Ignition and Pyrolysis

Burgers Program and Combustion Institute Summer School on Fire Safety Science - Wildland/WUI Fire Behavior

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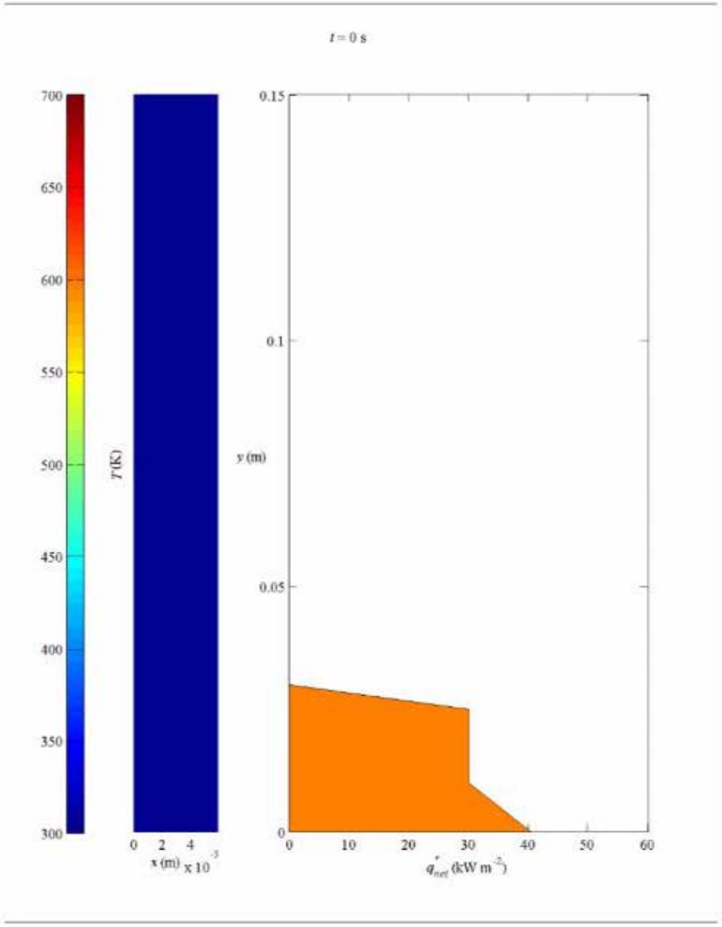
Definitions of Key Terms used in this Presentation

Thermal decomposition –	chemical reactions that occur in a combustible solid at elevated temperature
Pyrolysis –	thermal decomposition coupled with heat and mass transport inside and at the surface of the heated solid
Ignition –	refers to a piloted ignition of a flame at the surface of the heated solid

Outline

1. The role of pyrolysis in fire growth
2. Analytical pyrolysis model formulation and parameterization
3. Processes contributing to solid fuel pyrolysis and combustion
4. Key parameters that define piloted ignition of solids
5. Formulation of a comprehensive pyrolysis model
6. Parameterization of comprehensive pyrolysis models
7. Assessment of comprehensive pyrolysis model limitations

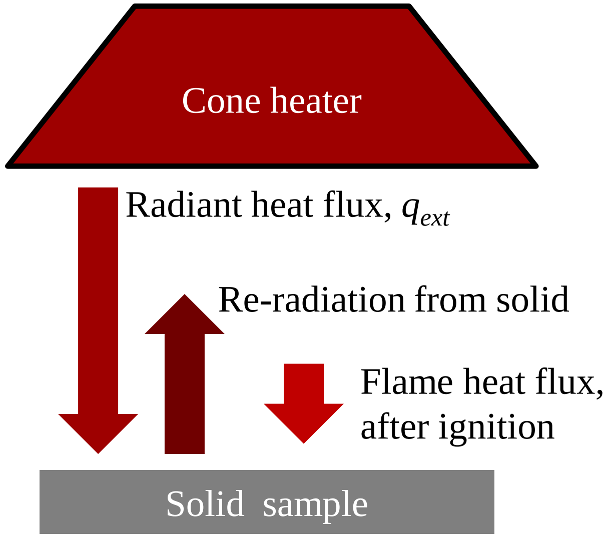
Fire Growth on a Solid Combustible Surface



Leventon I. T. et al. *A Flame Spread Simulation Based on a Comprehensive Solid Pyrolysis Model Coupled with a Detailed Empirical Flame Structure Representation;* Combustion and Flame; vol. 162; pp. 3884-3895 (2015)

Analytical Model of Ignition and Burning

Cone Calorimeter



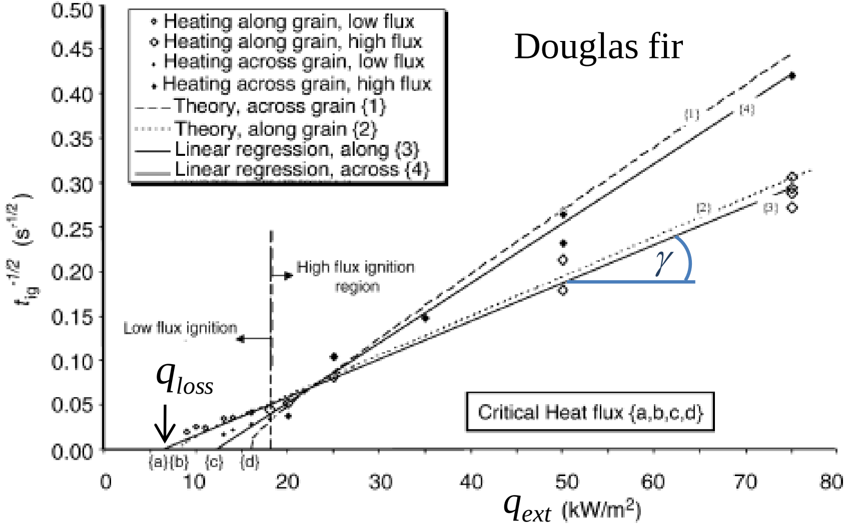
- Let us assume a thermally thick solid that decomposes at T_p:

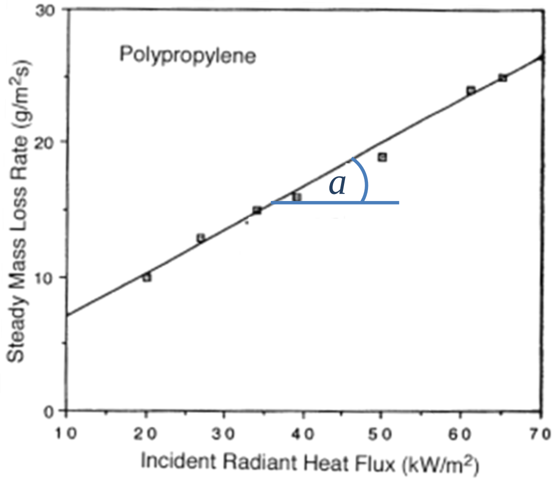
$$t_{ign} = \frac{\pi}{4} k\rho c \frac{\left(T_p - T_{env}\right)^2}{\left(\varepsilon q_{ext} \underbrace{- \varepsilon\sigma T_s^4 - h\left(T_s - T_{env}\right)}_{-q_{loss}\ \text{(assumed to be approximately constant)}}\right)^2}$$

$$\frac{1}{\sqrt{t_{ign}}} = \underbrace{\sqrt{\frac{4}{\pi}} \frac{1}{\sqrt{k\rho c}\left(T_p - T_{env}\right)}}_{\tan\gamma} \left(q_{ext} - q_{loss}\right)$$

- The burning rate is steady and expressed as:

$$mF = \frac{q_{ext} + q_{flame} - \sigma T_p^4}{\underbrace{\int_{T_{env}}^{T_p} c\,dT - \sum_{\substack{\text{reactions \&} \\ \text{transitions}}} \Delta H}_{\text{heat of gasification, } L}} = \frac{q_{flame} - \sigma T_p^4}{L} + \underbrace{\frac{1}{L}}_{\tan\alpha} q_{ext}$$

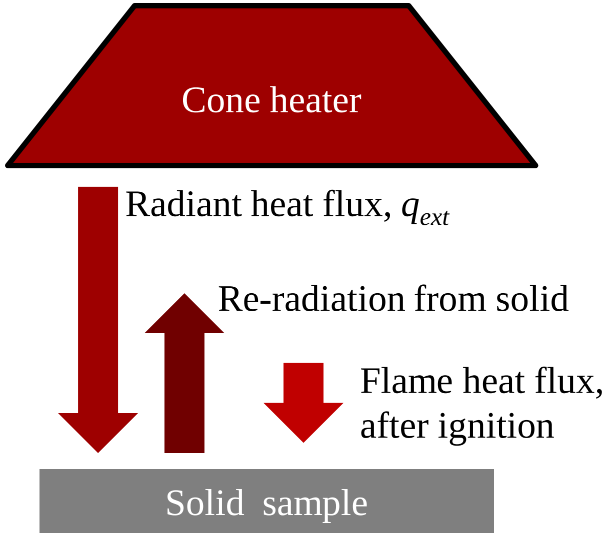




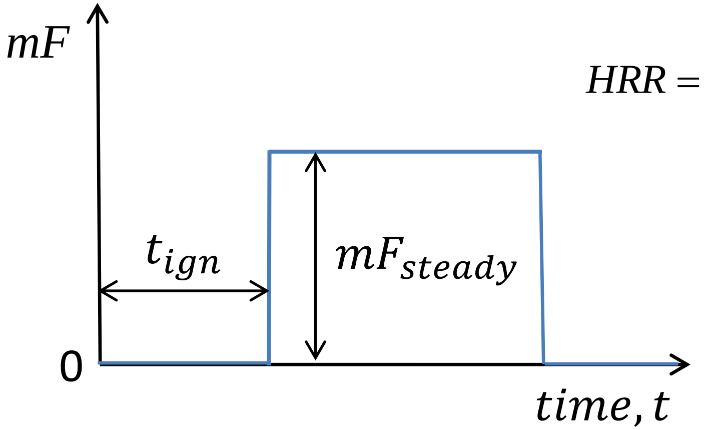
J. G. Quintiere; Fundamental of Fire Phenomena; John Wiley & Sons, Chichester, England; 2006

