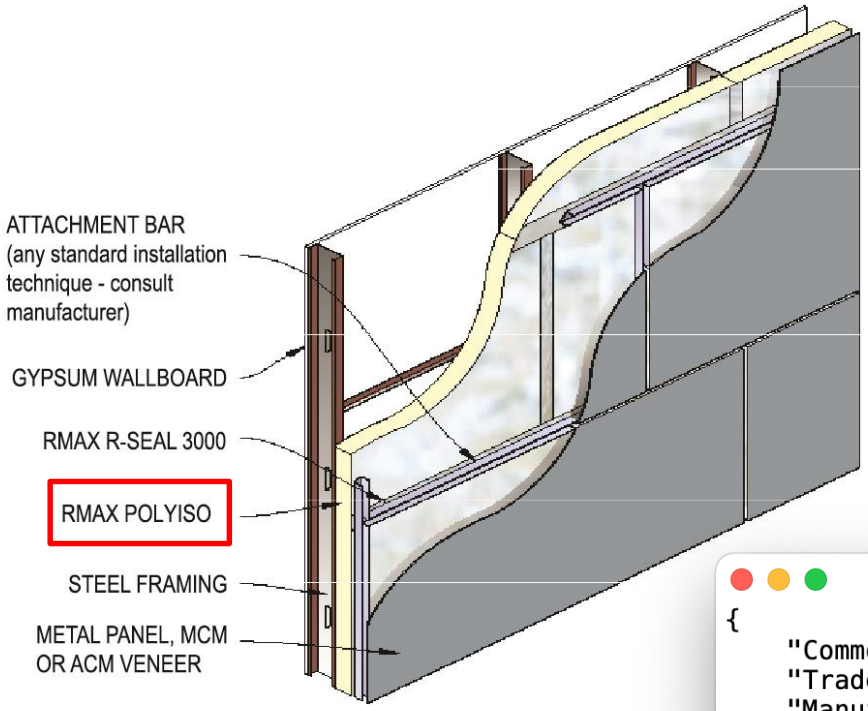




FACT: **F**lammability data **A**utomated **C**alibration **T**ools



Example: Polyisocyanurate Board Insulation



www.rmax.com

fact/Materials/metadata/PolyIso2.json

PolyIso2.json

```
{
    "Common Names": ["Poly(Isocyanurate) foam", "PolyIso foam"],
    "Trade Name": "Thermasheath",
    "Manufacturer": "RMAX",
    "Distributor": "Lowe's",
    "Date Acquired": "February 2020",
    "Description": "Yellow polyiso foam core bonded to Kraft-paper-
reinforced aluminum facers on each side; both sides have a reflective
surface; nominal thickness 2in. (50.5 to 51.7 mm)",
    "Categories": ["Synthetic Polymer", "Porous Foam", "Thermoset"]
}
```

Replicate TGA Data Files:

```
Time,Temperature,Mass
[s],[K],[mg]
0,300.772,5.64900711774
4.998,300.77222,5.65034706054
9.996,300.77115,5.64897096414
14.994,300.77005,5.64900768264
19.992,300.77194,5.64766717494
24.99,300.77516,5.64650687034
29.988,300.79185,5.64423088824
34.986,300.8111,5.64203116764
39.984,300.87397,5.63949985074
```

```
Time,Temperature,Mass
[s],[K],[mg]
0,303.653,4.53640016592
4.998,303.64491,4.53640016592
9.996,303.6319,4.53640016592
14.994,303.62205,4.53606994512
19.992,303.609,4.53472955712
24.99,303.60149,4.53220890192
29.988,303.591,4.52989826352
34.986,303.57958,4.52413981152
39.984,303.57796,4.51468270512
```

```
Time,Temperature,Mass
[s],[K],[mg]
0,298.818,4.88188150002
4.998,298.82011,4.88322139522
9.996,298.81941,4.88378928812
14.994,298.81898,4.88289179272
19.992,298.83343,4.88321602392
24.99,298.85833,4.88321700052
29.988,298.90316,4.88323457932
34.986,298.98718,4.88329171042
39.984,299.0697,4.88474342632
```

```
Time,Temperature,Mass
[s],[K],[mg]
0,301.008,4.23159800954
4.998,301.00631,4.23159800954
9.996,301.00344,4.23025805184
14.994,301.00297,4.23025805184
19.992,301.00235,4.23128787724
24.99,301.00844,4.22795131064
29.988,301.01631,4.22486945024
34.986,301.03529,4.22067695234
39.984,301.09055,4.21446457504
```

• • •

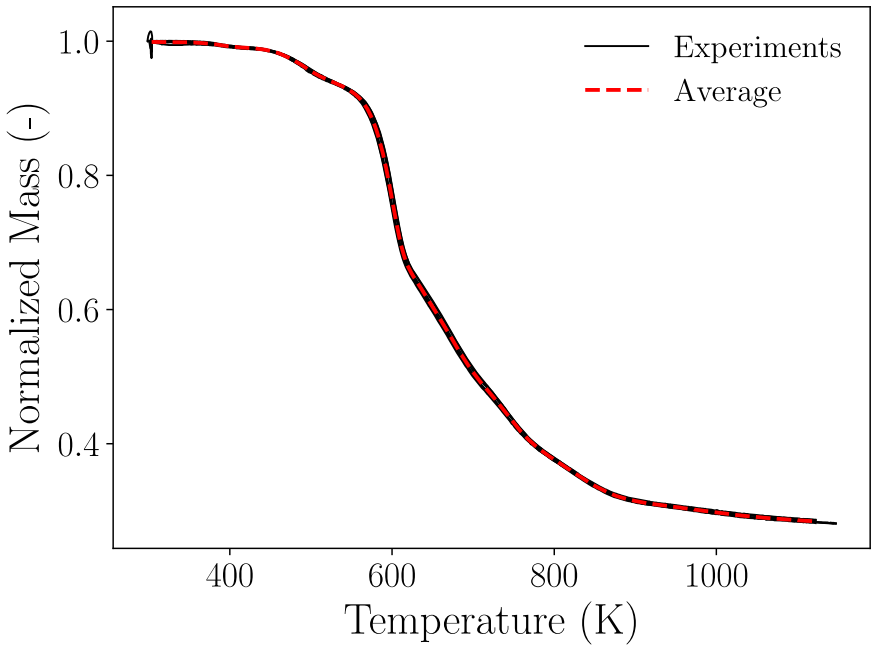
```
(base) Scripts $ python average_tga_series.py PolyIso2_Expt_TGA_N2_10K
================================================================

Reading data from:

   PolyIso2_Expt_TGA_N2_10K_r7.csv
   PolyIso2_Expt_TGA_N2_10K_r6.csv
   PolyIso2_Expt_TGA_N2_10K_r4.csv
   PolyIso2_Expt_TGA_N2_10K_r5.csv
   PolyIso2_Expt_TGA_N2_10K_r2.csv
   PolyIso2_Expt_TGA_N2_10K_r3.csv
   PolyIso2_Expt_TGA_N2_10K_r8.csv

Number of data sets in series =  7

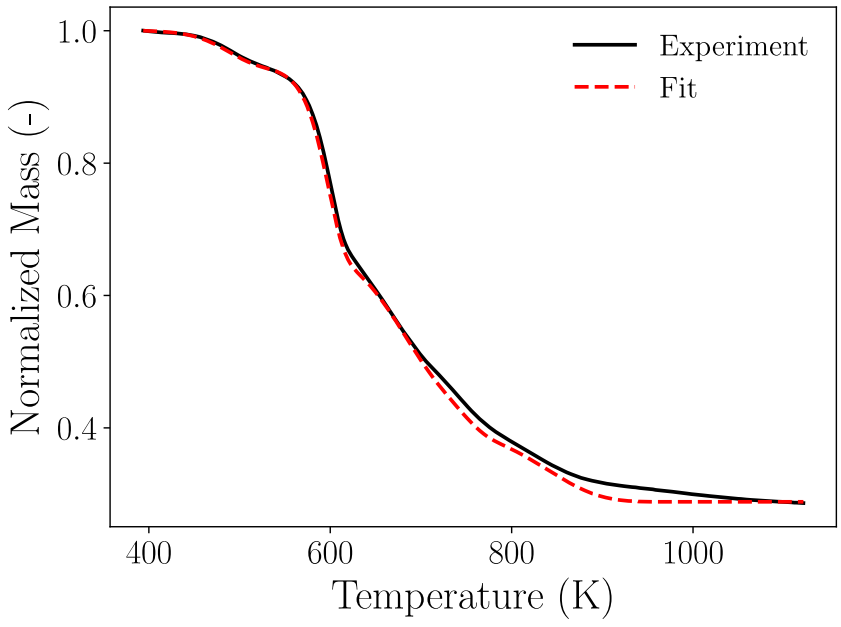
================================================================
```

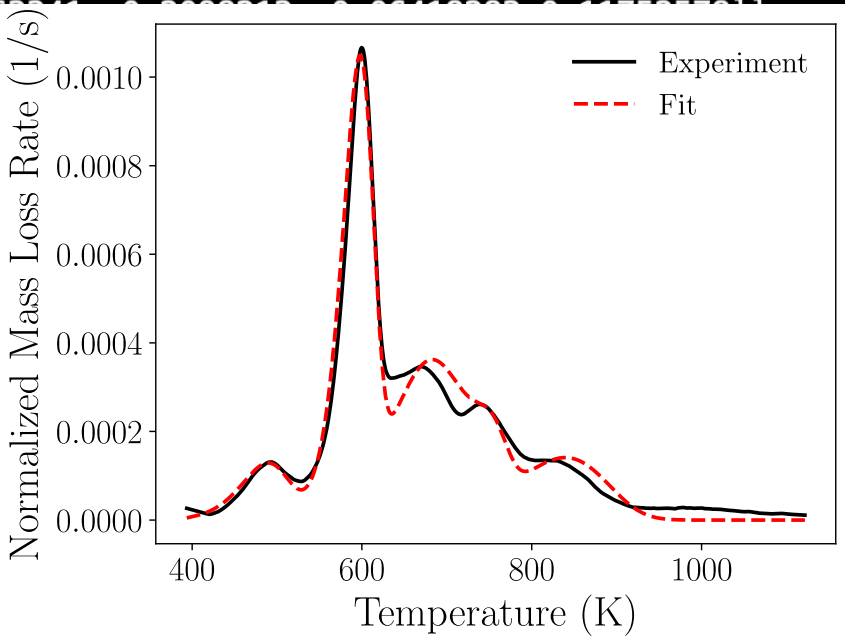


```
(base) Scripts $ python tga_fit.py PolyIso2_Expt_TGA_N2_10K_avg
```

PolyIso2_props.json

```
{
    "A": {
        "Name": "Pre-exponential Factor",
        "Units": "s^-1",
        "Values": [
            117257.20357330737,
            8420315447744.545,
            29625.162033341265,
            371893548781.6816,
            7241.320706107077
        ]
    },
    "E": {
        "Name": "Activation Energy",
        "Units": "kJ kmol^-1",
        "Values": [
```





