Kinetics and Thermodynamics of Condensed Phase Decomposition

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The Fire Problem

- Material burning behavior, flame spread, early fire growth governed by positive feedback between:
  - Gas phase heat transfer
    - Flame to surface heating
    - External radiation
  - Condensed phase pyrolysis

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Early Condensed–Phase Degradation Models

Introduction
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Pyrolysis Modeling
    Model Development
    Parameterization

Experimental
    TGA – Reaction Kinetics
    DSC – Reaction Thermodynamics
    MCC – Heat of Combustion

Conclusions

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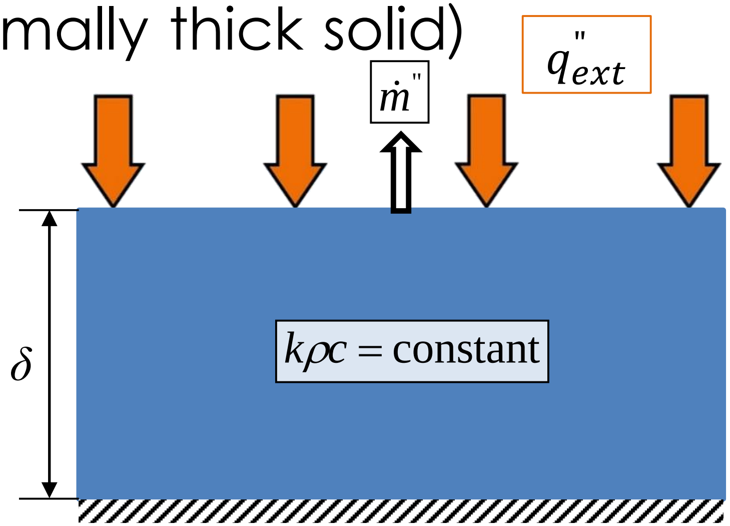
- Thermal models
    - Assume infinitely–fast reaction at a single pyrolysis temperature (e.g. ignition and burning of a thermally thick solid)

$$t_{ign} \approx \frac{\pi}{4} k\rho c \left(\frac{T_{ign} - T_{\infty}}{q''_{ext}}\right)^{2}$$

$$\dot{m}'' = \frac{q''_{net}}{L}$$



- Analytical and Algebraic Models
    - Bamford et al.[1] (1945)
    - Tewarson et al.[2] (1979)
    - Kanury[3] (1994)

State of the Art Computational Pyrolysis Solvers

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- FDS[4], Gpyro[5], ThermaKin[6]
  - Temperature–resolved thermophysical properties
  - Account for chemical degradation
  - Multiple components
  - In–depth radiation absorption/emission
  - Structural changes
    - Intumescence, burnout

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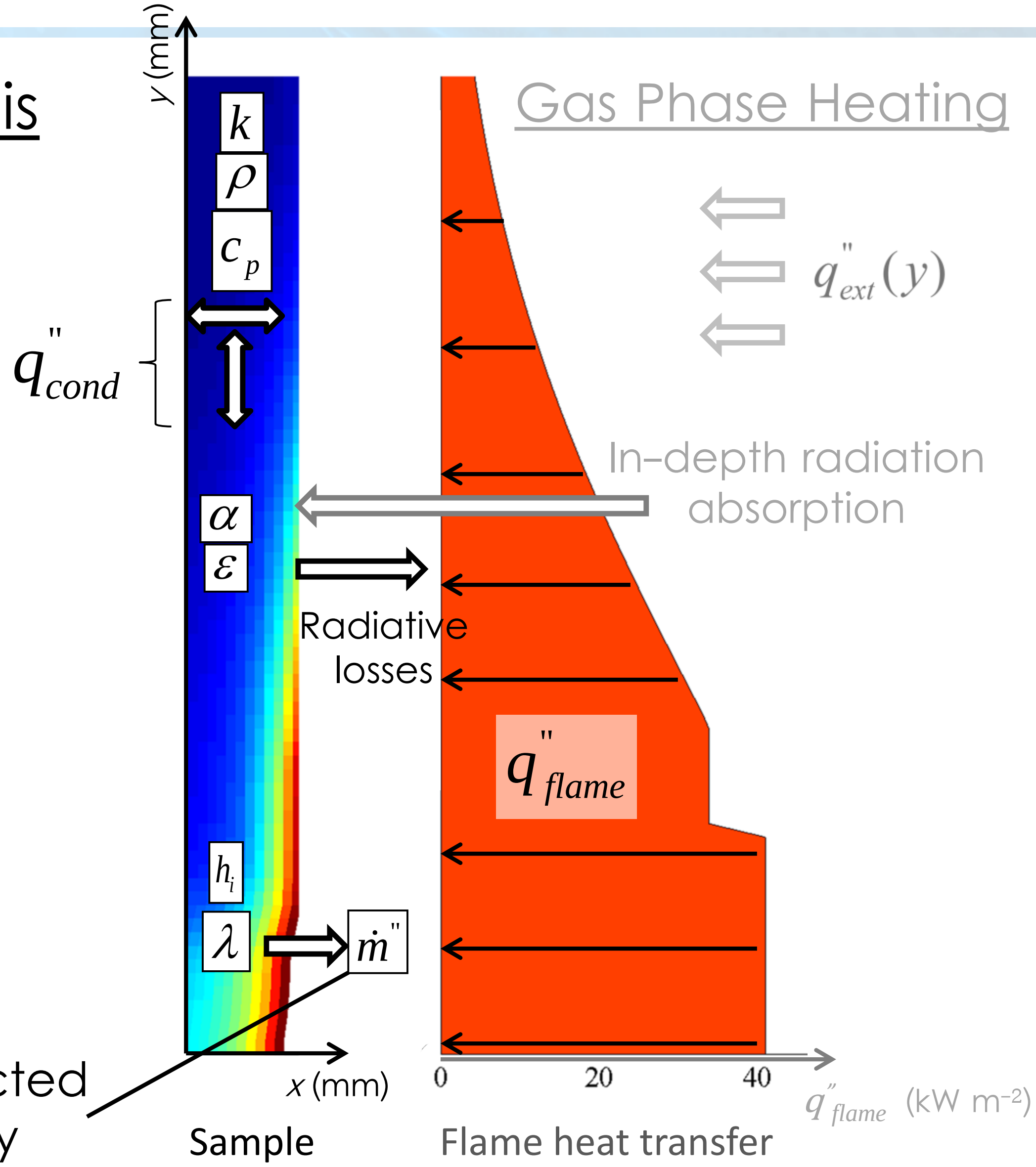
Modeling Framework