Analytical Model of Ignition and Burning

Cone Calorimeter



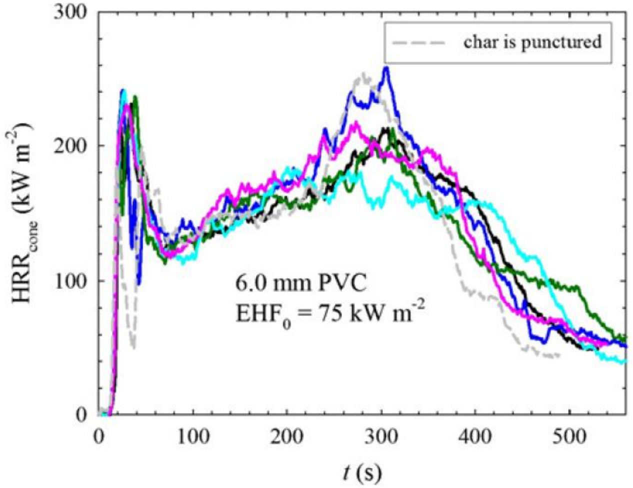
- Resulting representation of burning at a given q_{ext} :



$$HRR = mF \times \Delta H_{comb}^{eff}$$

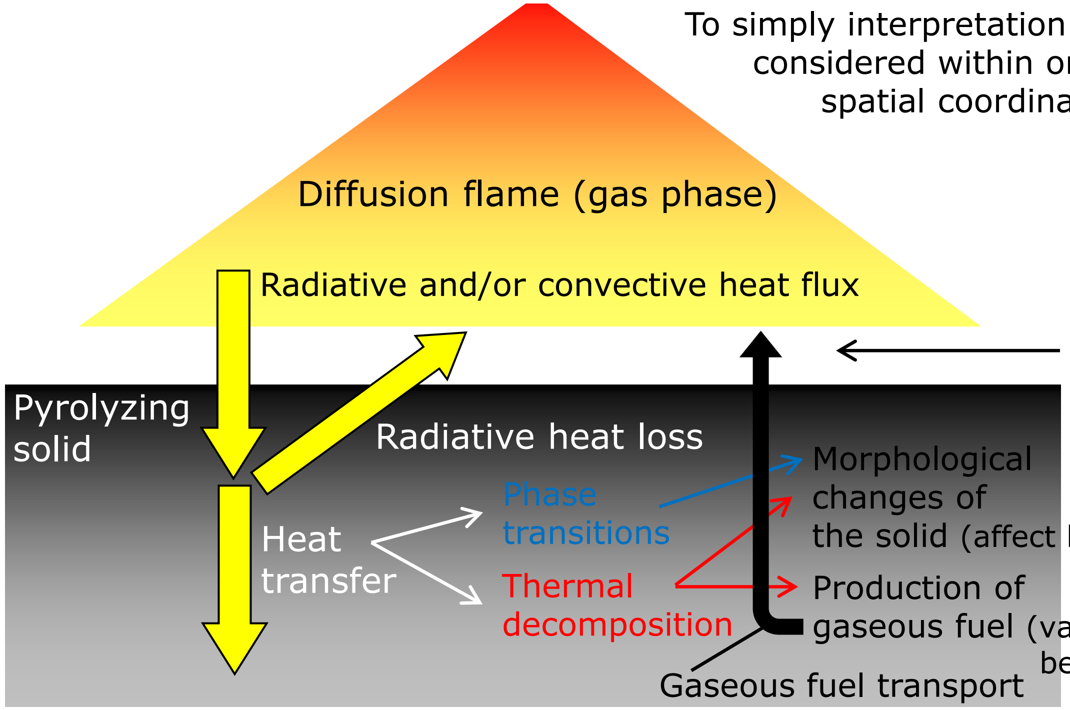
<u>Limitations:</u>

- Inability to fully capture measured *mF* or *HRR* temporal profiles
- Property values do not correspond to their original physical meaning leading to inability to extrapolate beyond specific scenarios explored during parameterization



Processes Contributing to Solid Pyrolysis and Combustion

To simply interpretation of key processes, the mechanism is considered within one-dimensional framework (only one spatial coordinate)



Diffusion flame (gas phase)

Radiative and/or convective heat flux

Pyrolyzing solid

Radiative heat loss

Heat transfer

Phase transitions

Thermal decomposition

Morphological changes of the solid (affect heat transfer)

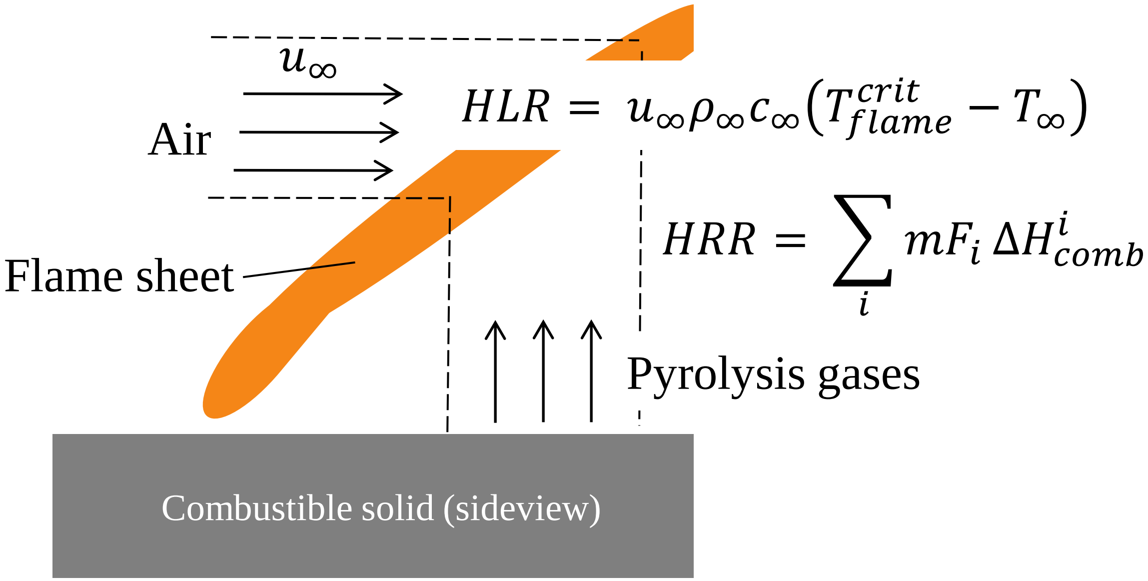
Production of gaseous fuel (vaporization is assumed to be a part of decomposition)

Gaseous fuel transport (and associated heat flow)

Flame consumes all oxygen (no oxygen at the surface)

Morphological changes may include
- formation of residue layer (char)
- bubbles and fissures
- melt flow

Key Parameters that Define Ignition



$$HLR = u_\infty \rho_\infty c_\infty \left(T_{flame}^{crit} - T_\infty\right)$$

$$HRR = \sum_i mF_i \, \Delta H_{comb}^i$$

$HRR \geq HLR$ → Stable flame is possible

mF_i and ΔH_{comb}^i are condensed-phase related parameters that define ignition

Formulation of a Comprehensive Pyrolysis Model: ThermaKin in 1D

Concentration of species j in kg m^{-3}

Conservation of species:

$$\frac{\partial \xi_j}{\partial t} = \boxed{\sum_{i=1}^{N_r} \theta_i^j r_i} - \boxed{\frac{\partial J_j{}^x}{\partial x}} + \boxed{\frac{\partial}{\partial x}\left(\xi_j \int_0^x \frac{1}{\rho}\frac{\partial \rho}{\partial t}\, dx\right)}$$

Expansion/Contraction

Chemical reactions

Gas transport

Conservation of energy:

$$\sum_{j=1}^{N} \xi_j c_j \frac{\partial T}{\partial t} = \boxed{-\sum_{i=1}^{N_r} h_i r_i} - \frac{\partial q_x}{\partial x} - \frac{\partial I_{ex}}{\partial x} + \frac{\partial I_{rr}}{\partial x} - \boxed{\sum_{g=1}^{N_g} c_g \left(J_g{}^x \frac{\partial T}{\partial x}\right)} + \boxed{c\rho \frac{\partial T}{\partial x} \int_0^x \frac{1}{\rho}\frac{\partial \rho}{\partial t}\, dx}$$

Conduction Radiation Re-radiation

Rate of reaction:

$$r_i = A_i\, exp\left(-\frac{E_i}{RT}\right) \xi_{\mathrm{REACT1}}\, \xi_{\mathrm{REACT2}}$$

Gas transport:

$$J_j = -\rho_j \lambda \frac{\partial \left(\xi_j / \rho_j\right)}{\partial x}$$

Radiation transport:

$$\frac{\partial I_{ex}}{\partial x} = -I_{ex} \sum_{j=1}^{N} \alpha_j \xi_j \qquad \frac{\partial I_{rr}}{\partial x} = \frac{\sigma T^4 \sum_{j=1}^{N} \varepsilon_j v_j}{I_{ex}^0} \frac{\partial I_{ex}}{\partial x}$$