Example: Lodgepole Pine Stems

fact/Materials/metadata/LodgepolePine-Stem.json

LodgepolePine-Stem.json

```
{
    "Common Names": "Lodgepole Pine Leaf",
    "Trade Name": "Pinus Contorta",
    "Manufacturer": "Natural Fuel",
    "Distributor": "Rocky Mountain Research Station (Missoula, Montana)",
    "Date Acquired": "May-July 2017",
    "Description": "Thin (<0.75 mm) flat slices of small branches picked
from a series of randomly selected individual Lodgepole Pine trees",
    "Categories": "Vegetation"
}
```

Replicate MCC Data Files:

```
(base) Scripts $ python average_mcc_series.py LodgepolePine-Stem_Expt_MCC_N2_10K
============================================================

 Reading data from:

    LodgepolePine-Stem_Expt_MCC_N2_10K_1.csv
    LodgepolePine-Stem_Expt_MCC_N2_10K_2.csv
    LodgepolePine-Stem_Expt_MCC_N2_10K_3.csv

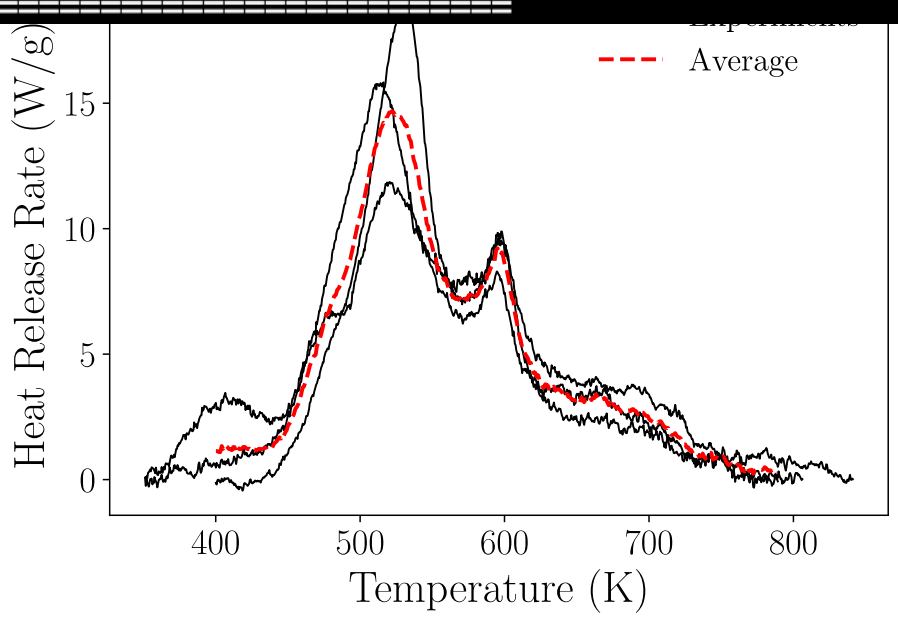
 Number of data sets in series =  3

============================================================
```

```
Ti
[s
6.
12
18
23
28
33
39
44
49
55,1,355,65,0,49
```

```
Time,Temperature,HRR
[s],[K],[W/g]
3,400.15,-0.13
5.8,400.65,-0.2
8.7,401.15,-0.03
11.9,401.65,-0
14.8,402.15,-0.05
17.7,402.65,-0.03
21,403.15,-0.12
23.8,403.65,-0.09
26.9,404.15,0.04
```

```
Time,Temperature,HRR
[s],[K],[W/g]
0.5,352.15,0.09
6.5,352.65,-0.12
11.6,353.15,-0.21
17.1,353.65,-0.28
22.3,354.15,-0.12
27.2,354.65,0.01
32.3,355.15,-0
37.4,355.65,0.04
42.2,356.15,-0.19
47,1,356,65,-0,09
```

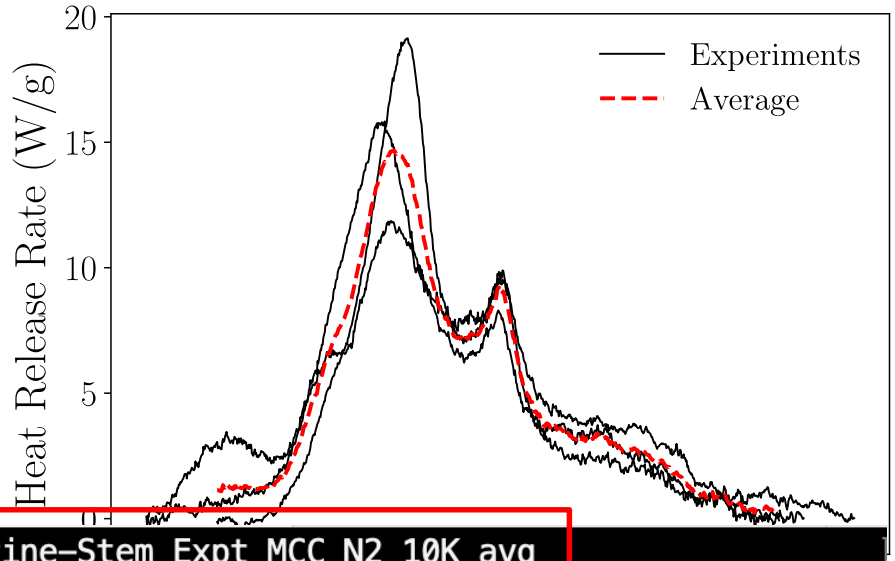


Pyrolysis Kinetics from TGA

LodgepolePine-Stem_props.json


```
{
    "A": {
        "Name": "Pre-exponential Factor",
        "Units": "s^-1",
        "Values": [
            4895170.775500201,
            235982.41393676633,
            241.86226531218318
        ]
    },
    "E": {
        "Name": "Activation Energy",
        "Units": "kJ kmol^-1",
        "Values": [
            90468.95723804967,
            88696.41047329734,
            65820.96613844081
        ]
    },
    "dmu": {
```


Average MCC Data




```
(base) Scripts $ python mcc_fit.py LodgepolePine-Stem_Expt_MCC_N2_10K_avg
------------------------------------------------------------

 Fitting MCC data from file:  ../Experiment/MCC/data/LodgepolePine-Stem_Expt_MCC_N2_10K_avg
.csv
   at heating rate of  10.0  K/min.

------------------------------------------------------------

Results:
  RMS HRR Error     =  0.9460753645395685
  dh_c_tot (J/g)    =  11054.7026255
  dh_c (J/g)        =  [19534.18875694 11315.38066012 11669.52953085]

============================================================
```

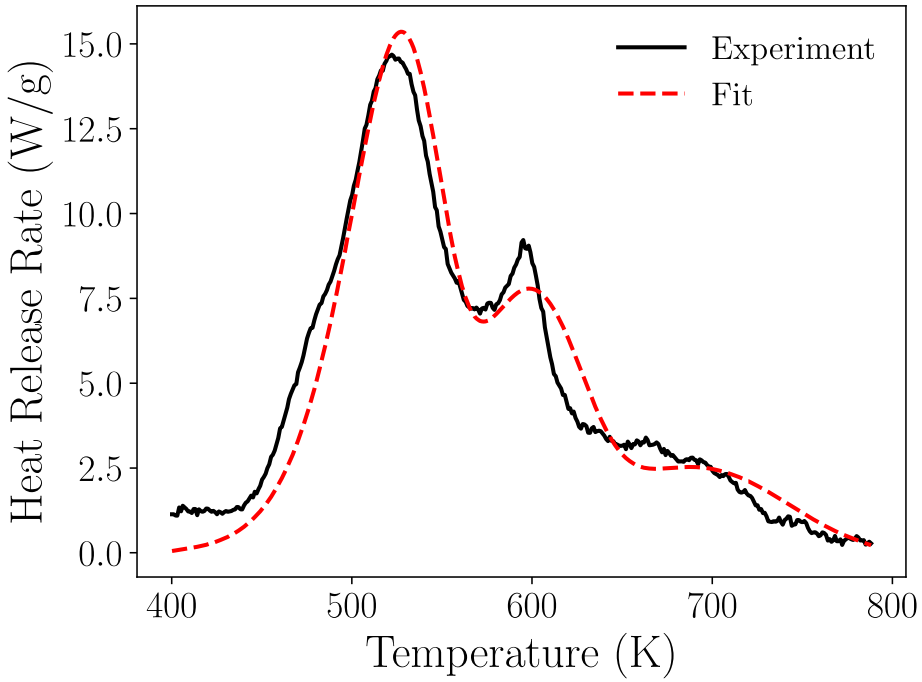
```
(base) Scripts $ python mcc_fit.py LodgepolePine-Stem_Expt_MCC_N2_10K_avg
============================================================

 Fitting MCC data from file:  ../Experiment/MCC/data/LodgepolePine-Stem_Expt_MCC_N2_10K_avg
.csv
   at heating rate of  10.0  K/min.

------------------------------------------------------------

Results:
  RMS HRR Error     =  0.9460753645395685
  dh_c_tot (J/g)    =  11054.7026255
  dh_c (J/g)        =  [19534.18875694 11315.38066012 11669.52953085]

============================================================
```