Condensed Phase Pyrolysis

- Degradation Reaction Mechanism
  - Degradation Kinetics (A, E, ν)
  - Heats of Reactions (h_i)
  - Heat Capacities (c_p)
  - Heats of Combustion (ΔH_c)
- Transport
  - Thermal Conductivity (k)
  - Absorption Coefficient (α)
  - Emissivity (ε)
  - Rheology/viscosity (η)
  - Gas Transfer (λ)



Key predicted quantity

Modeling Framework

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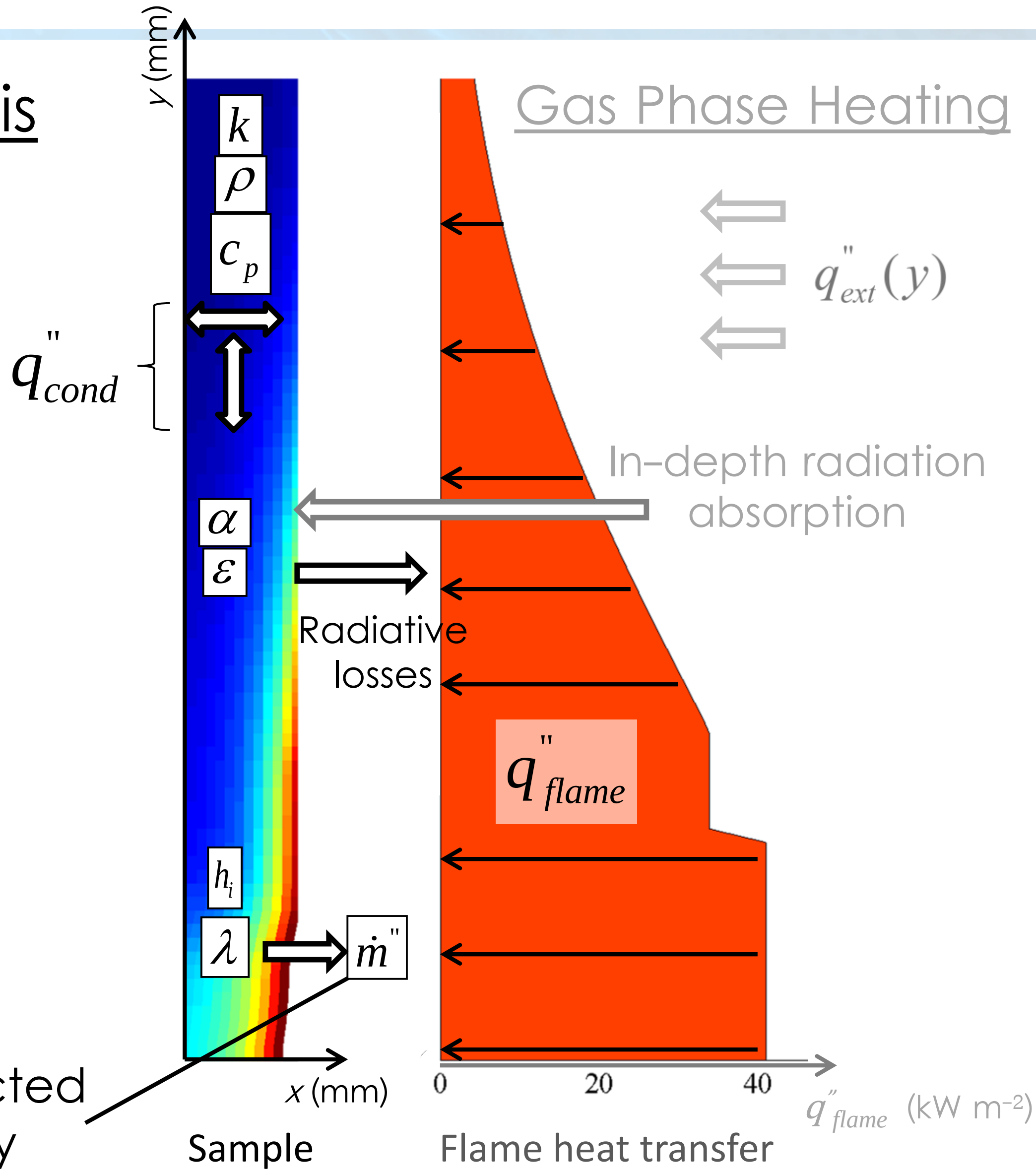

Pyrolysis Model Parameterization

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Conclusions

- Goal:
  - Develop a systematic methodology to parameterize and validate condensed phase pyrolysis models
- Model Parameterization
  - Literature Review
  - Direct Measurement
  - Semi-Empirical Correlations
  - Inverse Analysis of Experiments
    - Multi-Dimensional Optimization Algorithms[7–9]
    - Manually Iterative Analyses[10–12]