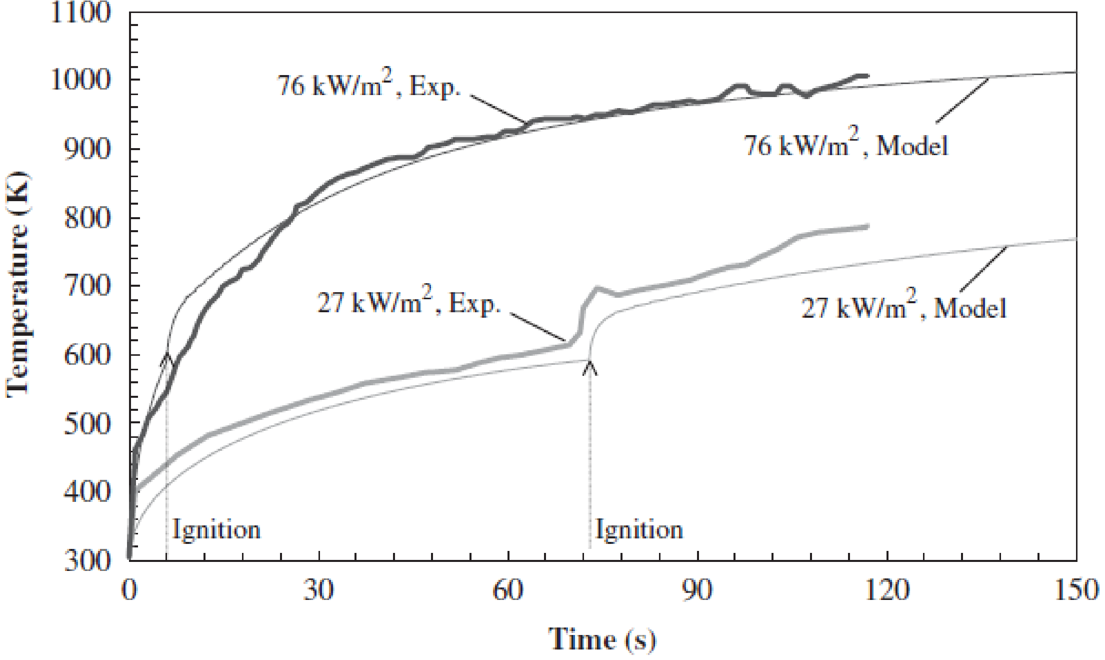
Stoliarov S. I. et al. *Two-dimensional Model of Burning for Pyrolyzable Solids;* Fire and Materials; vol. 38; pp. 391-408 (2014)

Global Approach to Comprehensive Pyrolysis Model Parameterization

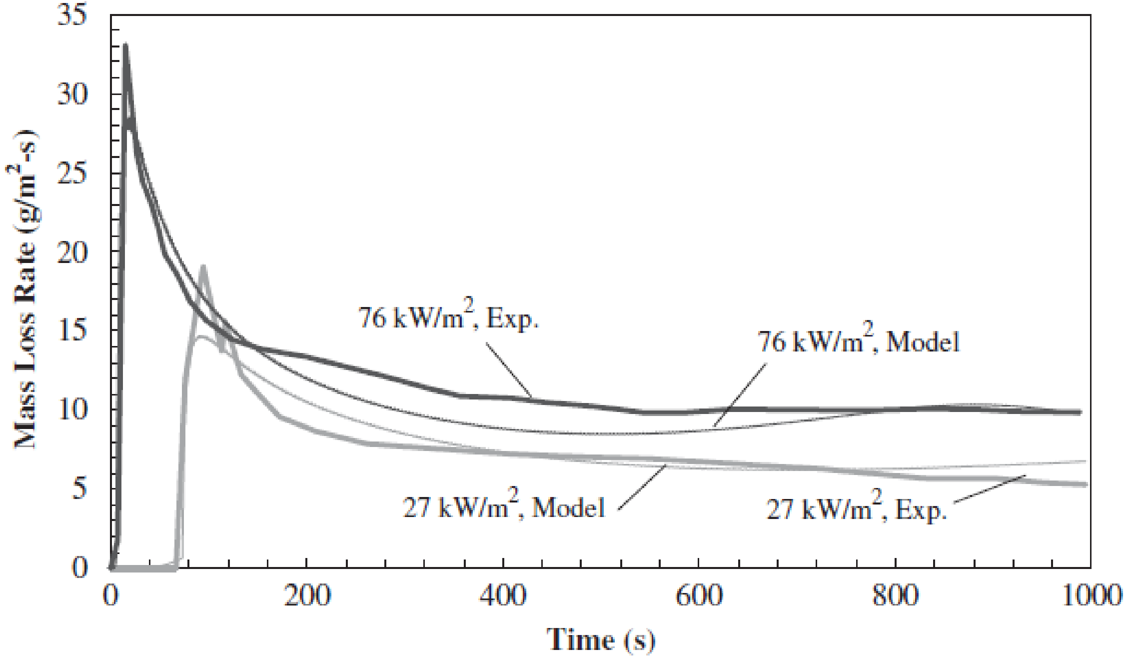
- An assumption is made about the thermal decomposition mechanism

- All pyrolysis properties with the exception of initial density are fitted into fire calorimetry data using a genetic algorithm

Red oak – exposed surface temperature

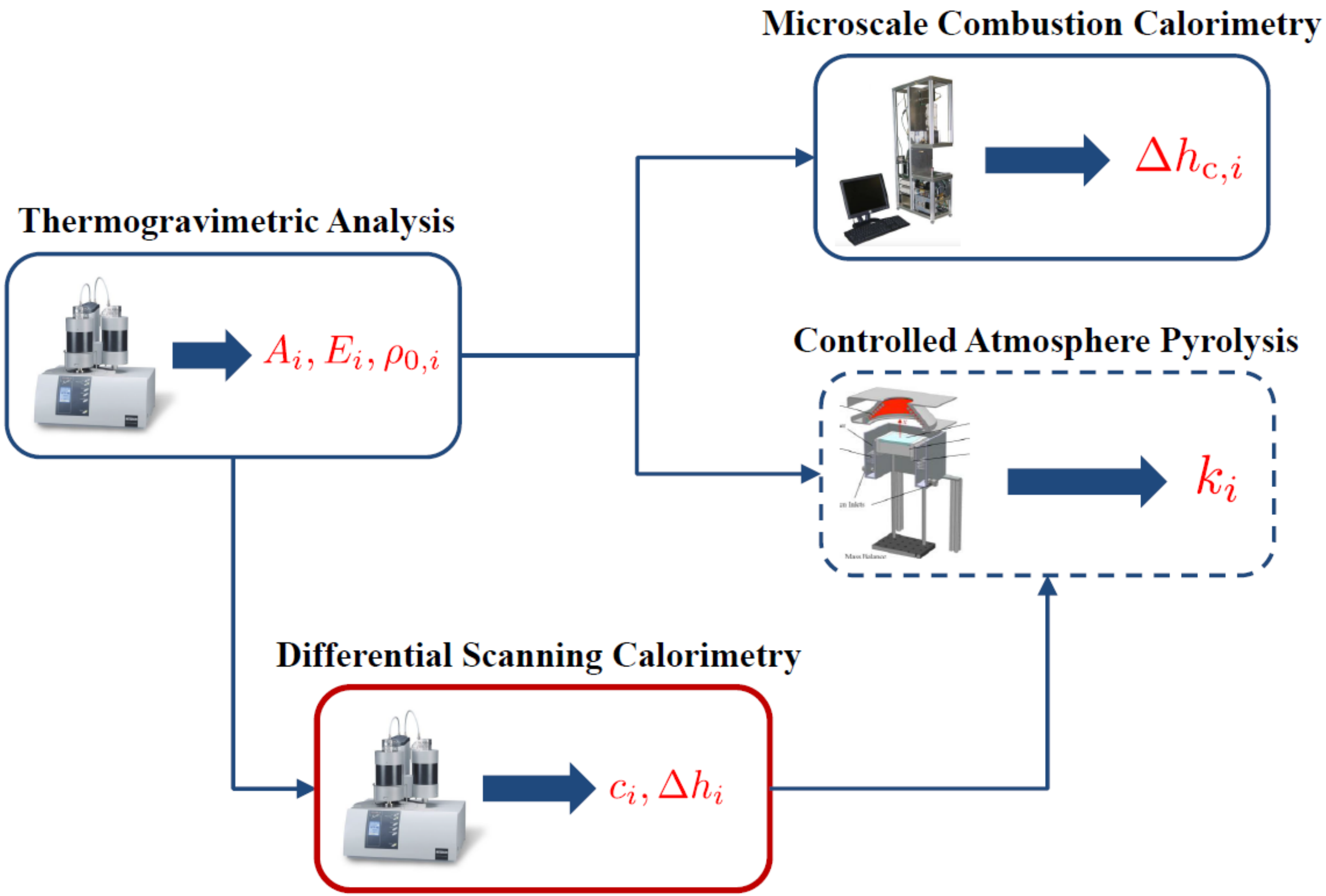


Red oak – mass loss rate



C. Lautenberger et al. *The Application of a Genetic Algorithm to Estimate Material Properties for Fire Modeling from Bench-scale Fire Test Data;* Fire Safety Journal; vol. 41; pp. 204–214 (2006)

Hierarchical Approach to Comprehensive Pyrolysis Model Parameterization



Thermogravimetric Analysis

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

Microscale Combustion Calorimetry

$\Delta h_{c,i}$

Controlled Atmosphere Pyrolysis

k_i

Differential Scanning Calorimetry

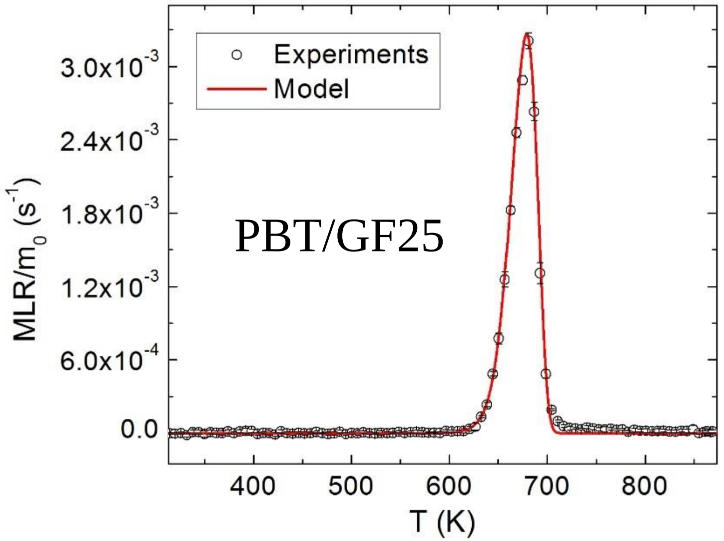
$c_i, \Delta h_i$

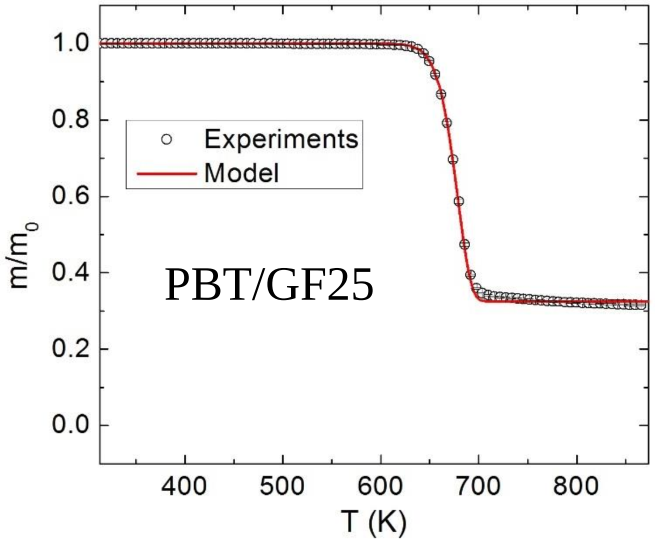
The diagram is a courtesy of Dr. Morgan Bruns of St. Mary’s University