LodgepolePine-Stem_props.json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            11669.52953084592
        ]
    }
}
```

Material Flammability

Not secure | https://flammability.el.nist.gov

Not syncing

Material Flammability Database

This database contains data from the Materials database. The data is organized by material and the kinetic parameters is available for download in the form of a csv file.

Material

Chamise-Stem

- ABS
- BigBerry-Leaf
- BigBerry-Stem
- Chamise-Leaf
- **Chamise-Stem**
- Chaparral-Leaf

Acquired	
Description	Thin (<0.75 mm) flat slices of small branches picked from a series of randomly selected individual Desert Chamise plants
Categories	Vegetation

TGA

Chamise-Stem_Expt_TGA_N2_1...

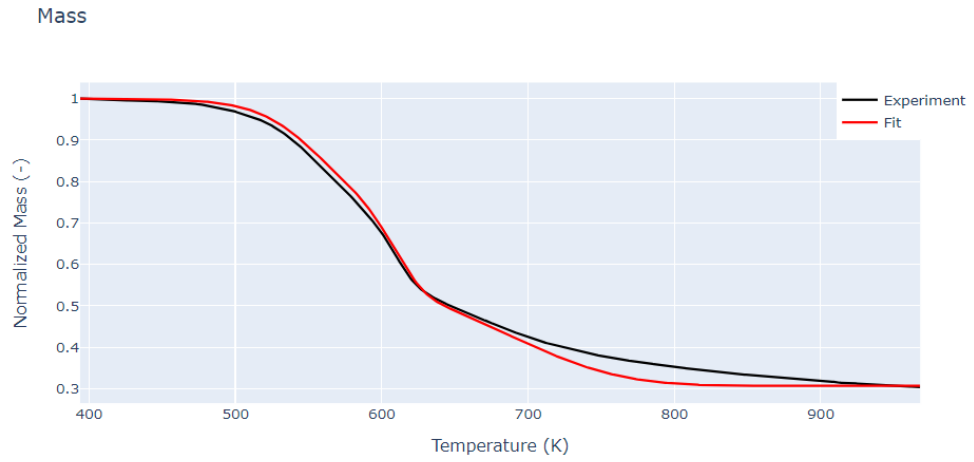
MCC

Chamise-Stem_Expt_MCC_N2_1...

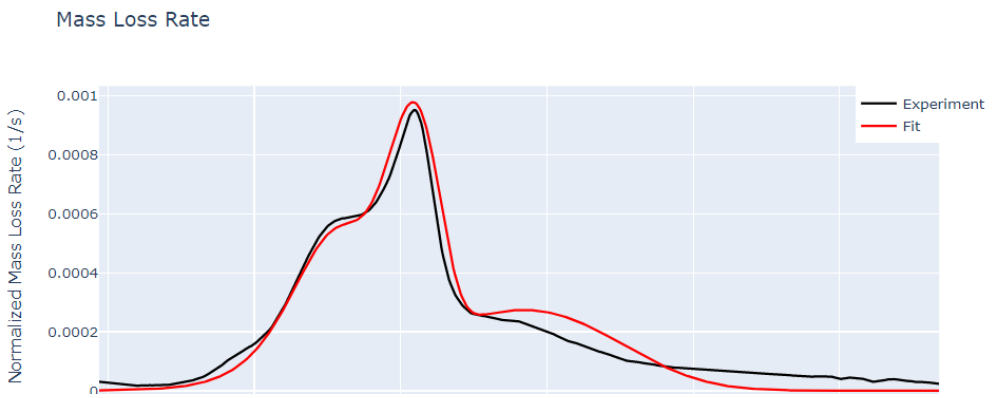
Kinetic Params

Name	Units	Values
Pre-exponential Factor	1/s	2.732E+07, 7.219E+10, 1.474E+01
Activation Energy	kJ/mol	1.008E+05, 1.507E+05, 5.022E+04
Normalized Mass of Reaction	-	1.409E-01, 2.608E-01, 2.915E-01
Heat of Combustion	J/g	1.145E+04, 9.040E+03, 1.823E+03

TGA Mass



TGA Mass Loss Rate



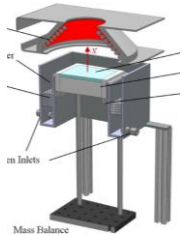
Micro Combustion Calorimeter

$\Delta h_{c,i}$

Thermogravimetric Analysis

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

Controlled Atmosphere Pyrolysis



k_i

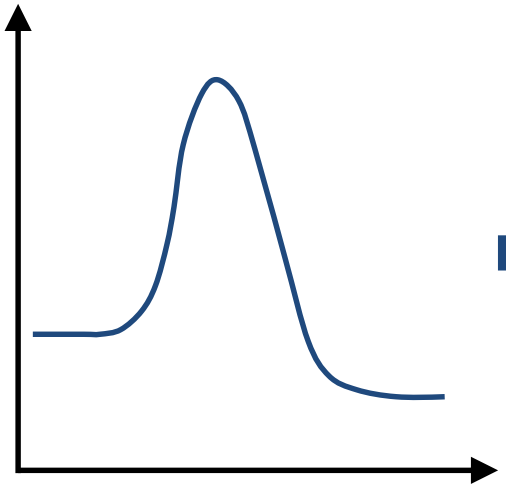
Differential Scanning Calorimetry

$c_i, \Delta h_i$

Analysis of DSC Data

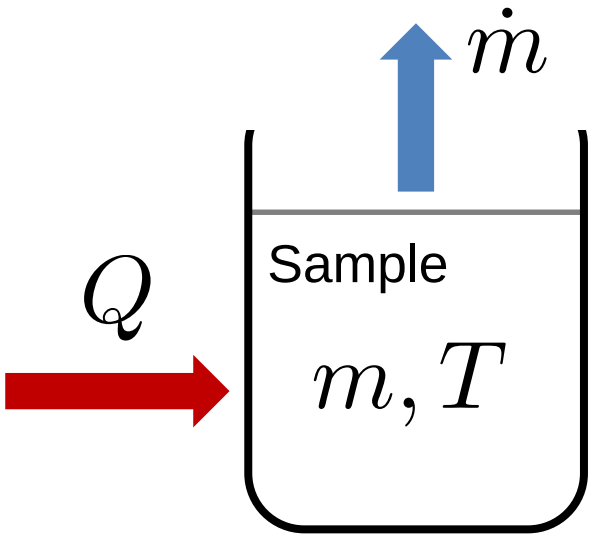
How should we estimate component specific heat capacities ($c_{p,i}$) and heats of gasification (Δh_i) from raw DSC data?