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Pyrolysis Model Parameterization

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

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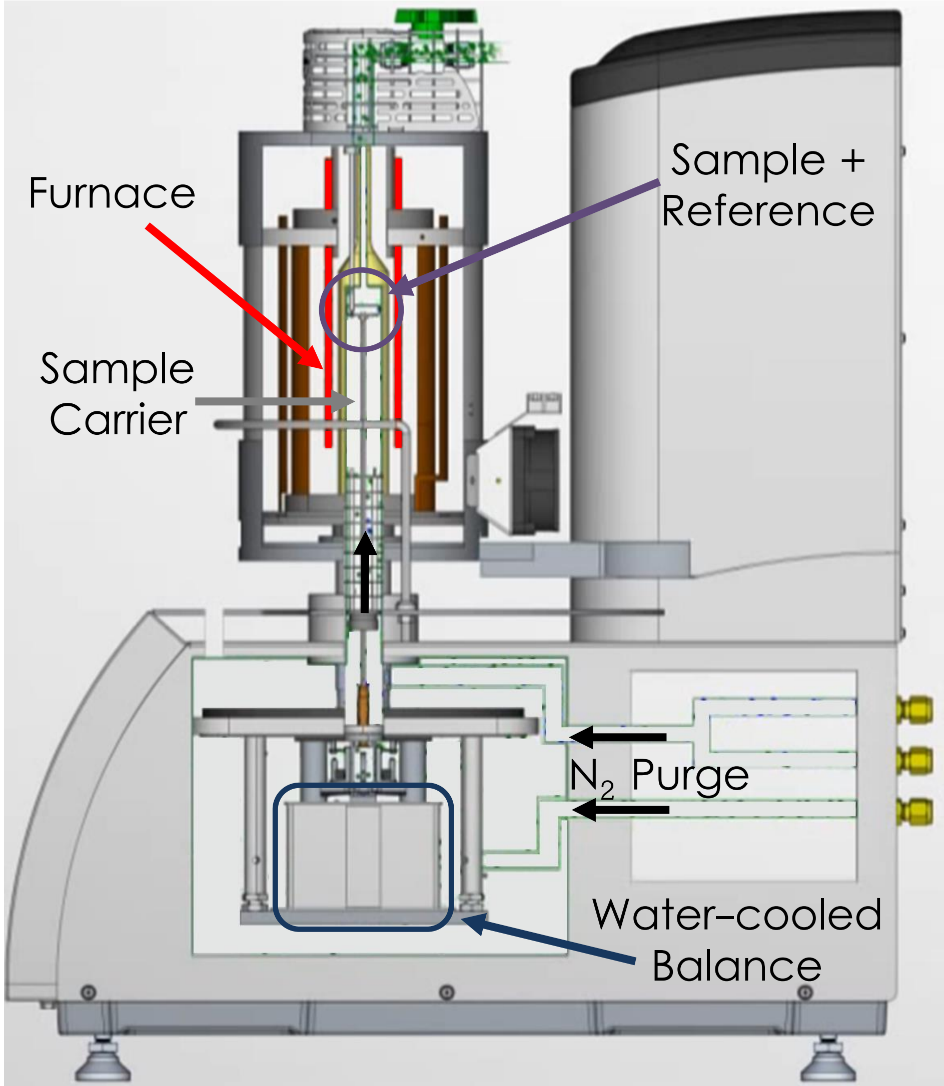
- Thermogravimetric Analysis (TGA)
  - Degradation Reaction Mechanism
  - Thermal Degradation Kinetics (A, E, ν)
- Differential Scanning Calorimetry (DSC)
  - Heat Capacities of Components (c_p)
  - Heats of Degradation Reactions (h_i)
- Microscale Combustion Calorimetry (MCC)
  - Degradation Reaction Mechanism
  - Thermal Degradation Kinetics (A, E, ν)
  - Heats of Combustion of volatiles (ΔH_c)

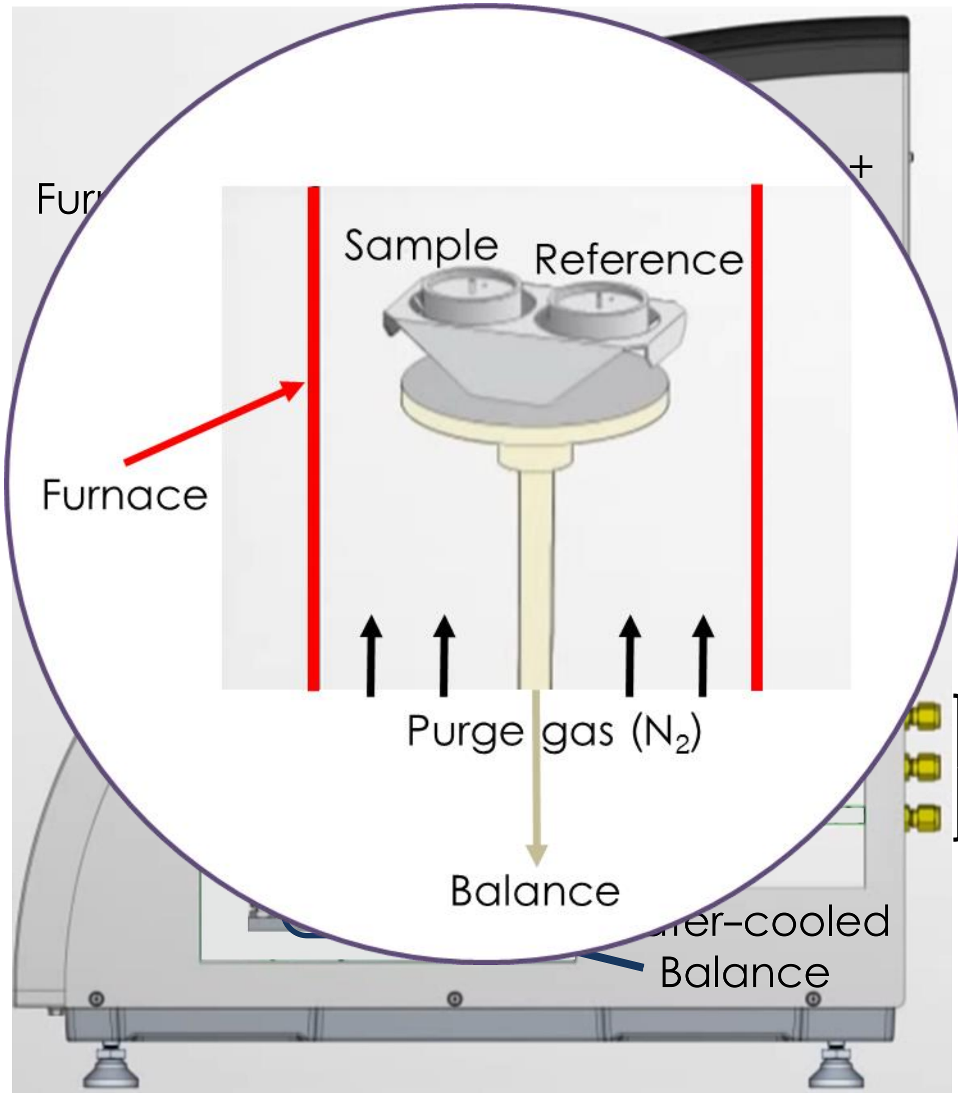
Case Study: Poly(butylene terepthalate) (PBT)