Thermogravimetric Analysis (TGA) for Determination of Kinetics

Milligram-sized, thermally thin solid sample heated at a constant heating rate between 3 and 30 K min^{-1}

Example: polybutylene terephthalate (PBT) reinforced with glass fiber (GF)





Reaction equation: $PBT \rightarrow \theta Res + (1-\theta)Gas$

$$E = \frac{eRT_p^2 \frac{MLR_p}{m_0}}{(1-\theta)\frac{dT}{dt}}$$

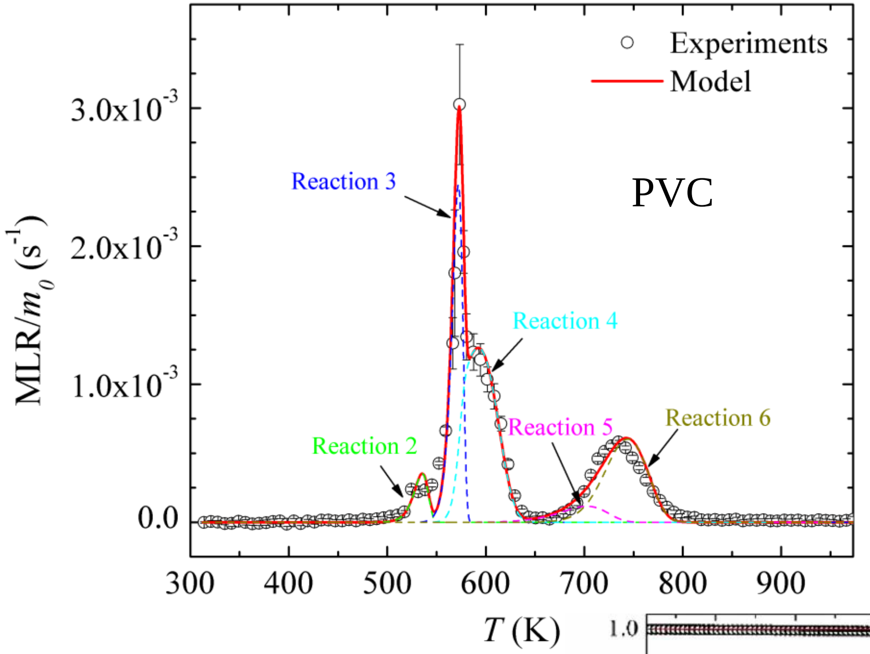
$$A = \frac{MLR_p}{\left(\frac{m(T_p) - m_o\theta}{1-\theta}\right)} e^{\frac{E}{RT_p}}$$

Initial Estimate

A, E, θ

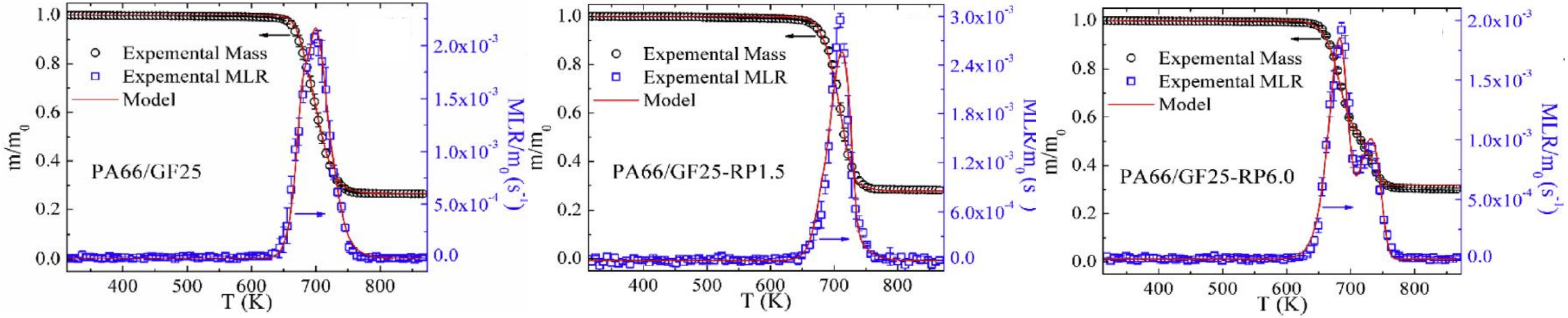
More Complex Thermal Decomposition Mechanisms Based on TGA

Poly(vinyl chloride) (PVC): 6 reactions



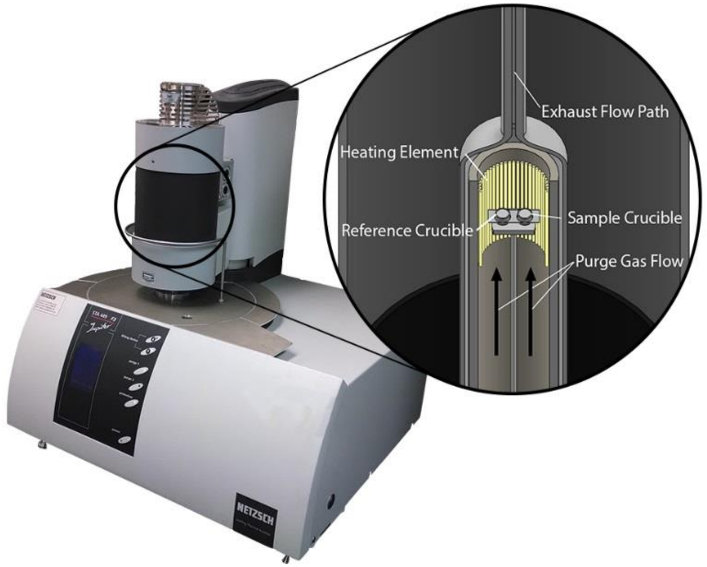
Nylon 6,6 (PA66) with red phosphorus (RP): 9 reactions

#	Reaction
1	PA66 → PA66_Melt
2	PA66_Melt → 0.83 PA66_Res1 + 0.17 PA66_Gas1
3	PA66_Res1 → 0.40 PA66_Res2 + 0.60 PA66_Gas2
4	PA66_Res2 + PA66_Res2 → 0.14 PA66_Res3 + 1.86 PA66_Gas3
5	RP → RP_Gas
6	PA66_Melt + 0.03 RP → 1.03 PA66_RP
7	PA66_RP → 0.04 PA66_RP_Res1 + 0.96 PA66_RP_Gas1
8	PA66_RP + 0.02 RP → 0.49 PA66_RP_Res2 + 0.53 PA66_RP_Gas2
9	PA66_RP_Res2 → 0.21 PA66_RP_Res3 + 0.79 PA66_RP_Gas3

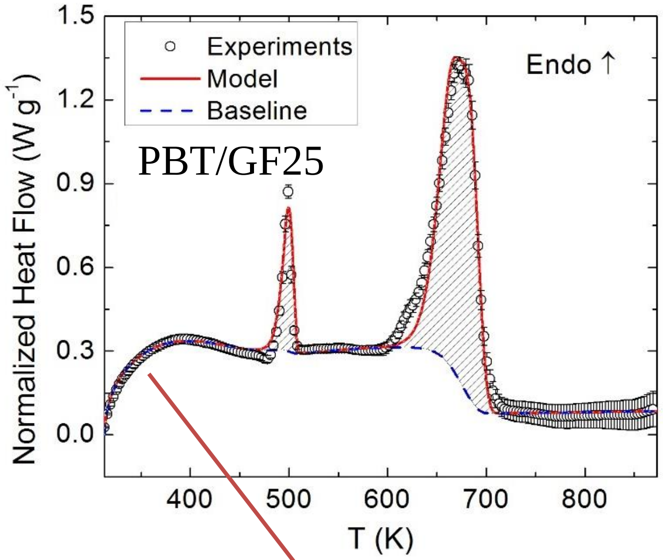


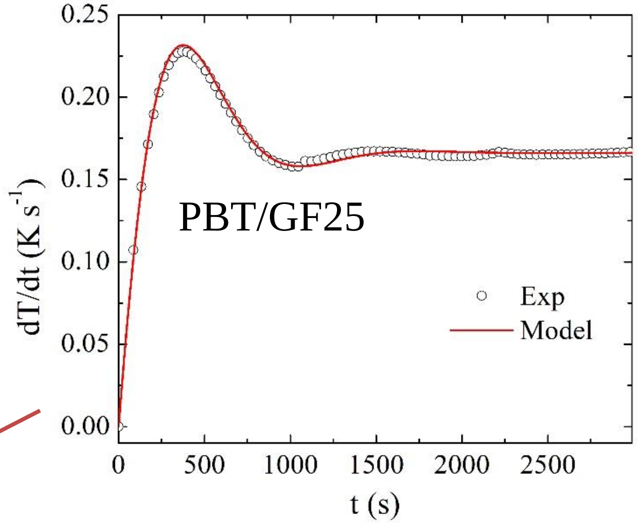
Ding Y. et al. *Development of a Semi-global Reaction Mechanism for Thermal Decomposition of a Polymer Containing Reactive Flame Retardant;* Proceedings of the Combustion Institute; vol. 37; pp. 4247–4255 (2019)

Heat Capacities and Heats of Decomposition Reactions from Differential Scanning Calorimetry (DSC)



