Automated Fitting of Thermogravimetric Analysis Data

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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?

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

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

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

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

\[ k = f (\rho_1, \ldots, \rho_N, k_1, \ldots, k_N) \]

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

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

Neglecting
- Radiation
- Mass transport
- Charring
- Temperature dependence

At least \( \sim 6N \) 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
\[ (10^1 \text{ Parameters}) \times (10^3 \text{ Materials}) = 10^4 \text{ Properties for reliable fire growth predictions} \]

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

Hierarchical Approach

Fire Model

\[ A_i, E_i, c_i, k_i, \Delta h_i, \rho_{0,i} \]
Analysis of TGA Data

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

1. Parameters predict data $\rightarrow$ Accurate
2. Many different materials $\rightarrow$ Efficient
3. Many different responses $\rightarrow$ Robust
4. Parameters do not vary $\rightarrow$ Consistent
How to be Consistent

1. No free parameters
2. No random numbers

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

~John von Neumann
Pyrolysis Model: Independent Unimolecular Reactions

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

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

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

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:

\[ E = \frac{RT_p^2}{\Delta T} \]

\[ A = \frac{\beta}{\Delta T} \exp \left( \frac{T_p}{\Delta T} \right) \]
Nondimensional Form

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

\[ \mu \equiv \frac{m}{m_0} \]

\[ \theta \equiv \frac{T - T_p}{\Delta T} \]

\[ \xi \equiv \frac{\Delta T}{T_p} \]
Approximate Solution

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

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

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

Also applies for multiple, independent reactions.
Estimating Parameters

TGA Data

Approximate Solution

\[ \Delta T = \sqrt{-\frac{m'_p}{m''_p}} \]

\[ \Delta m = -em'_p \Delta T \]
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

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

![Temperature vs. Residual Mass Fraction](image1)

![Temperature vs. Residual Mass Loss Rate](image2)

- Graph 1: Residual Mass Fraction vs. Temperature (°C)
  - Lines for different ΔT values: ΔT = 10 K, ΔT = 20 K, ΔT = 40 K

- Graph 2: Residual Mass Loss Rate vs. Temperature (°C)
  - Lines for different ΔT values: ΔT = 10 K, ΔT = 20 K, ΔT = 40 K
# Single Reaction Verification

## $\Delta T = 10 \text{ K}$:

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

## $\Delta T = 20 \text{ K}$:

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

## $\Delta T = 40 \text{ K}$:

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

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

<table>
<thead>
<tr>
<th>Kinetic Parameter</th>
<th>Reaction 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_p$ (K)</td>
<td>716.3</td>
</tr>
<tr>
<td>$\Delta T$ (K)</td>
<td>22.11</td>
</tr>
<tr>
<td>$\Delta m$</td>
<td>0.9754</td>
</tr>
<tr>
<td>$\xi$</td>
<td>0.03087</td>
</tr>
<tr>
<td>$\ln[A \ (s^{-1})]$</td>
<td>27.50</td>
</tr>
<tr>
<td>$E$ (kJ/kmol)</td>
<td>192.9×10³</td>
</tr>
</tbody>
</table>
Validation: Polyurethane Foam

<table>
<thead>
<tr>
<th>Kinetic Parameter</th>
<th>Reaction 1</th>
<th>Reaction 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_p$ (K)</td>
<td>562.7</td>
<td>648.5</td>
</tr>
<tr>
<td>$\Delta T$ (K)</td>
<td>14.50</td>
<td>13.69</td>
</tr>
<tr>
<td>$\Delta m$</td>
<td>0.2511</td>
<td>0.7280</td>
</tr>
<tr>
<td>$\xi$</td>
<td>0.02577</td>
<td>0.02112</td>
</tr>
<tr>
<td>$\ln[A$ (s$^{-1}$)]</td>
<td>34.34</td>
<td>42.95</td>
</tr>
<tr>
<td>$E$ (kJ/kmol)</td>
<td>$181.5 \times 10^3$</td>
<td>$255.3 \times 10^3$</td>
</tr>
</tbody>
</table>
Validation: PVC

<table>
<thead>
<tr>
<th>Kinetic Parameter</th>
<th>Reaction 1</th>
<th>Reaction 2</th>
<th>Reaction 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_p$ (K)</td>
<td>568.5</td>
<td>731.7</td>
<td>588.1</td>
</tr>
<tr>
<td>$\Delta T$ (K)</td>
<td>12.15</td>
<td>22.39</td>
<td>9.62</td>
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<tr>
<td>$\Delta m$</td>
<td>0.4200</td>
<td>0.2238</td>
<td>0.1999</td>
</tr>
<tr>
<td>$\xi$</td>
<td>0.02138</td>
<td>0.03060</td>
<td>0.01636</td>
</tr>
<tr>
<td>$\ln[A \ (s^{-1})]$</td>
<td>42.49</td>
<td>27.78</td>
<td>57.06</td>
</tr>
<tr>
<td>$E \ (kJ/kmol)$</td>
<td>$221.1 \times 10^3$</td>
<td>$198.8 \times 10^3$</td>
<td>$298.8 \times 10^3$</td>
</tr>
</tbody>
</table>
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 Phenomena (MaCFP)—Condensed Phase Workshop

April 26, 2020
Waterloo, Canada

https://iafss.org/macfp/