Simultaneous Thermal Analysis



- Simultaneously conduct TGA/DSC
  - Sample masses 4–7 mg
  - Heating rates of 10, 5, and 20 K min^{-1} (typically up to T = 873 K)
  - Continuously purged N_2 atmosphere
  - TGA: measure mass of sample as a function of temperature
  - DSC: measure heat flow to sample as a function of temperature

Simultaneous Thermal Analysis



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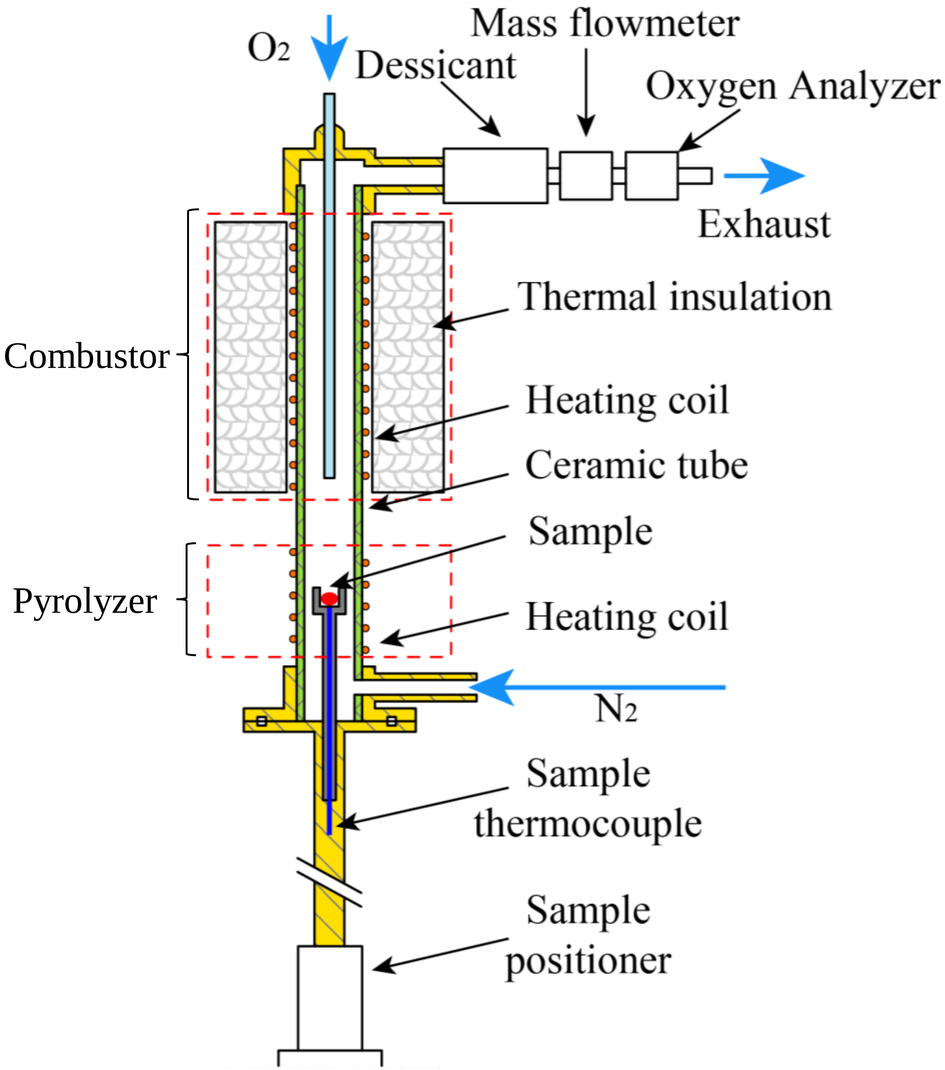
Microscale Combustion Calorimeter (MCC)