Heat Flow



$c_{p,i}$, Δh_i

Modeling DSC



Controlled **Measured**

$$mc_p \frac{dT}{dt} = Q - Q_{\mathrm{r}}$$

Calibrated

Assumptions:

- No spatial variations in temperature and composition
- No work

Normalized Model

Divide energy equation by initial mass, m_0

$$\mu c_p \frac{dT}{dt} = q - q_{\mathrm{r}}$$

where

$$\mu \equiv m/m_0$$

$$q \equiv Q/m_0$$

$$q_{\mathrm{r}} \equiv Q_{\mathrm{r}}/m_0$$

Material and Reaction Models

- Consistent with TGA analysis
- Mass information from pyrolysis kinetics
- **$2N_{\mathrm{r}} + 1$ unknown material properties**

Char Specific Heat

Reactant Specific Heat

$$\mu c_p = \mu_{\mathrm{c}} c_{p,\mathrm{c}} + \sum_{i=1}^{N_{\mathrm{r}}} \mu_i c_{p,i}$$

$$q_{\mathrm{r}} = \sum_{i=1}^{N_{\mathrm{r}}} \Delta h_i \left(-\frac{d\mu_i}{dt} \right)$$

Heats of Gasification

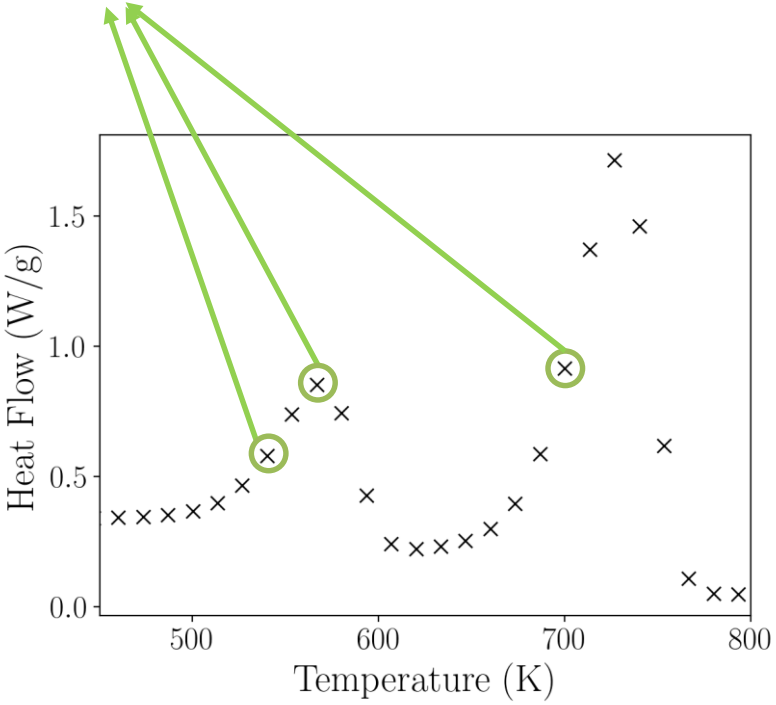
Linear Problem—Heat Flow

$$\mu_{\mathrm{c}} c_{p,\mathrm{c}} + \sum_{i=1}^{N_{\mathrm{r}}} \mu_i c_{p,i} - \sum_{i=1}^{N_{\mathrm{r}}} \frac{d\mu_i}{dt} \Delta h_i = q$$

$$\mu_{\mathrm{c},k} c_{p,\mathrm{c}} + \sum_{i=1}^{N_{\mathrm{r}}} \mu_{i,k} c_{p,i} - \sum_{i=1}^{N_{\mathrm{r}}} \left(\frac{d\mu_i}{dt} \right)_k \Delta h_i = q_k, \quad k = 1, \ldots, N_{\mathrm{d}} \gg N_{\mathrm{r}}$$

$2N_{\mathrm{r}} + 1$ unknowns

Normalized masses (μ_{c}, μ_i) and mass change rates ($d\mu_i/dt$) are obtained from kinetic model of pyrolysis



Integral Heat Flow Form

Hypothesis: total heat absorbed by material is more important for predicting flame spread

$$\theta_{\mathrm{c}} c_{p,\mathrm{c}} + \sum_{i=1}^{N_{\mathrm{r}}} \theta_i c_{p,i} + \sum_{i=1}^{N_{\mathrm{r}}} \Delta\mu_i \Delta h_i = \Delta e_q$$