Milligram-sized, thermally thin solid sample heated at a constant heating rate between 3 and 30 K min^{-1}





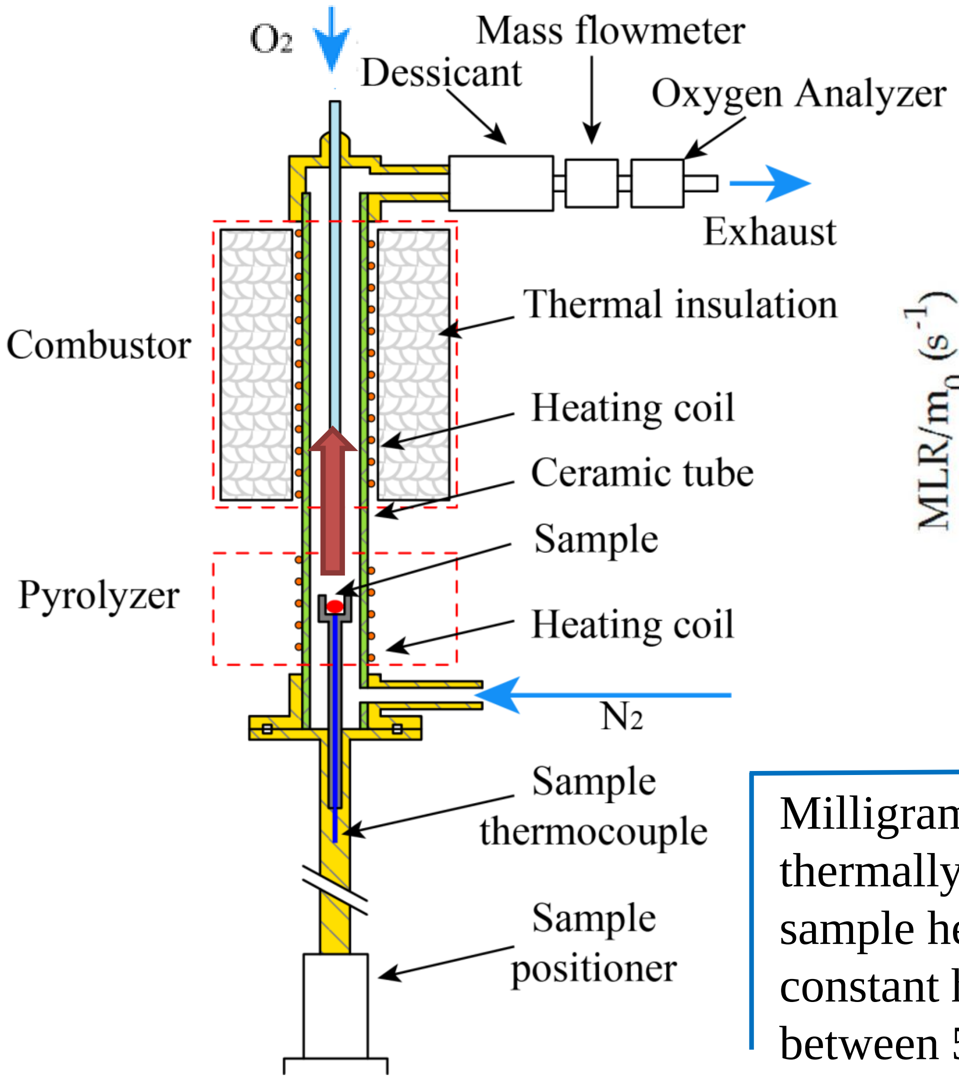
$$\frac{\dot{q}}{m_0} = \underbrace{\sum_{j=1}^{N_c} \frac{V}{m_0} \xi_j c_j \frac{\partial T}{\partial t}}_{\text{Sensible Heat}} + \underbrace{\sum_{i=1}^{N_r} \frac{V}{m_0} r_i h_i}_{\text{Heats of Reactions}}$$

$$PBT \rightarrow PBT_{Melt}$$

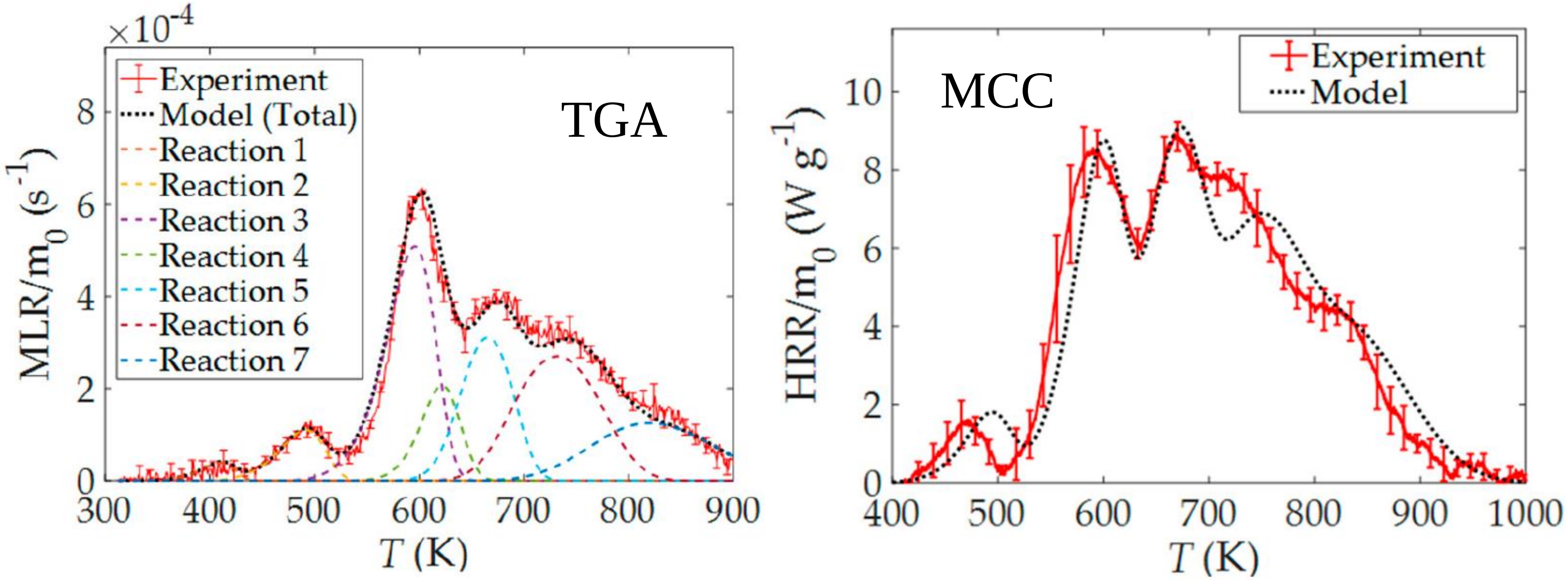
$$PBT_{Melt} \rightarrow \theta\ Res + (1-\theta) Gas$$

$$\boxed{c_j, h_i}$$

Heats of Combustion from Microscale Combustion Calorimetry (MCC)



Example: polyisocyanurate (PIR) foam

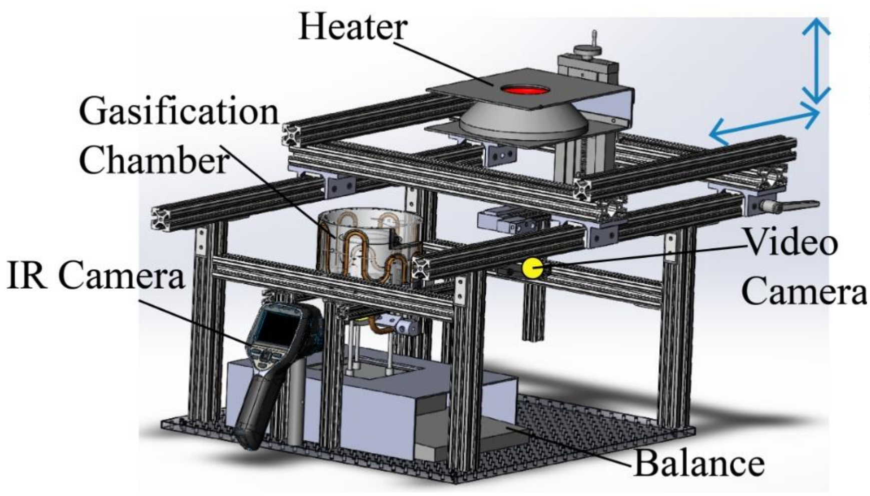


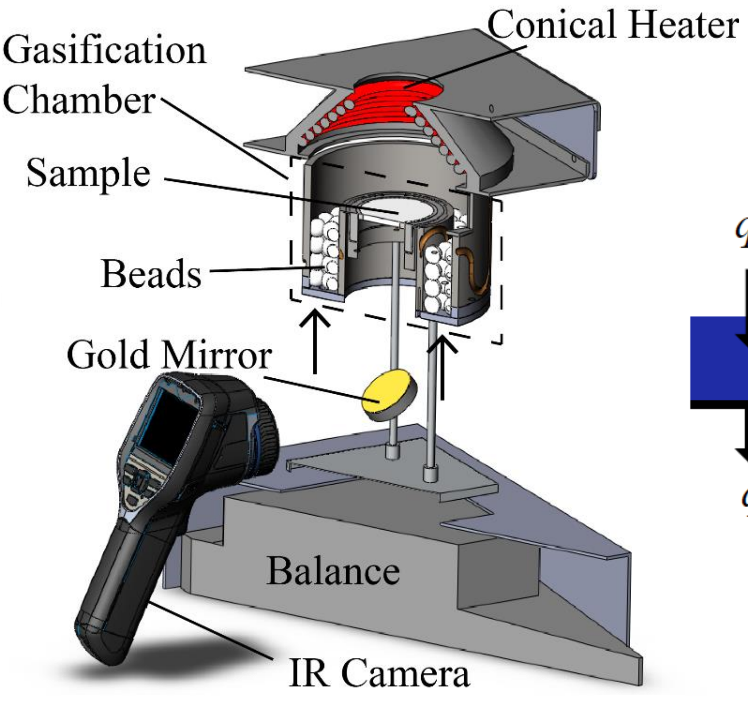
Milligram-sized, thermally thin solid sample heated at a constant heating rate between 5 and 30 K min^{-1}