MCC

- Sample mass 3–5 mg
- Heating rate of 10 K min^{-1}

Pyrolyzer

- Continuously purged with N_2
- Well-defined temperature program
- Gaseous pyrolyzate freely flows to combustion chamber

$$HRR = \sum_{i=1}^{N_r} \nu_j r_i \Delta H_c^j$$

Combustor

- Pyrolyzate reacts with excess O_2
- HRR measured by oxygen consumption calorimetry

Inverse Analysis of TGA Data: Reaction Kinetics

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Conclusions

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- Maintain simplest model that captures defining characteristics of mass & mass loss rate data from STA tests

- First (and second) order reactions arranged in series or parallel

Reaction Rate

$$r_i = A_i \exp(-E_i/RT)\underbrace{\xi_k \xi_l}_{\to \text{Component Concentrations}}$$

  - Reaction: a mass loss or heat flow event that can be mathematically represented by the Arrhenius equation
  - Component: a collection of chemical species that exist over a common temperature range

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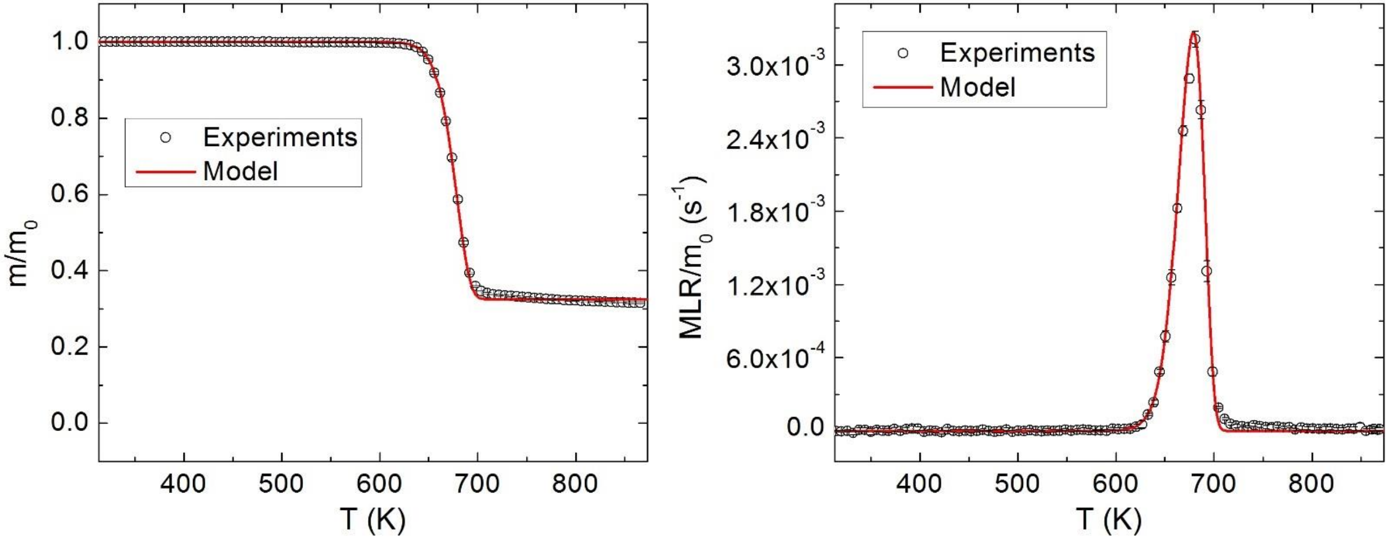

- Arrhenius Reaction: $PBT \rightarrow v(PBT_{Res}) + (1 - v)(PBT_{Gas})$
- Criteria for iterative inverse analysis:
  - $\Delta T_{peak} \leq 5K$
  - Height of MLR peak within 5%
  - Prediction of mass residue within 3%

$$\boxed{A, E, v}$$

Case Study: Poly(butylene terepthalate) (PBT)

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Inverse Analysis of DSC Data: Reaction Thermodynamics

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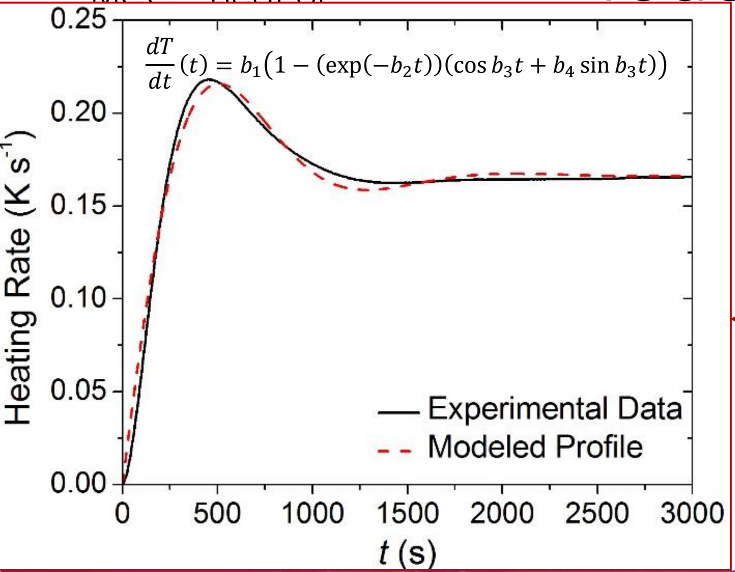
Experimental
    TGA – Reaction Kinetics
    DSC – Reaction Thermodynamics
    MCC – Heat of

- Maintain simplest model that captures heat flow rate data from STA tests
  - Maintain consistency with TGA mass & mass flow rate data

- Determine heat capacities (c_p) and reaction energetics (h_i)