Mass-weighted temperature changes

$$\theta_{\mathrm{c}} \equiv \int_{T_0}^{T} \mu_{\mathrm{c}}\, dT$$

$$\theta_i \equiv \int_{T_0}^{T} \mu_i\, dT$$

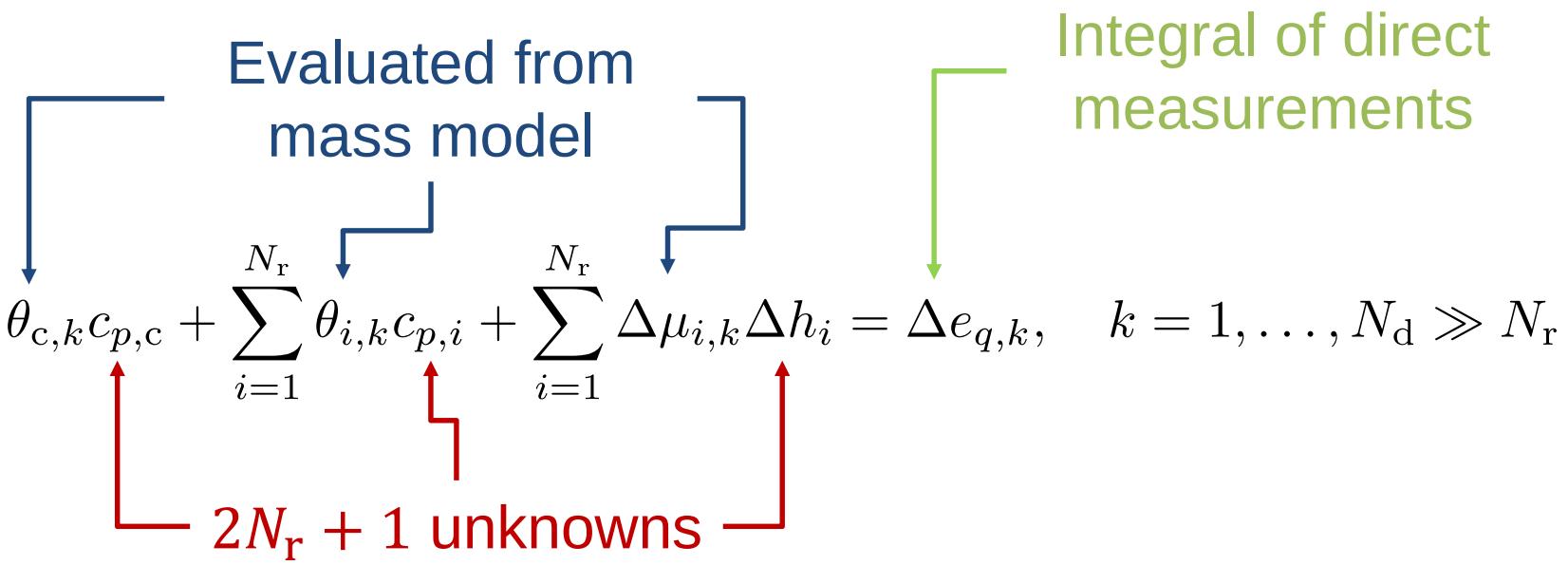
Component mass change

$$\Delta\mu_i \equiv \mu_{i,0} - \mu_i$$

Total heat in to sample

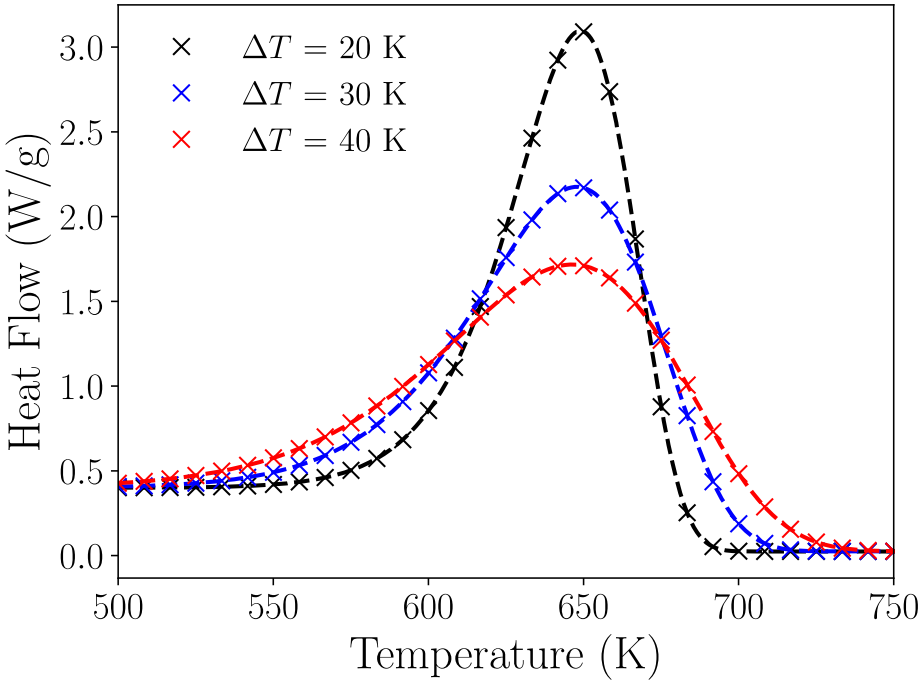
$$\Delta e_q \equiv \int_{t_0}^{t} q\, dt$$

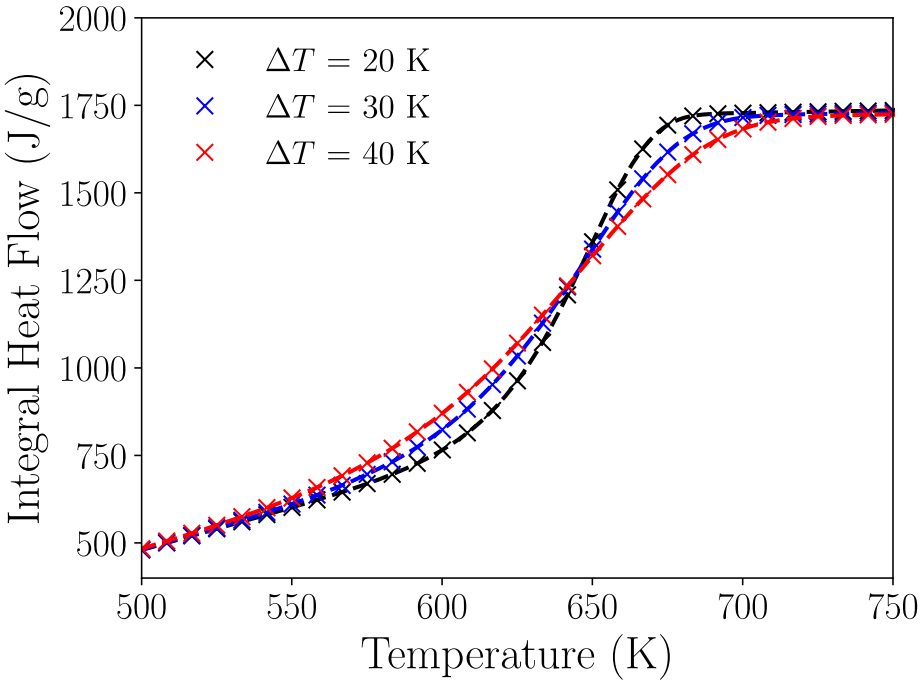
Linear Problem—Total Heat Flow



- N_d equations for $2N_r + 1$ unknowns
- Linear least-squares problem is well-posed* → unique solution exists

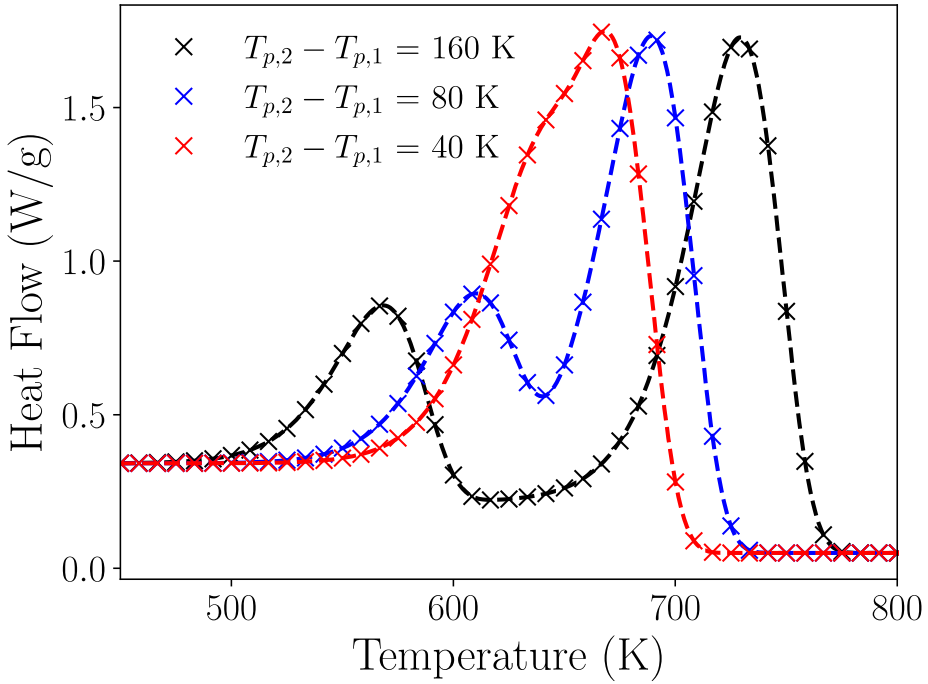
DSC: Single Reaction Verification

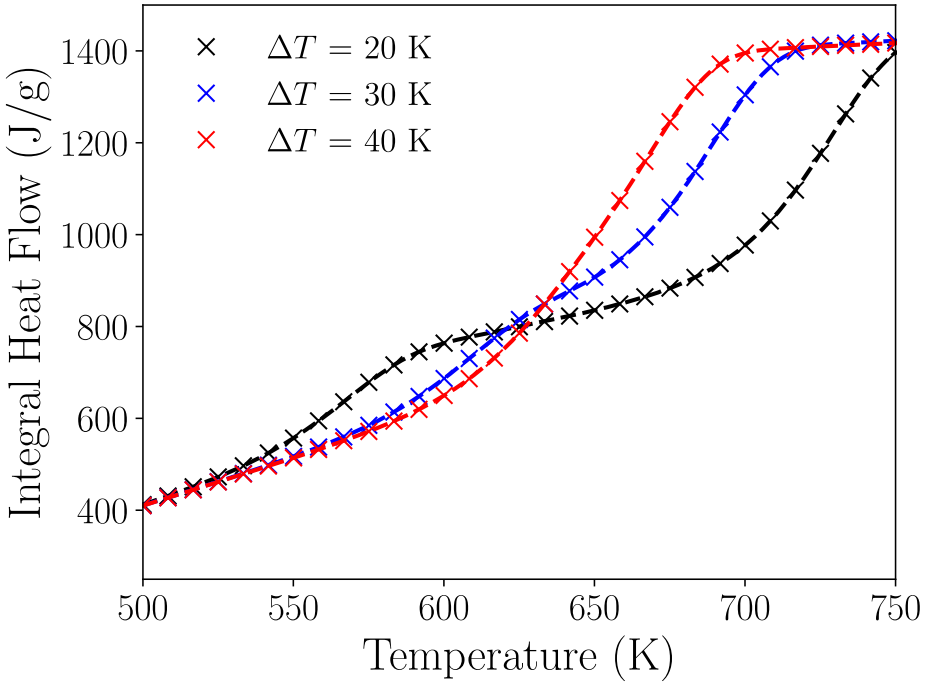




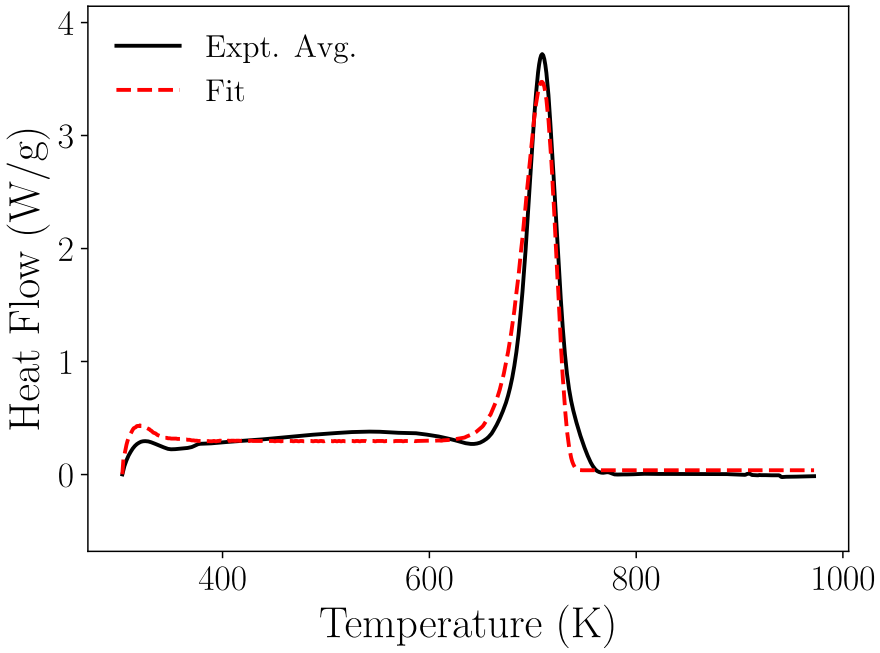
- **Markers**: simulated data using assumed specific heats and heats of gasification
- **Lines**: fits using calibrated parameters

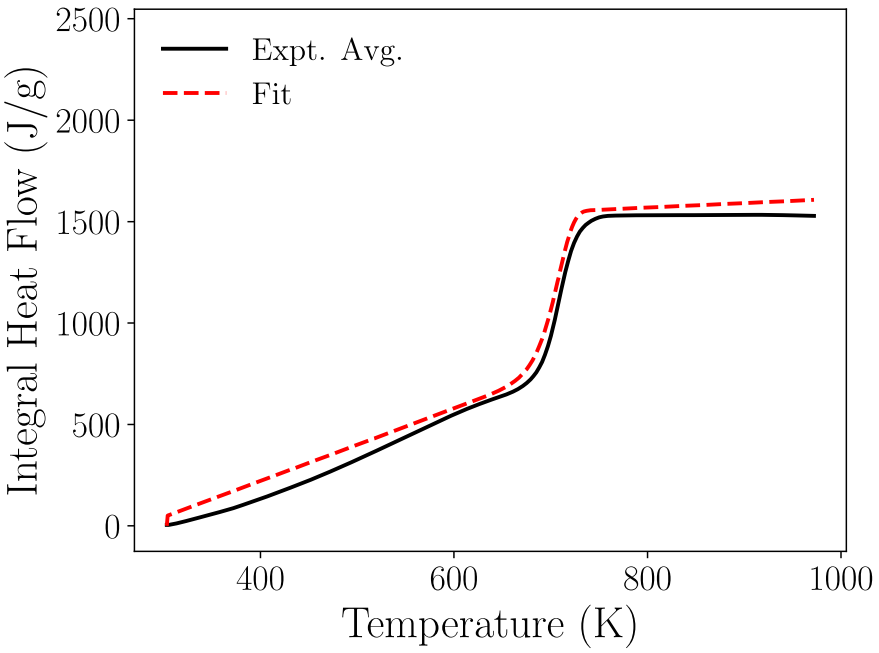
DSC: Two Reaction Verification





Validation: HIPS

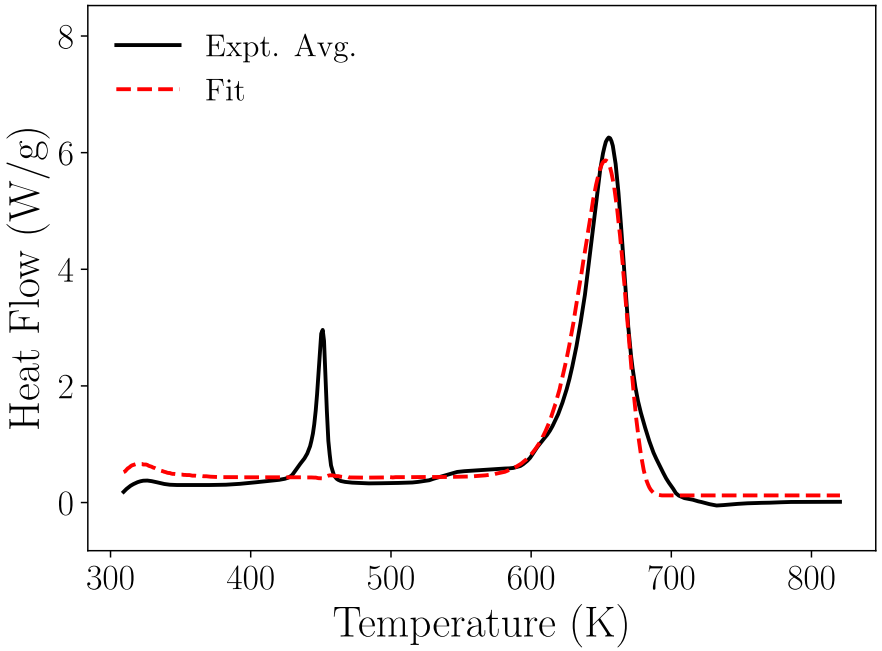


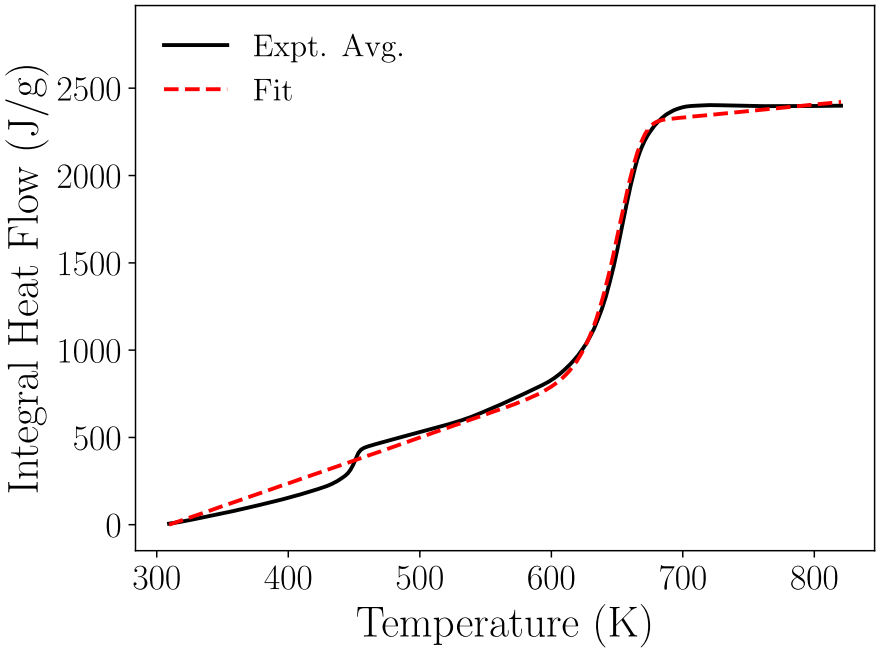


Based on 7 replicate DSC experiments at 10 K/min

Property	Calibrated Value	Stoliarov and Walters (2008)
Specific Heat Capacity (J/g-K)	1.61	2.0
Heat of Gasification (J/g)	818	1000

Validation: POMGF





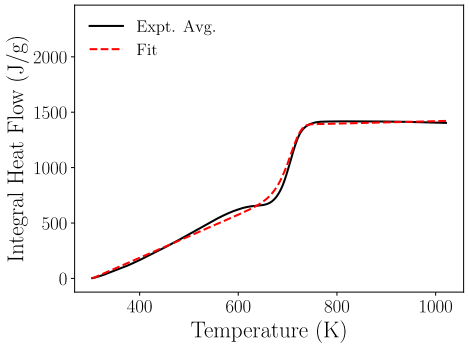
Based on 7 replicate DSC experiments at 10 K/min

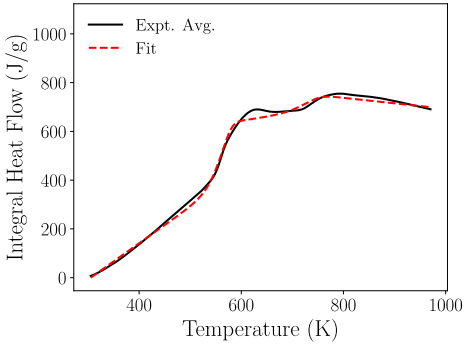
Property	Calibrated Value	Stoliarov, Lyon, and Linteris (2012)
Specific Heat Capacity (J/g-K)	2.27	1.88
Heat of Gasification (J/g)	1720	1570

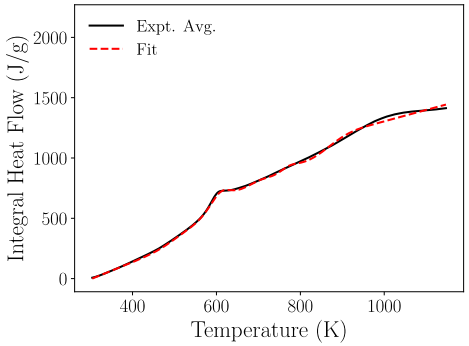
DSC Validation Cases

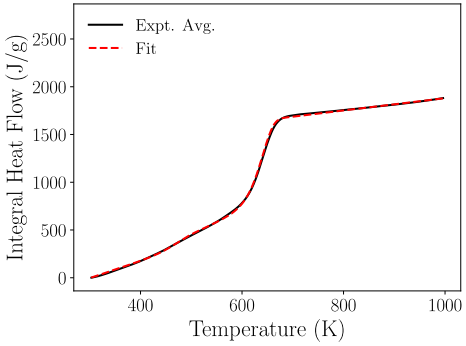
11 materials:

```
# list of all current DSC test series
dsc_tests = [
    'ABS_Expt_DSC_N2_10K',
    'HDPE_Expt_DSC_N2_10K',
    'HIPS_Expt_DSC_N2_10K',
    'Kydex_Expt_DSC_N2_10K',
    'MaCFP_PMMA_Expt_DSC_N2_10K',
    'PolyIso1_Expt_DSC_N2_10K',
    'PolyIso2_Expt_DSC_N2_10K',
    'PolyIso05_Expt_DSC_N2_10K',
    'POMGF_Expt_DSC_N2_10K',
    'XPSgreen_Expt_DSC_N2_10K',
    'XPSpink_Expt_DSC_N2_10K'
]
```





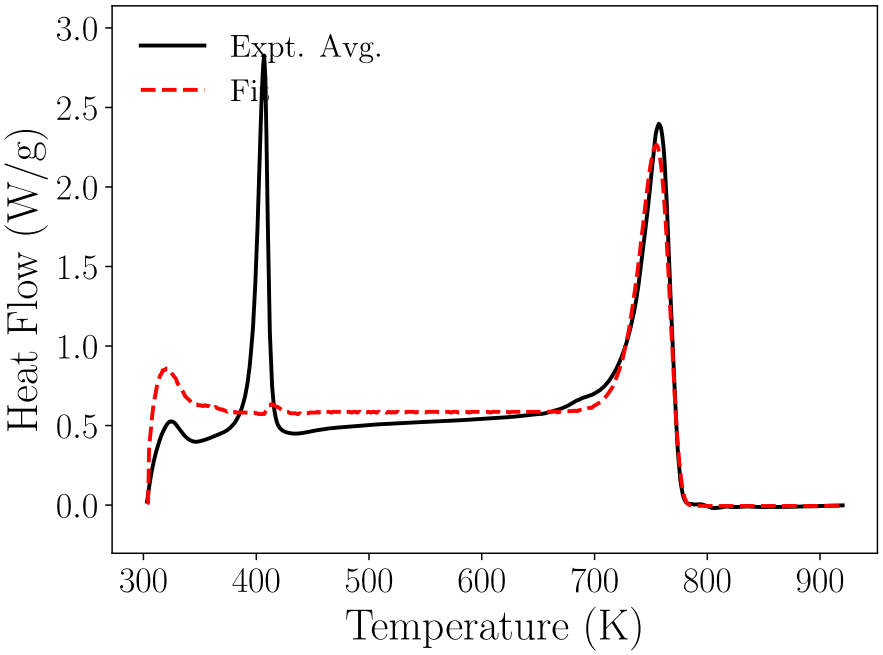




Next Steps

- Phase changes: get both kinetics and enthalpy changes from DSC
- Negative specific heats:
  - Improve pyrolysis kinetics, or
  - Get more data
- Consider non-constant specific heats

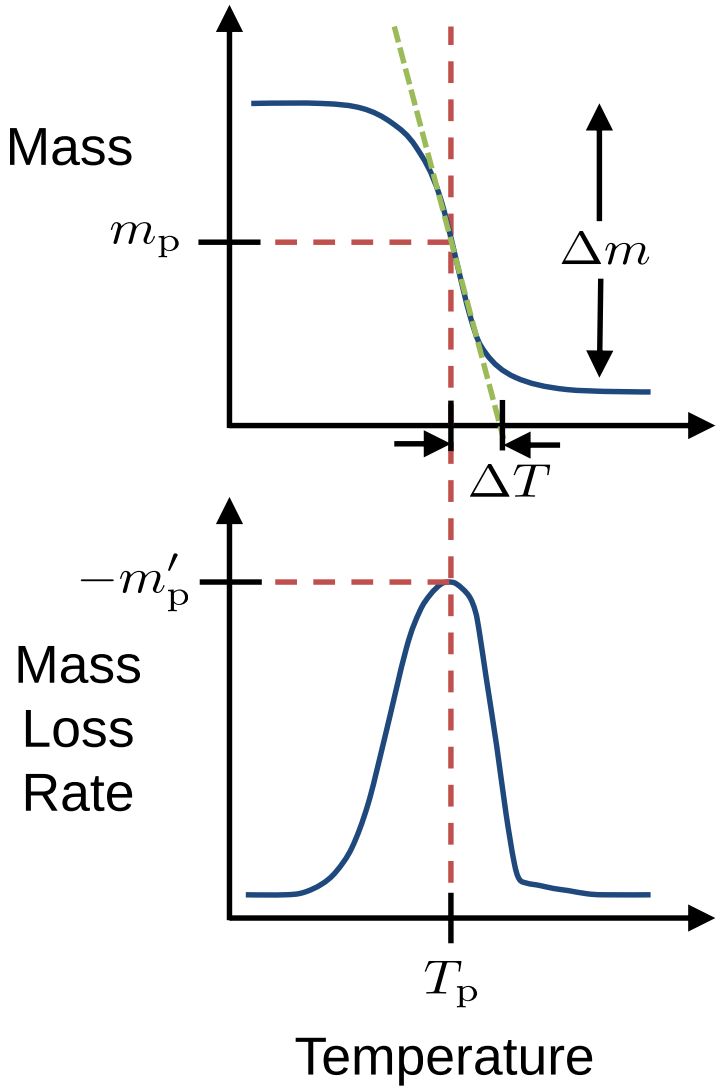
HDPE Calibration:



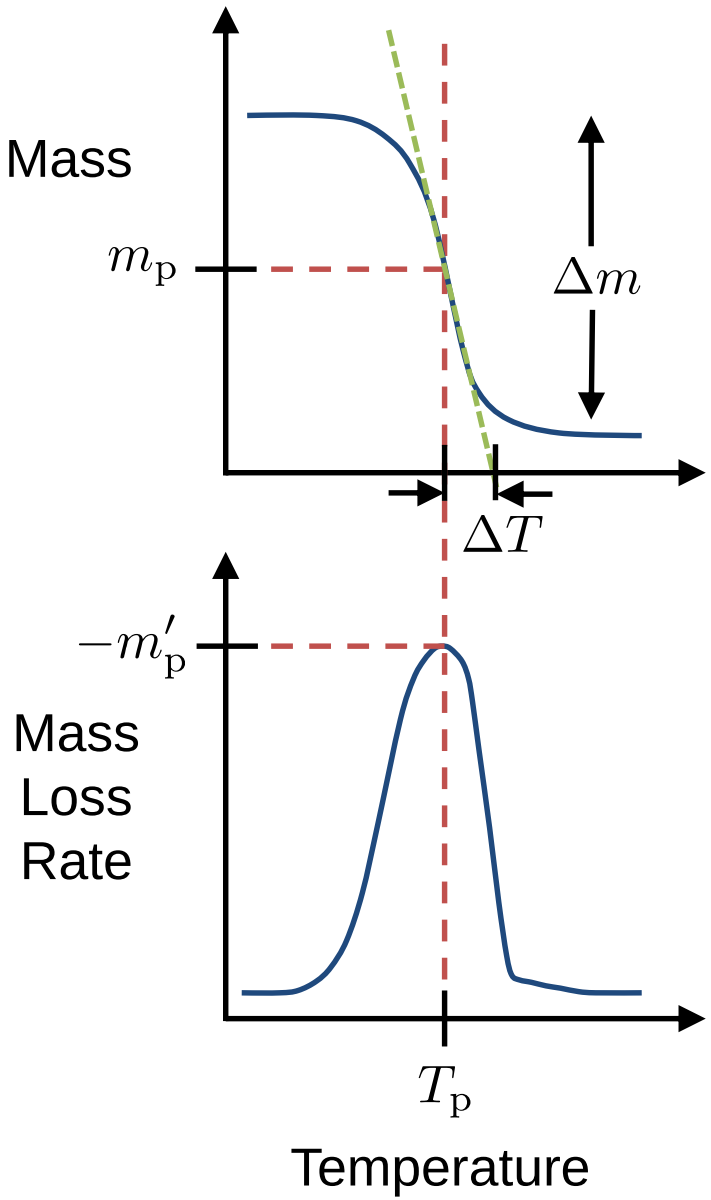
Summary

- **Predicting** fire growth requires material properties
- To obtain material properties:
  - Small-scale tests (TGA, MCC, DSC, etc.)
  - **Calibration algorithms**
- A new calibration algorithm is presented for obtaining specific heat capacities and heats of gasification from DSC data
- Algorithm performs well with simulated data and DSC for several thermoplastics
- Future work is needed to
  - Characterize phase change energetics
  - Eliminate negative specific heat capacities (not **realistic**)
  - Allow for temperature dependent specific heat capacities

TGA Calibration Method



- Based on iterative analysis of reaction peaks
- Peaks found from conditions on derivatives of data
- Two free parameters:
  1. Tolerance on what counts as a peak
  2. Critical peak width for smoothing