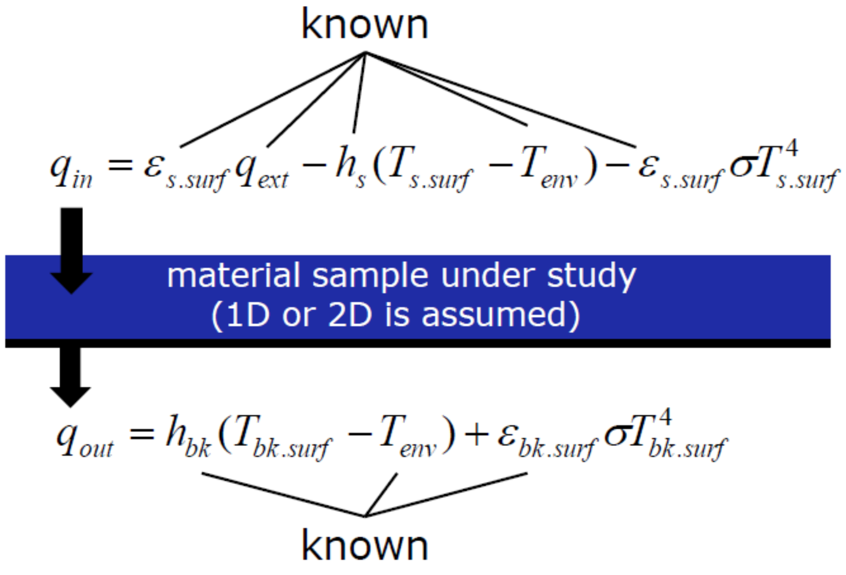
$$\boxed{\Delta H^{j}_{comb}}$$

Parameterization of Transport Processes Inside the Solid

Controlled Atmosphere Pyrolysis Apparatus II (CAPA II)

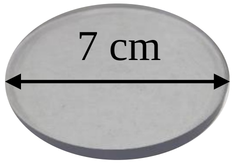






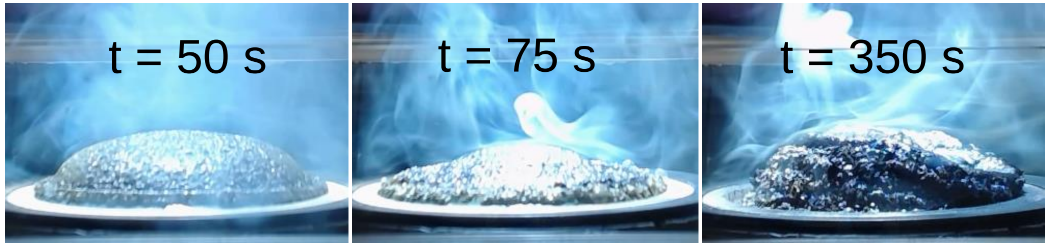
$$q_{in} = \varepsilon_{s.surf} q_{ext} - h_s (T_{s.surf} - T_{env}) - \varepsilon_{s.surf} \sigma T^4_{s.surf}$$

$$q_{out} = h_{bk} (T_{bk.surf} - T_{env}) + \varepsilon_{bk.surf} \sigma T^4_{bk.surf}$$



5 - 40 gram sample heated using a well-defined radiant heat flux

Sample may expand or contract with time:



Inverse Analysis of Transport Processes for PBT

Conservation of species: $$\frac{\partial \xi_j}{\partial t} = \boxed{\sum_{i=1}^{N_r} \theta_i^j r_i} - \boxed{\frac{\partial J_j{}^x}{\partial x}} + \boxed{\frac{\partial}{\partial x}\left(\xi_j \int_0^x \frac{1}{\rho}\frac{\partial \rho}{\partial t}\,dx\right)}$$

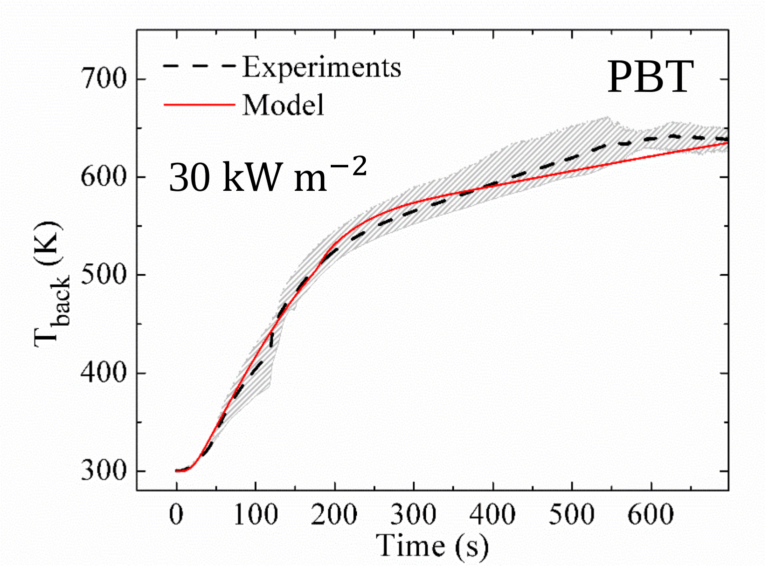
Chemical Reactions

Gas Transport

Expansion/Contraction

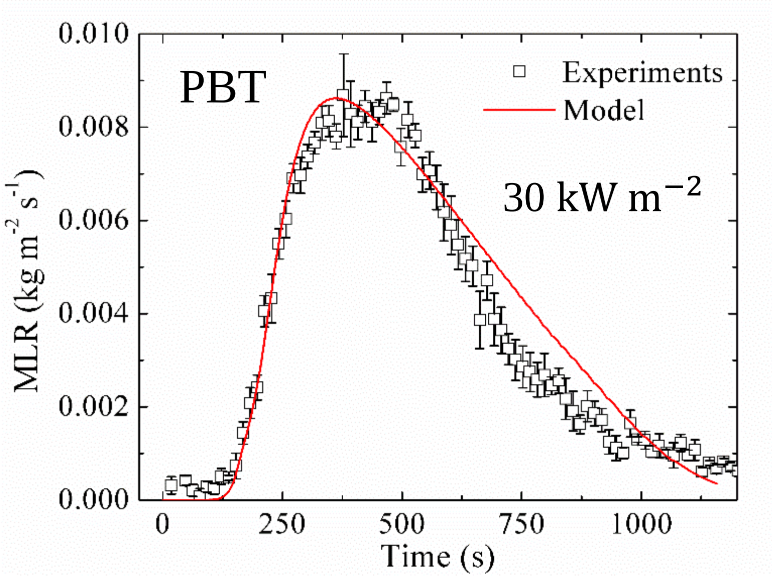
Conservation of energy: $$\sum_{j=1}^{N} \xi_j c_j \frac{\partial T}{\partial t} = \boxed{-\sum_{i=1}^{N_r} h_i r_i} - \frac{\partial q_x}{\partial x} - \frac{\partial I_{ex}}{\partial x} + \frac{\partial I_{rr}}{\partial x} - \boxed{\sum_{g=1}^{N_g} c_g \left(J_g{}^x \frac{\partial T}{\partial x}\right)} + \boxed{c\rho \frac{\partial T}{\partial x}\int_0^x \frac{1}{\rho}\frac{\partial \rho}{\partial t}\,dx}$$

Conduction Radiation Re-radiation

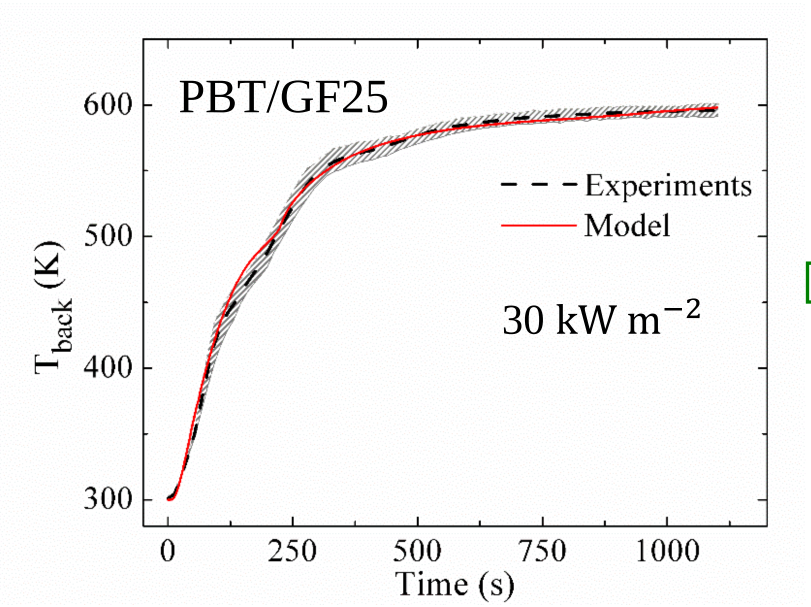


$\boxed{\boldsymbol{k_j}}$

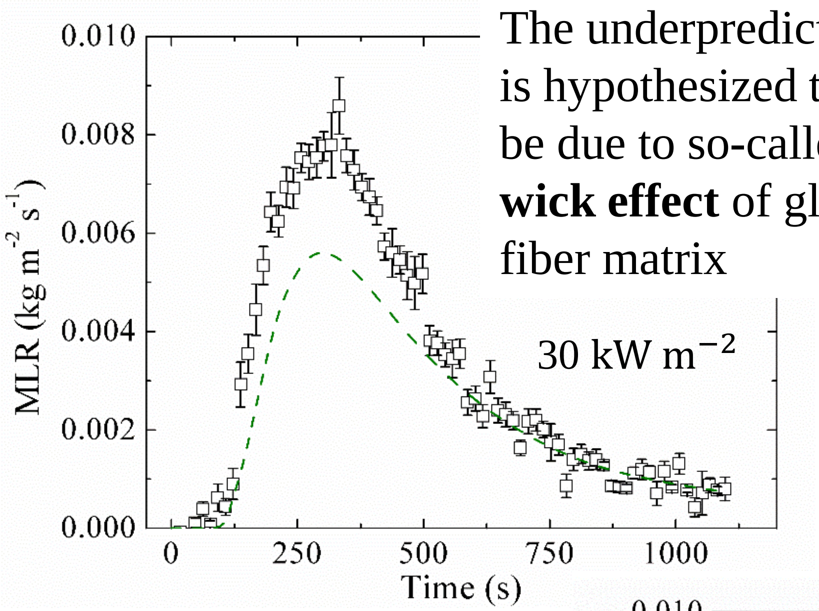
Prediction ⇒



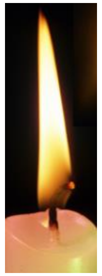
Inverse Analysis of Transport Processes for PBT with GF