Temperature dependent; determined from degradation kinetics

$$\dot{q} = \sum_{j=1}^{N_c}\left(\underbrace{\boxed{\xi_j}\, c_{p,j} \boxed{\frac{\partial T}{\partial t}}}_{\text{Sensible Enthalpy}} + \underbrace{\sum_{i=1}^{N_r} \boxed{r_i}\, h_i}_{\text{Heats of Reactions}}\right)$$



Inverse Analysis of DSC Data: Reaction Thermodynamics

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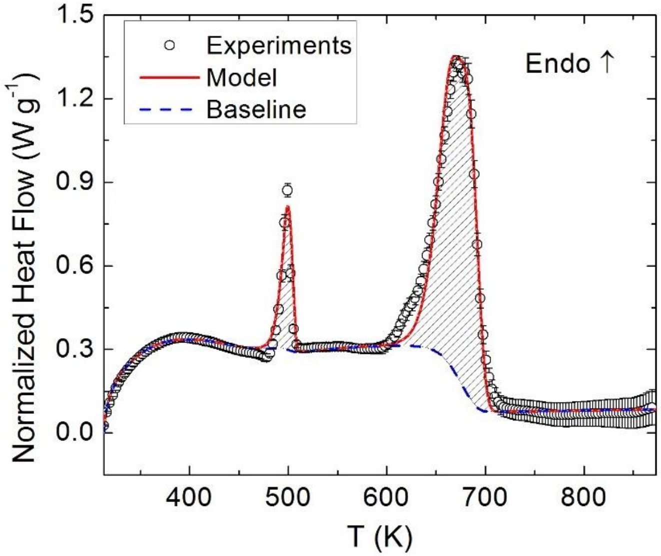

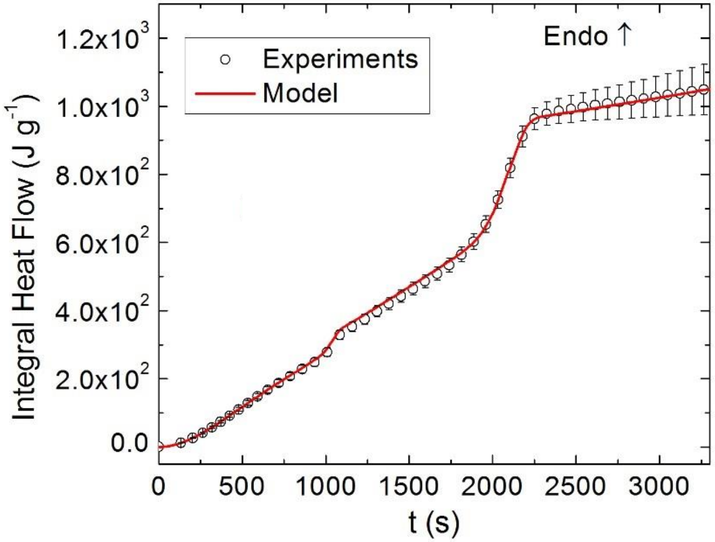

$$PBT \rightarrow v(PBT_{Res}) + (1-v)(PBT_{Gas})$$

$$\boxed{c_{p,j}, h_i}$$

➡

$$PBT \rightarrow PBT_{Melt}$$

$$PBT_{Melt} \rightarrow v(PBT_{Res}) + (1-v)(PBT_{Gas})$$

- Criteria for inverse analysis:
  - $\Delta T_{peak} \leq 5K$
  - Average mean error within 10%
  - Prediction of integral heat flow within 5%

From kinetics

$$\dot{q} = \sum_{j=1}^{N_c} \left(\boxed{\xi_j} c_{p,j} \frac{\partial T}{\partial t} + \sum_{i=1}^{N_r} \boxed{r_i} h_i \right)$$

Inverse Analysis of MCC Data: Heat of Combustion

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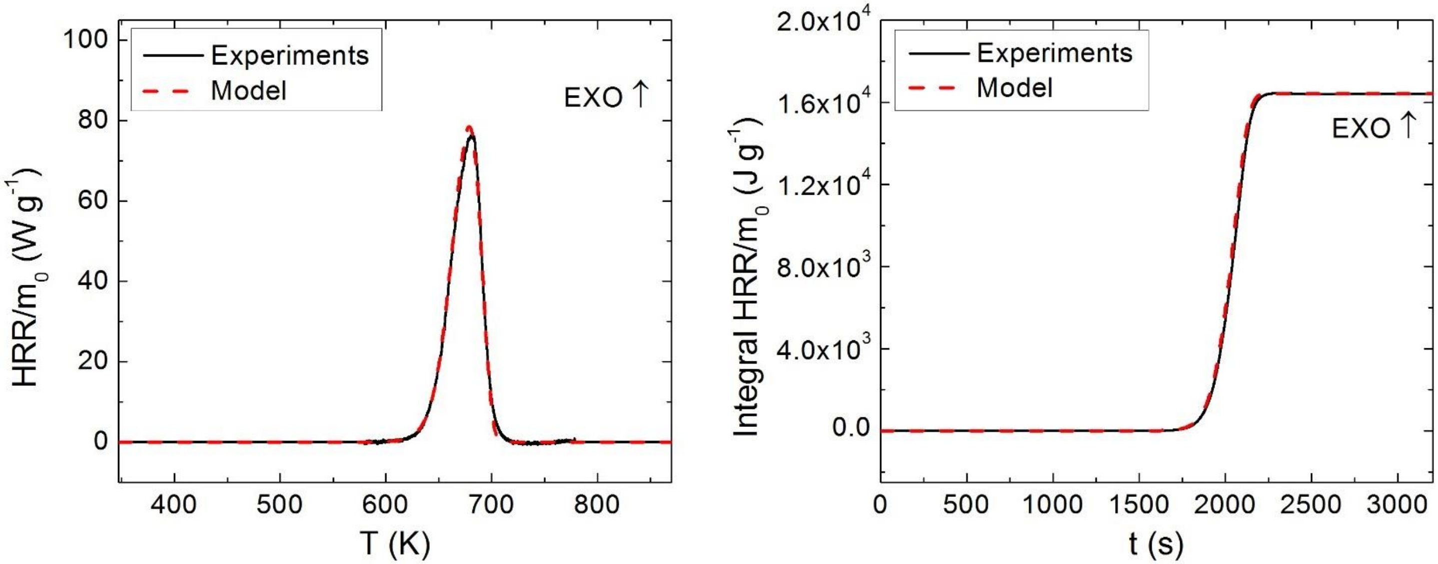
Conclusions