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

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

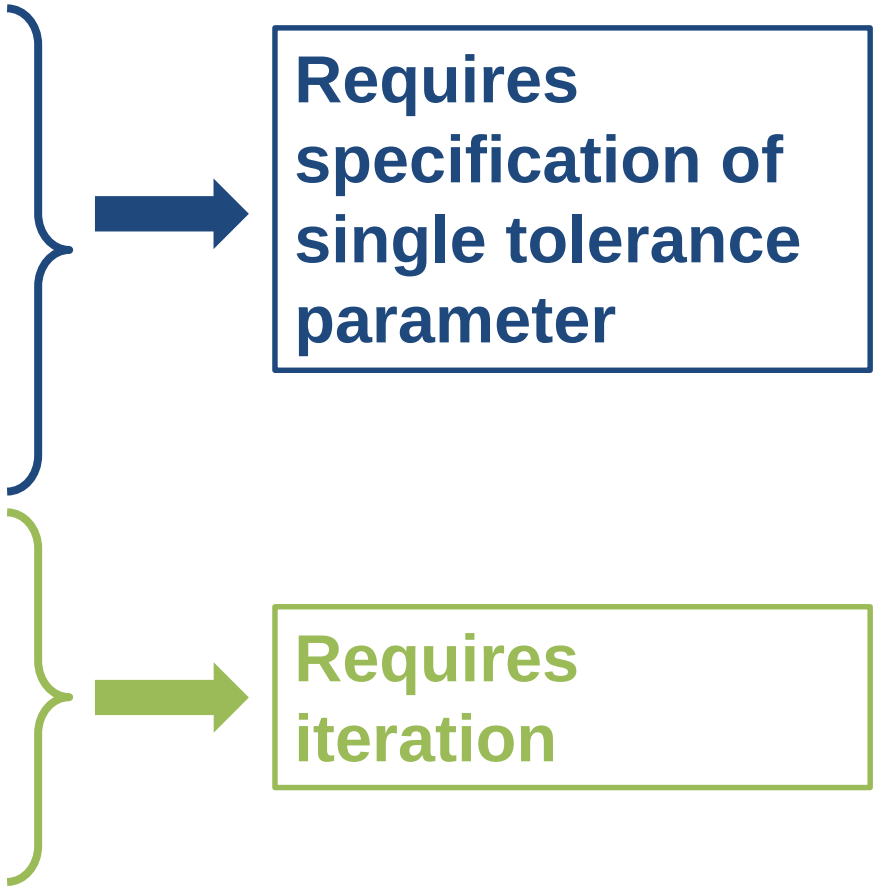
Approximate Solution

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

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

Some Details

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



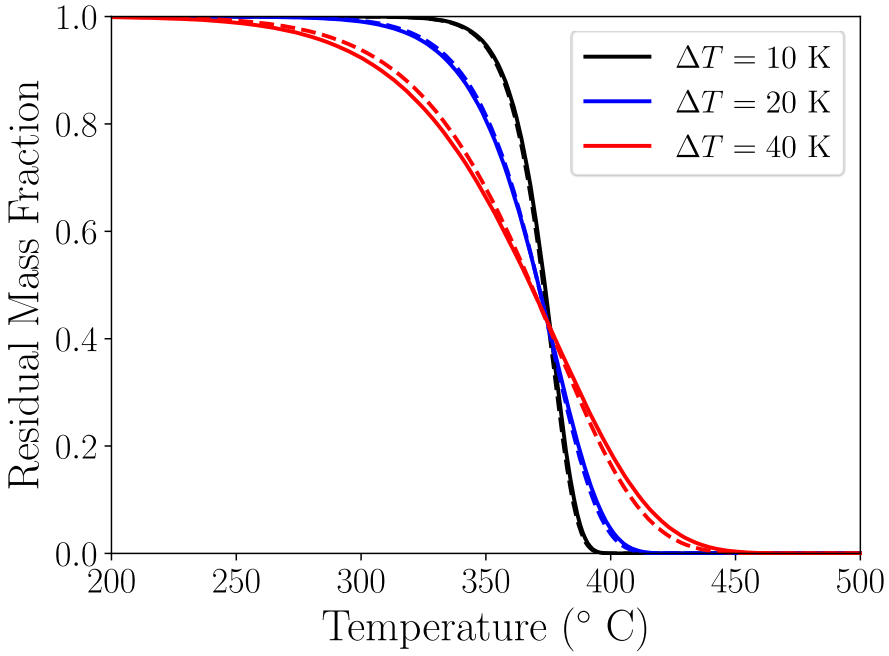
TGA Fit Verification

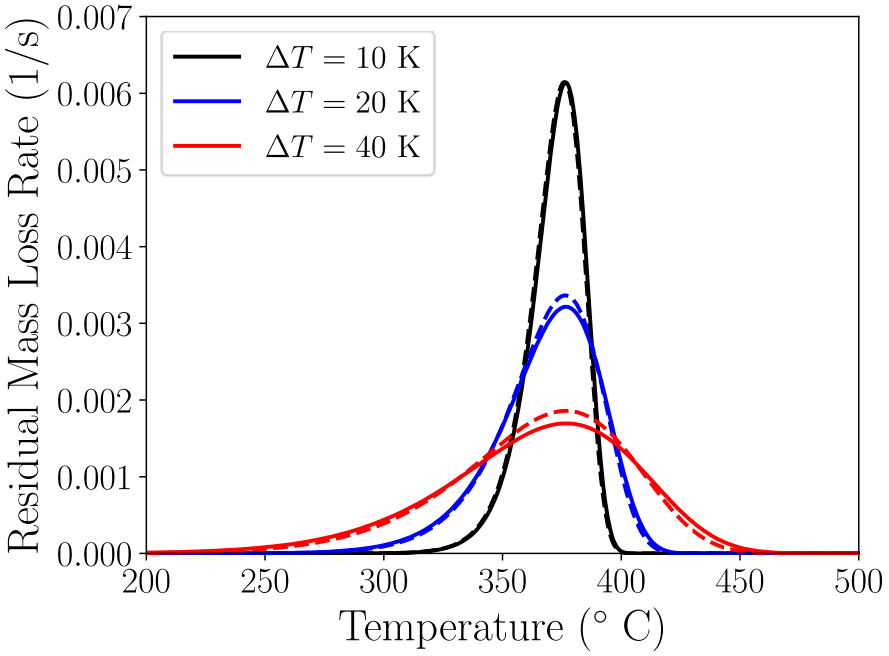
1. Assume **kinetic parameters**
2. Generate simulated TGA data
3. Use algorithm to find assumed parameters

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:

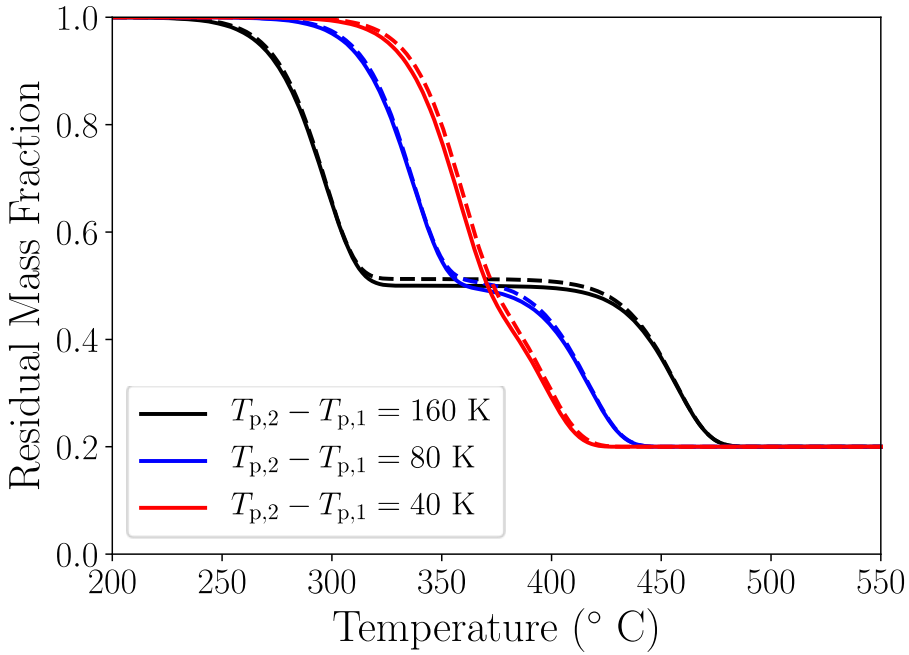
Kinetic Parameter	Specified Value	Calibrated Value
T_p (K)	650	649.4
ΔT (K)	20	19.07
ξ	0.03077	0.02935
$\ln[A\ (s^{-1})]$	27.71	29.34
E (kJ/kmol)	175.6×10^3	184.1×10^3

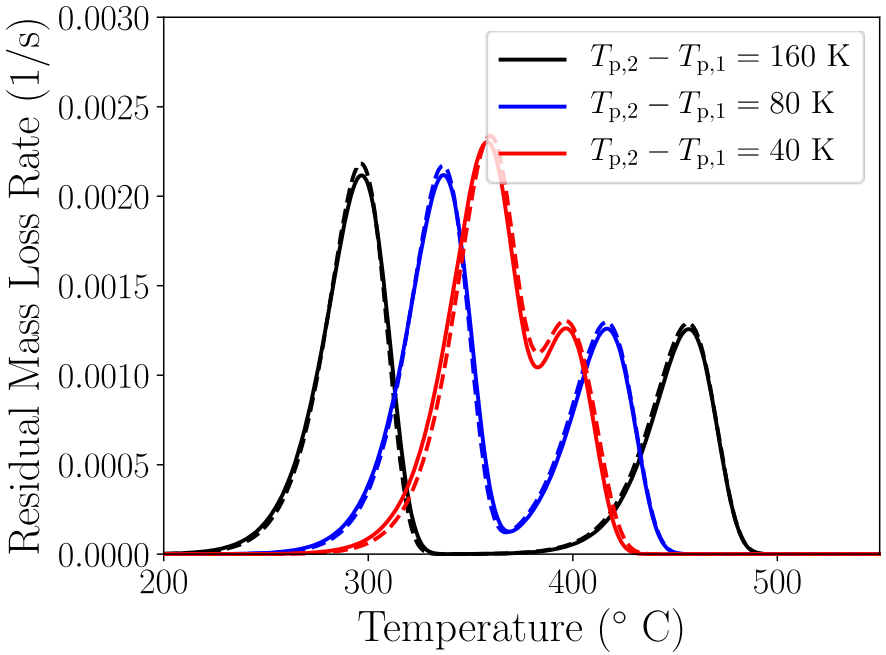
ΔT = 40 K:

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 ΔT
Increasing accuracy

Two Reactions Verification





Closer fit for more separated reactions

Validation

Purpose:

1. Test algorithm with real TGA data

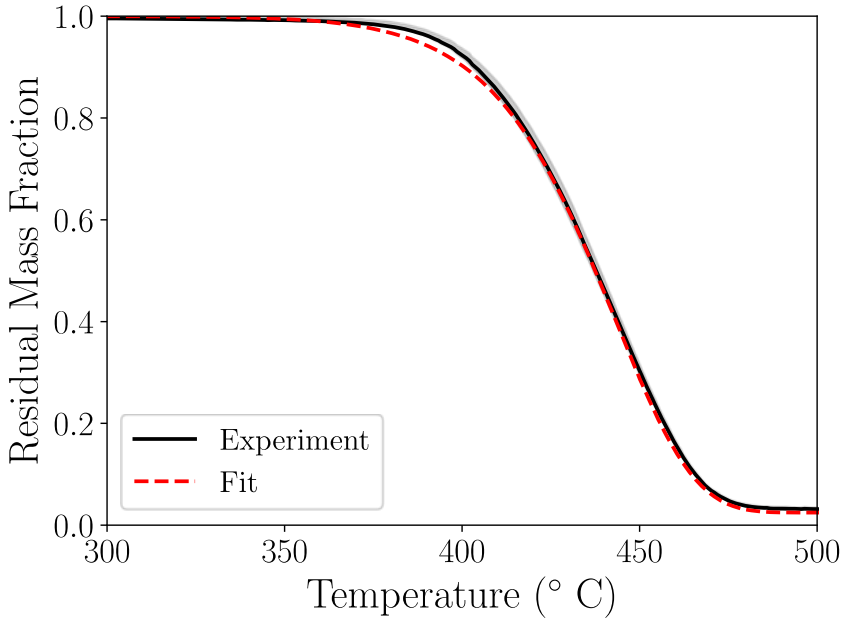
Test Materials:

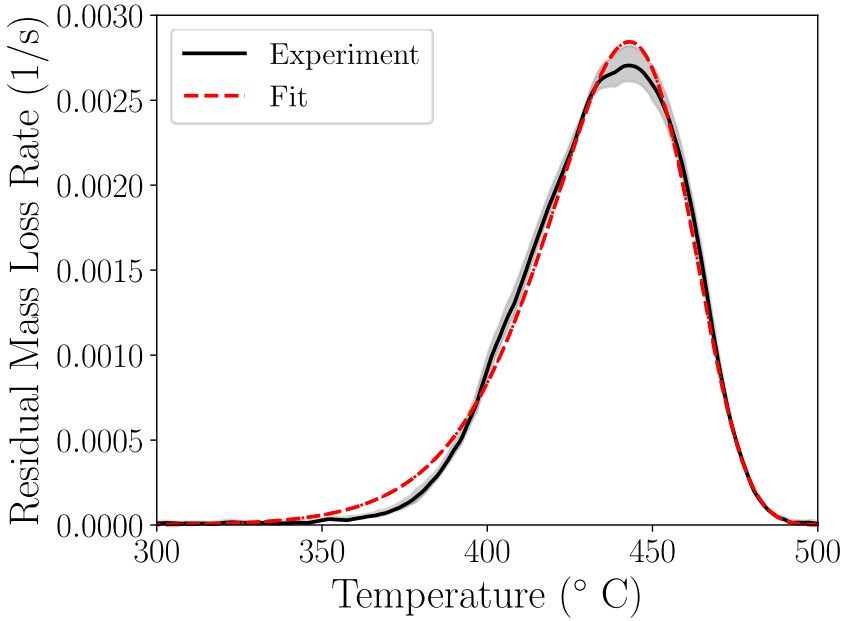
1. Nylon 6,6
2. Flexible polyurethane (PU) foam
3. Polyvinyl Chloride (PVC)

Procedure:

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

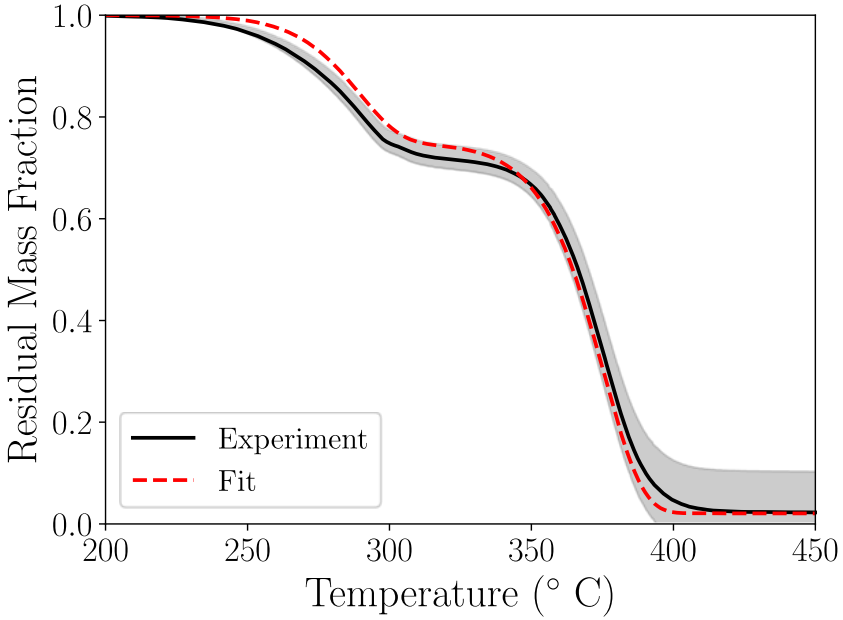
Validation: Nylon 6,6

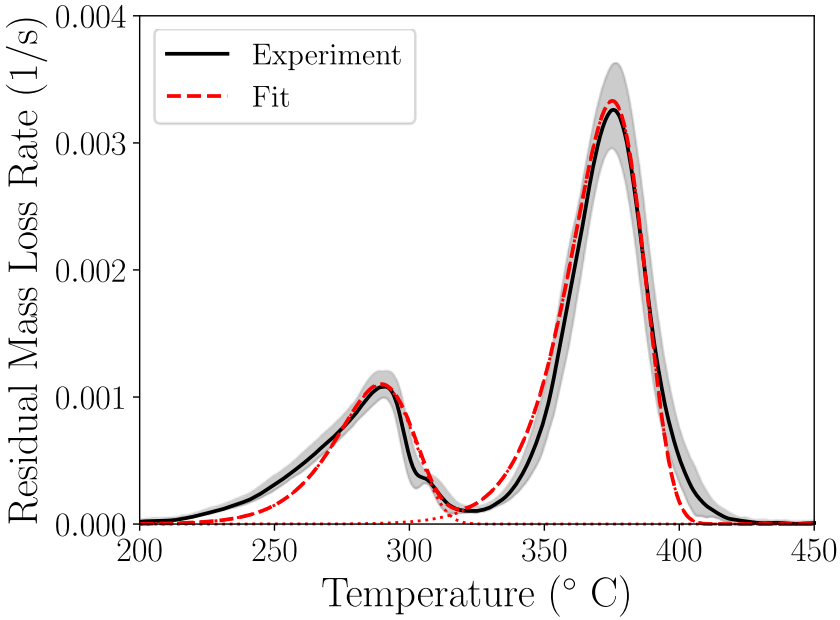




Kinetic Parameter	Reaction 1
T_p (K)	716.3
ΔT (K)	22.11
Δm	0.9754
ξ	0.03087
$\ln[A\ (s^{-1})]$	27.50
E (kJ/kmol)	192.9×10^3

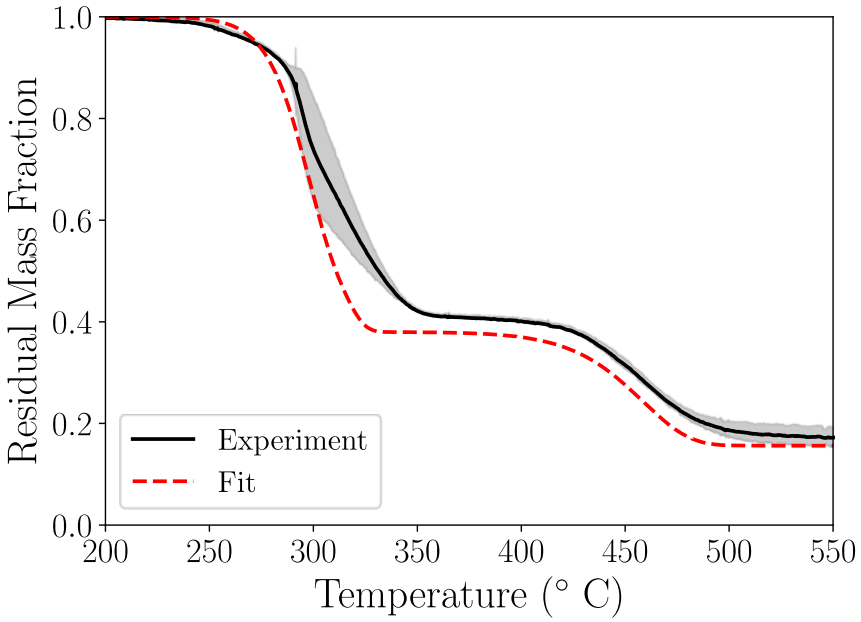