- MCC data further validates reaction mechanism developed from STA experiments

- Criteria for inverse analysis:
  - $\Delta T_{peak} \leq 5K$
  - Average mean error within 10%
  - Prediction of integral heat flow within 5%

$$\boxed{\Delta H_c}$$

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Conclusions

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Conclusions

- A reaction mechanism is developed that simultaneously reproduces test data from TGA, DSC, and MCC experiments

- Extrapolate reaction mechanism to:
  - Varied heating rates
  - Unified models of material degradation and burning

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Model Validation at Varied Heating Rates (5, 20 K min^{-1})

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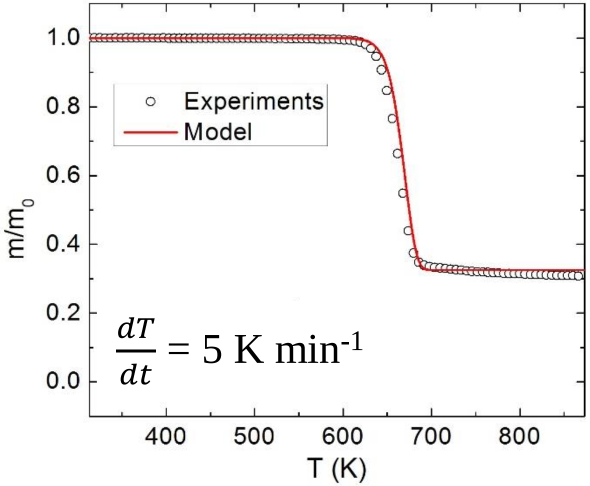

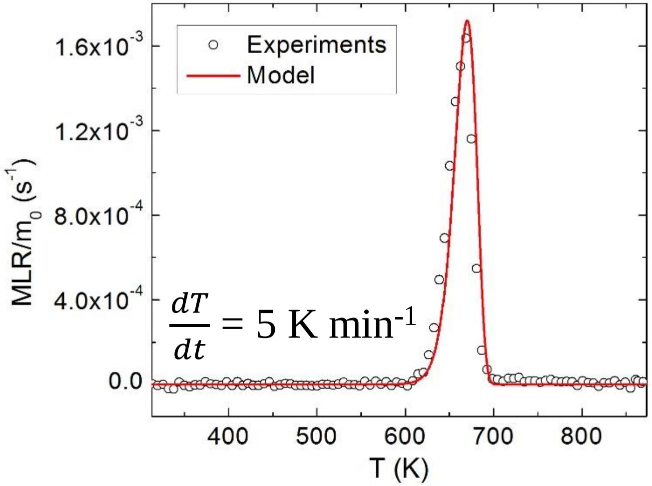

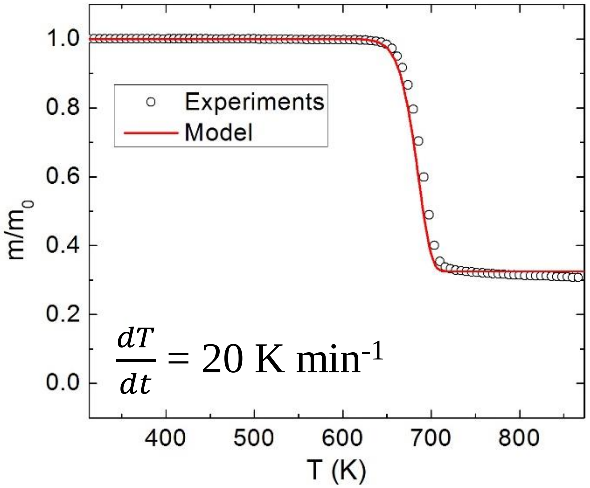

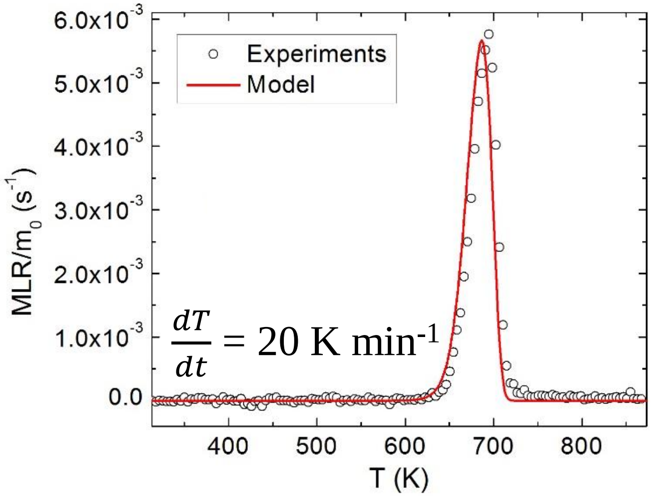

Application to Complex Systems

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    TGA – Reaction Kinetics
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Conclusions

- Polyamide66 (PA66) + Red Phosphorous
  - Interactions between components
  - Parallel and series reactions
  - Varied compositions, heating rates