Validation: Polyurethane Foam

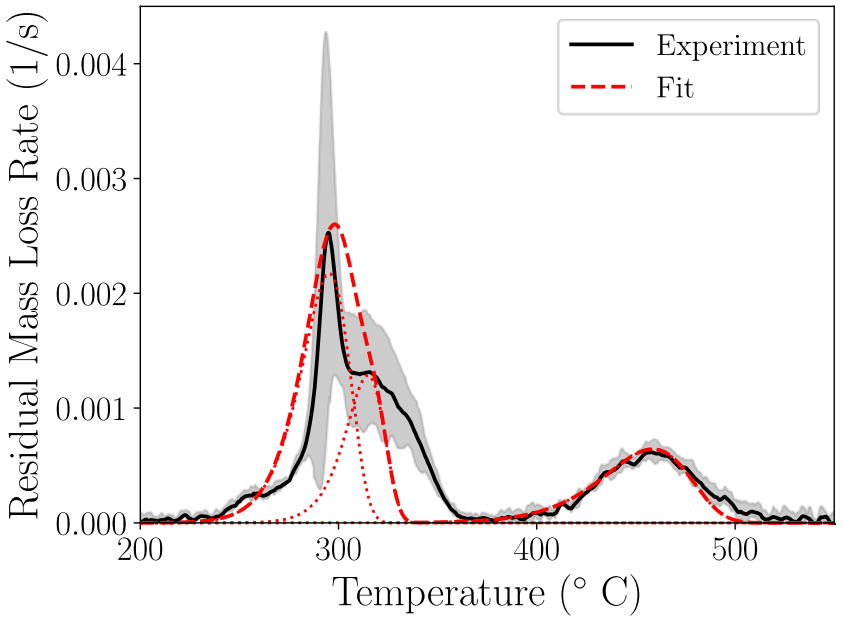




Kinetic Parameter	Reaction 1	Reaction 2
T_p (K)	562.7	648.5
ΔT (K)	14.50	13.69
Δm	0.2511	0.7280
ξ	0.02577	0.02112
$\ln[A\ (s^{-1})]$	34.34	42.95
E (kJ/kmol)	181.5×10^3	255.3×10^3

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

Single Reaction

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

1) Value at Peak Temperature: T_{p}

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

2) Simple Average: N_{d} data points

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

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

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

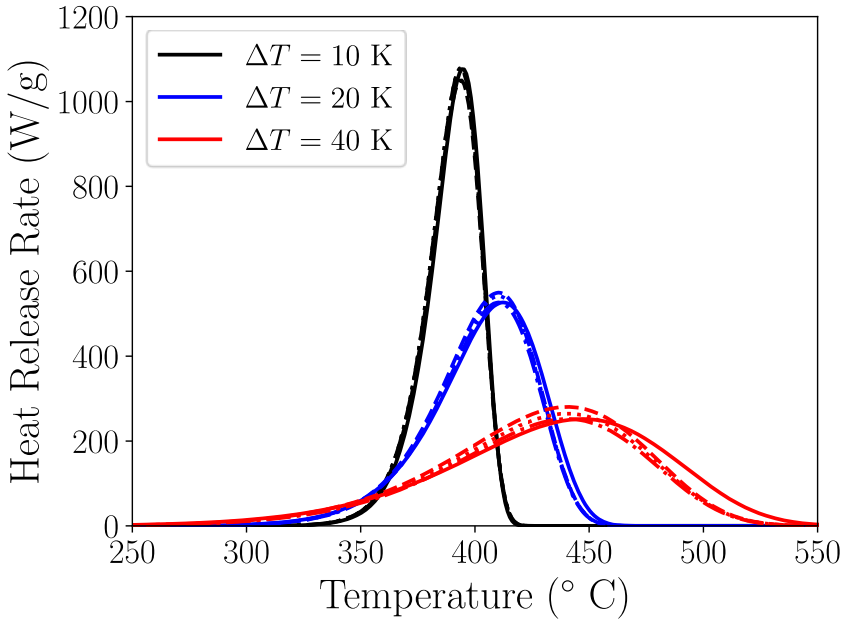
MCC Fit Verification

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



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

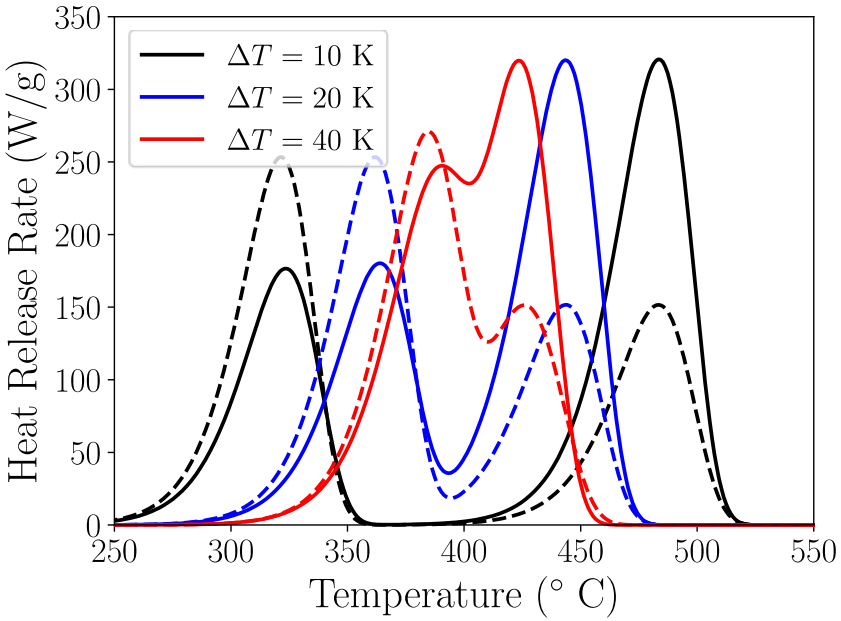
- TGA Data
  - 10 K/min
  - T_p = 650 K
- MCC Data
  - 60 K/min
  - Δh = 30 kJ/g

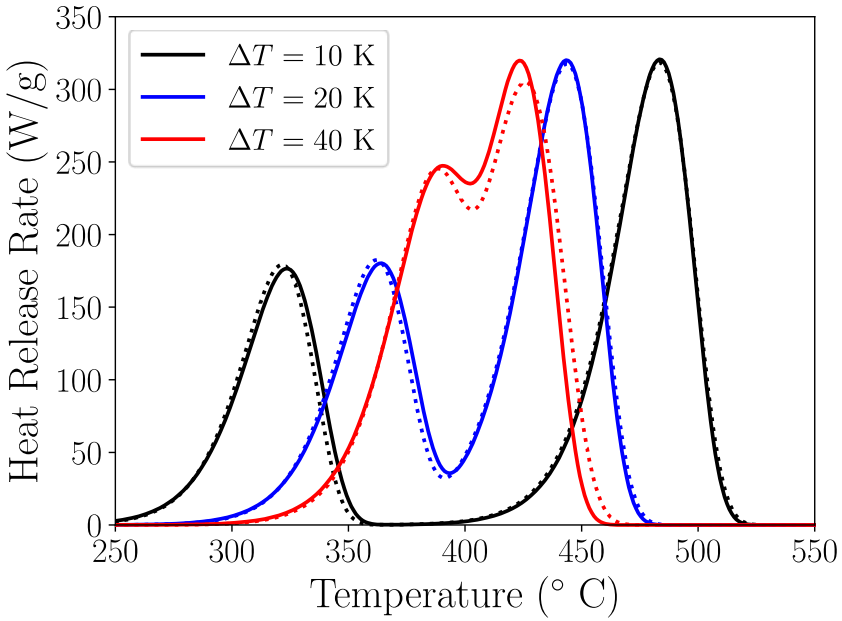
MCC: Single Reaction Verification

Scenario	Δh (kJ/g) (Total HR/mass)	Method 1: Peak Ratio Δh (kJ/g)	Method 2: Simple Average Δh (kJ/g)
ΔT = 10 K	30.026	30.792	30.849
ΔT = 20 K	29.997	28.731	29.556
ΔT = 40 K	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	Simple Integration	--	--	20.998
	Linear Regression	14.854	44.085	21.021
ΔT = 20 K	Simple Integration	--	--	20.998
	Linear Regression	14.953	43.973	21.061
ΔT = 40 K	Simple Integration	--	--	20.998
	Linear Regression	15.415	42.304	21.501

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