#	Reaction
1	$\text{PA66} \rightarrow \text{PA66-Melt}$
2	$\text{PA66-Melt} \rightarrow \theta\text{PA66-Res1} + (1\text{-}\theta)\ \text{PA66-Gas1}$
3	$\text{PA66-Res1} \rightarrow \theta\ \text{PA66-Res2} + (1\text{-}\theta)\ \text{PA66-Gas2}$
4	$\text{PA66-Res2} + \text{PA66-Res2} \rightarrow \theta\ \text{PA66-Res3} + (2\text{-}\theta)\ \text{PA66-Gas3}$
5	$\text{RP} \rightarrow \text{RP-Gas}$
6	$\text{PA66-Melt} + \alpha\ \text{RP} \rightarrow (1+\alpha)\text{PA66-RP}$
7	$\text{PA66-RP} \rightarrow \theta\ \text{PA66-RP-Res1} + (1\text{-}\theta)\ \text{PA66-RP-Gas1}$
8	$\text{PA66-RP} + \alpha\ \text{RP} \rightarrow \theta\ \text{PA66-RP-Res2} + (1+\alpha\ \text{-}\theta)\ \text{PA66-RP-Gas2}$
9	$\text{PA66-RP-Res2} \rightarrow \theta\ \text{PA66-RP-Res3} + (1\text{-}\theta)\ \text{PA66-RP-Gas3}$

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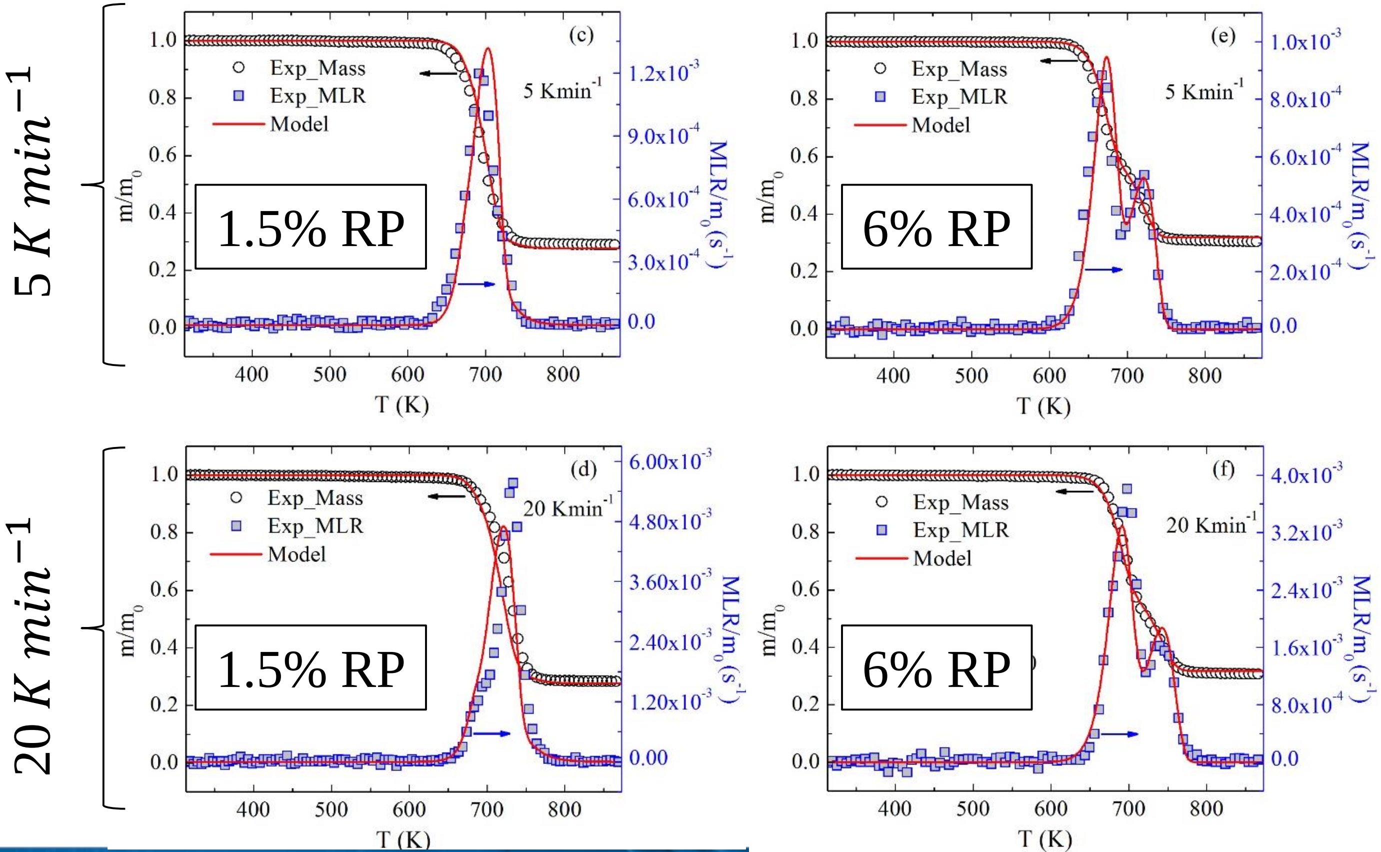

Conclusions

- Systematic methodology to characterize materials for pyrolysis models applied to:
  - Non-charring polymers[13]
  - Charing-polymers[14]
  - Composite materials (cardboard, carpet, carbon-fiber/epoxy, fiberglass)[15–18]
  - Polymers with fire retardants active in the solid phase (i.e. red phosphorous)[19]

- Foundation for prediction of material degradation and burning:
  - 1D gasification[11,12,20,21]
  - 2D Flame spread[22]

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