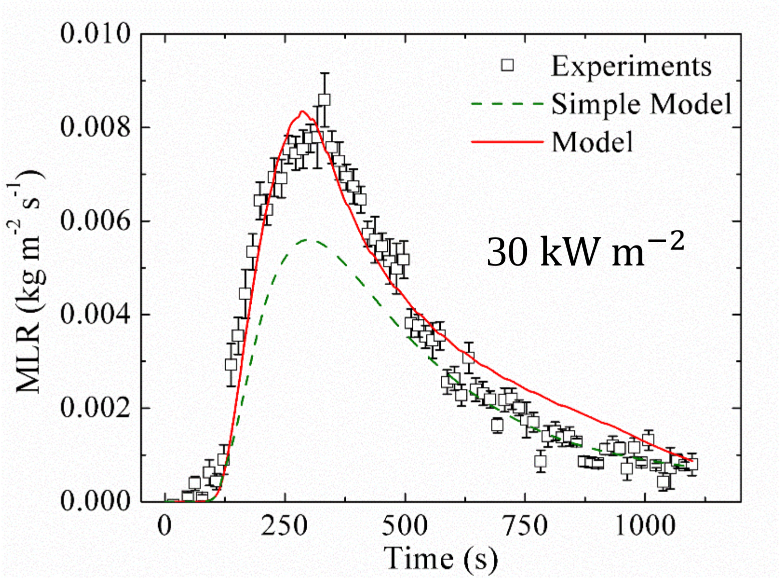
Prediction



The underprediction is hypothesized to be due to so-called **wick effect** of glass fiber matrix



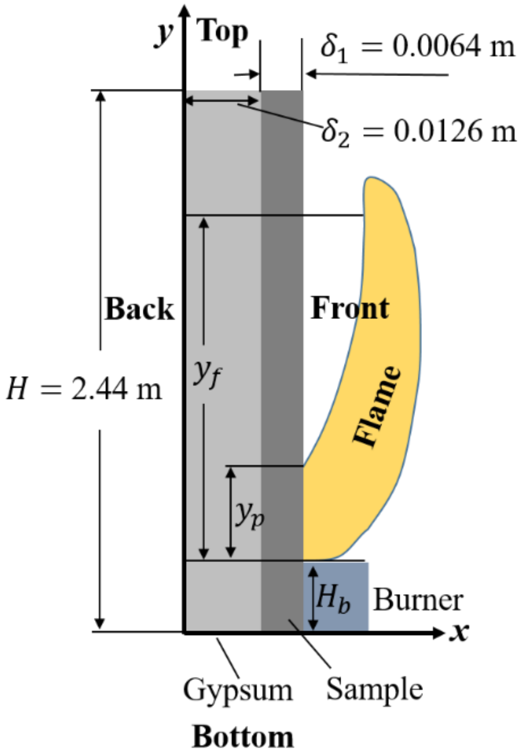
Capillary transport of PBT_{Melt} is added



Ding Y. et al. *Pyrolysis Model Development for a Polymeric Material Containing Multiple Flame Retardants: Relationship between Heat Release Rate and Material Composition;* Combustion and Flame; vol. 202; pp. 43-57 (2019)

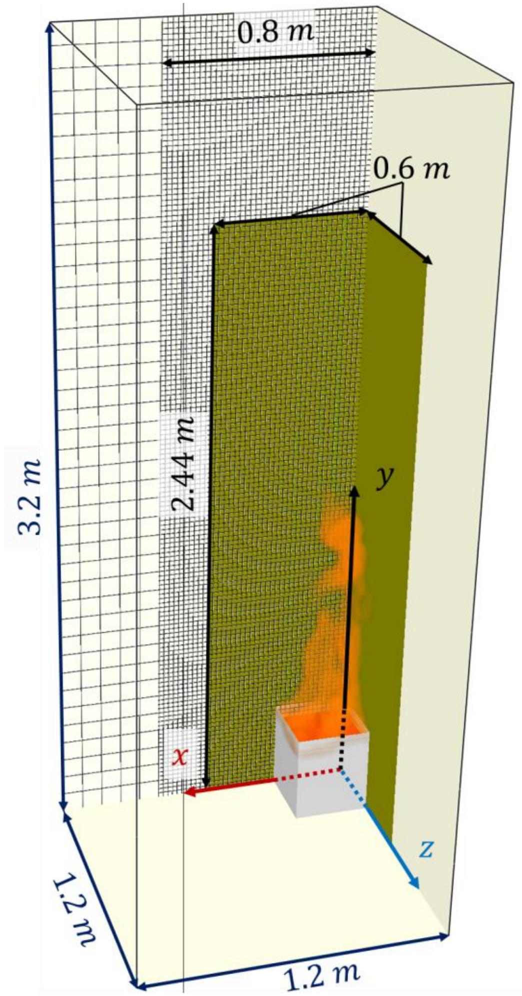
Sensitivity of the Rate of Fire Growth to Uncertainties in the Pyrolysis Properties

Simulation setup in ThermaKin

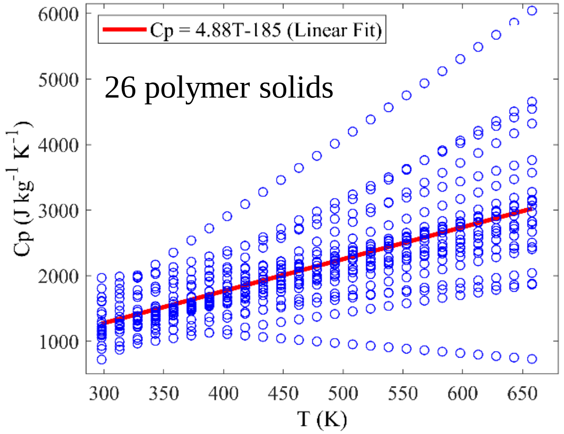


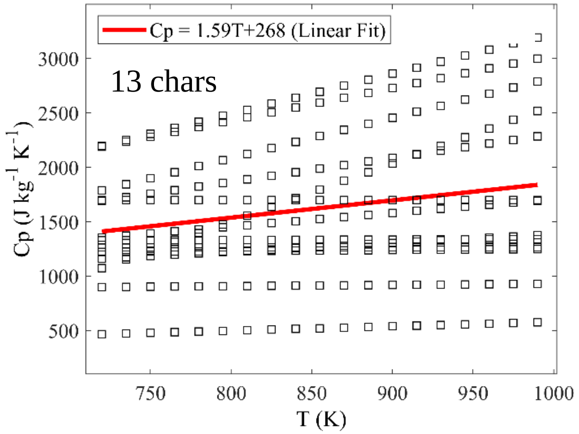
Similar to NFPA 286

Simulation setup in FDS

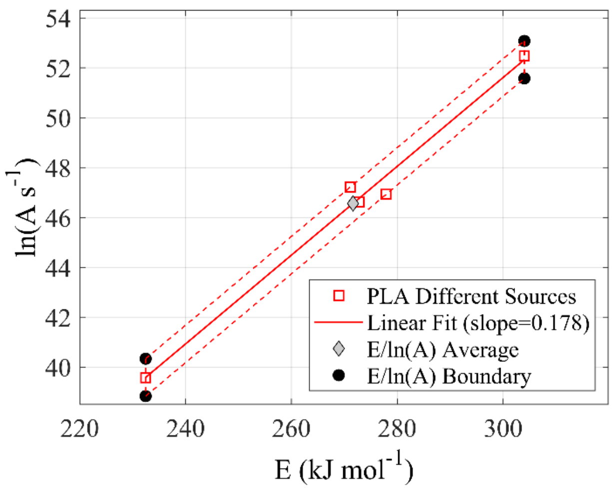


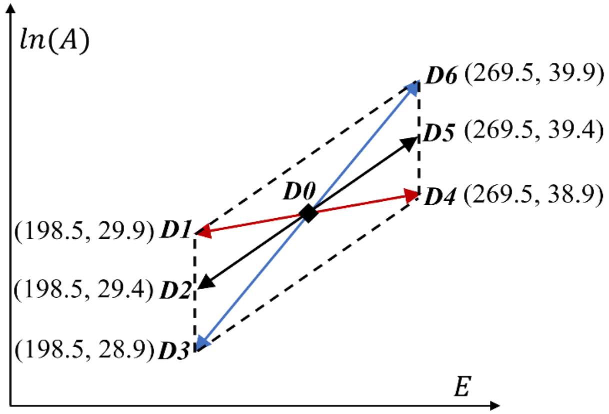
Average heat capacities:





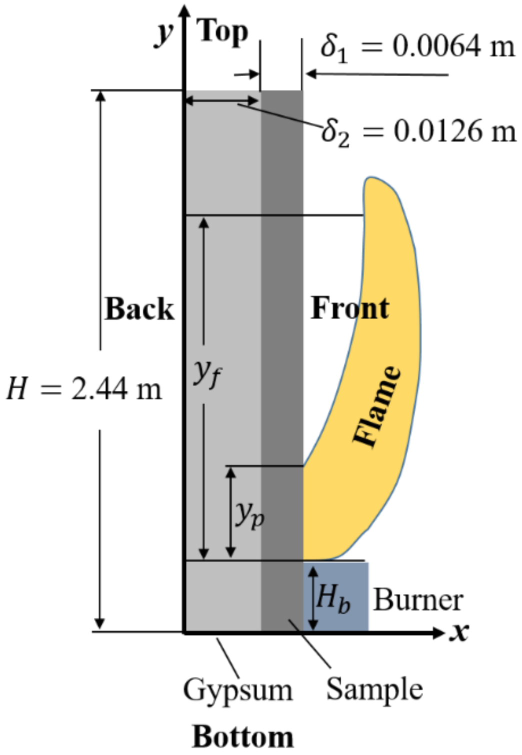
Uncertainties in decomposition kinetics:



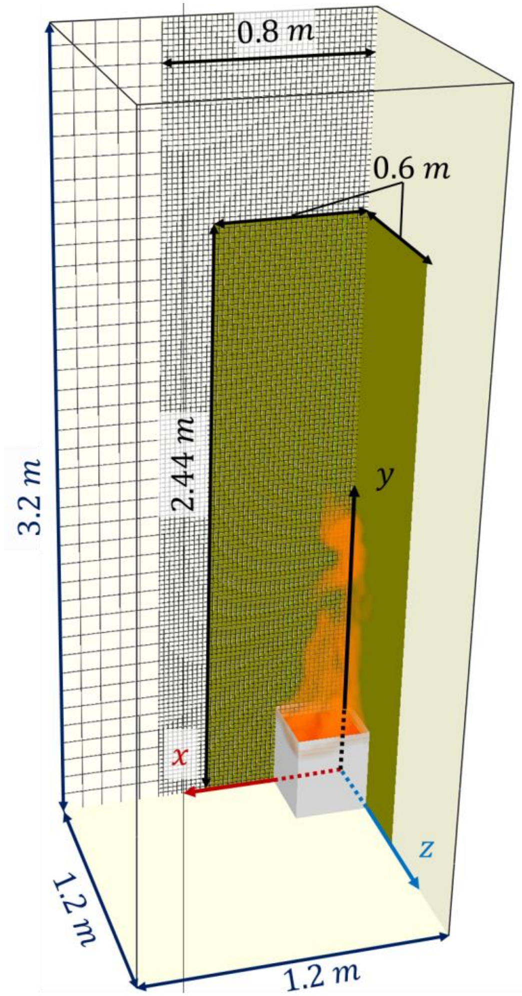


Sensitivity of the Rate of Fire Growth to Uncertainties in the Pyrolysis Properties

<u>Simulation setup in ThermaKin</u>

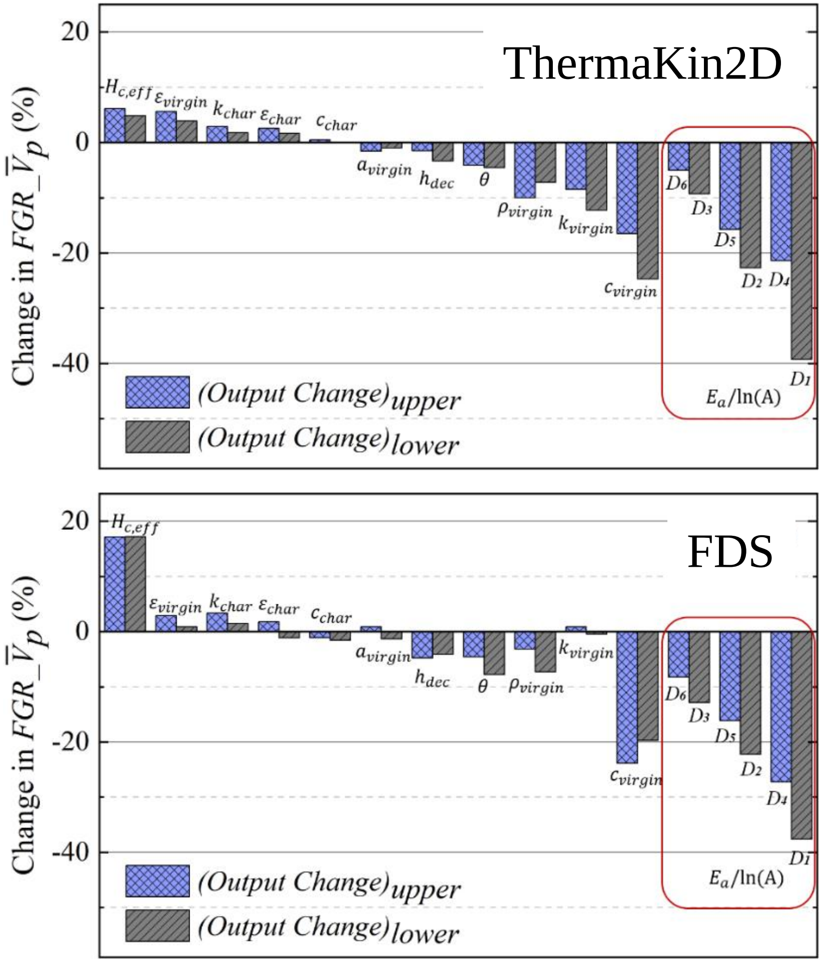


<u>Simulation setup in FDS</u>



<u>Average flame spread rate sensitivity:</u>

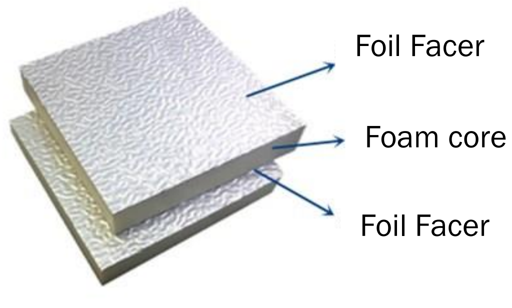
$$FGR\_\overline{V}_p = \frac{1.8 - y_{p,sustained}}{t_{y_p=1.8m} - t_{sustained}}$$



Ding Y. et al. *An Analysis of the Sensitivity of the Rate of Buoyancy-driven Flame Spread on a Solid Material to Uncertainties in the Pyrolysis and Combustion Properties*; Polymer Degradation and Stability; vol 214; 110405 (2023); https://doi.org/10.1016/j.polymdegradstab.2023.110405

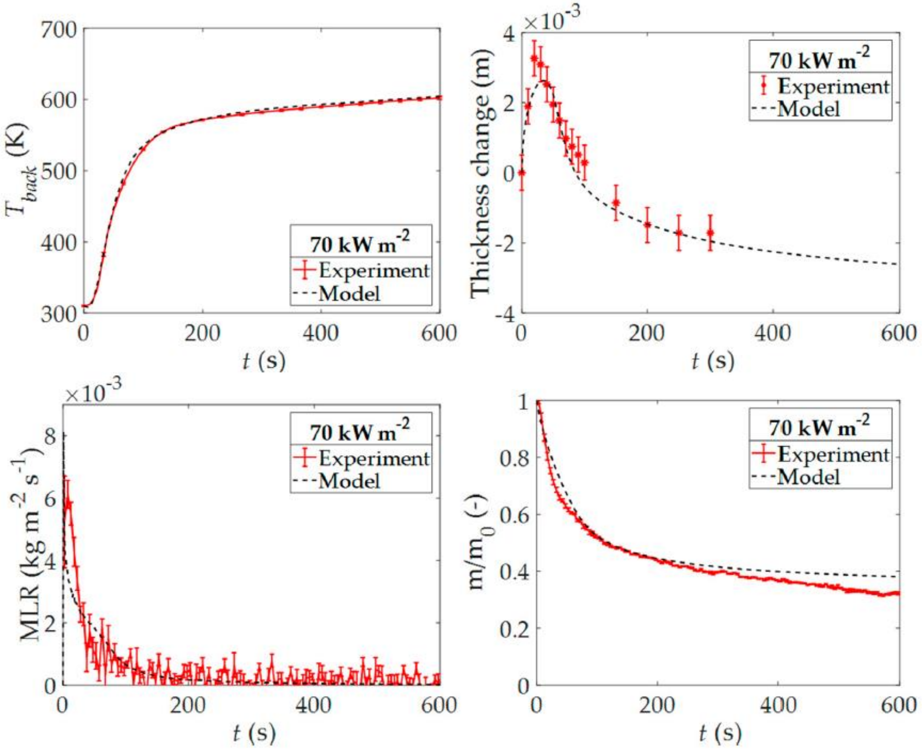
Complications in Material Behavior Observed at Larger Scale

PIR Foam

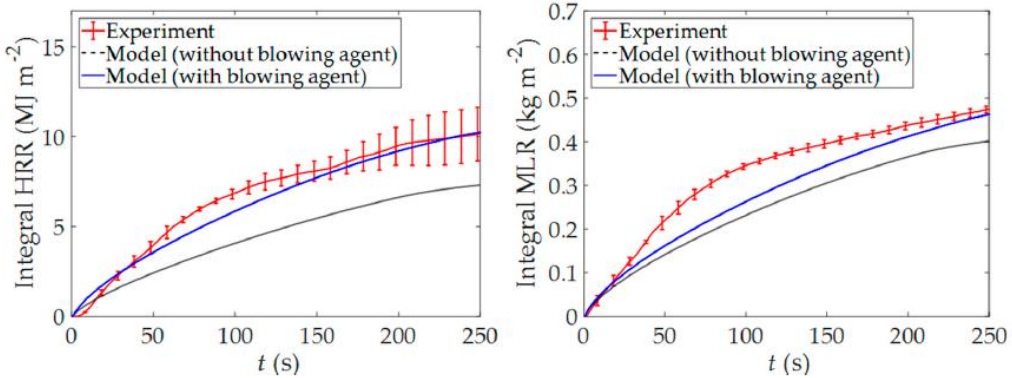


Tuff-R™ foam

CAPA II modeling results
for 1.3 cm thick samples:

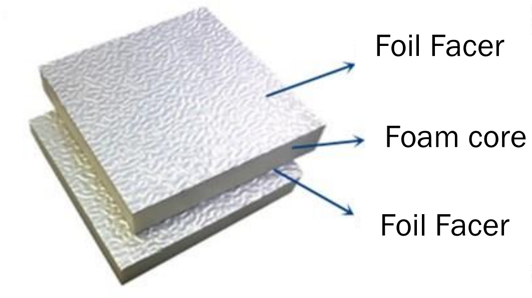


Cone calorimetry modeling results
for 2.5 cm thick samples:



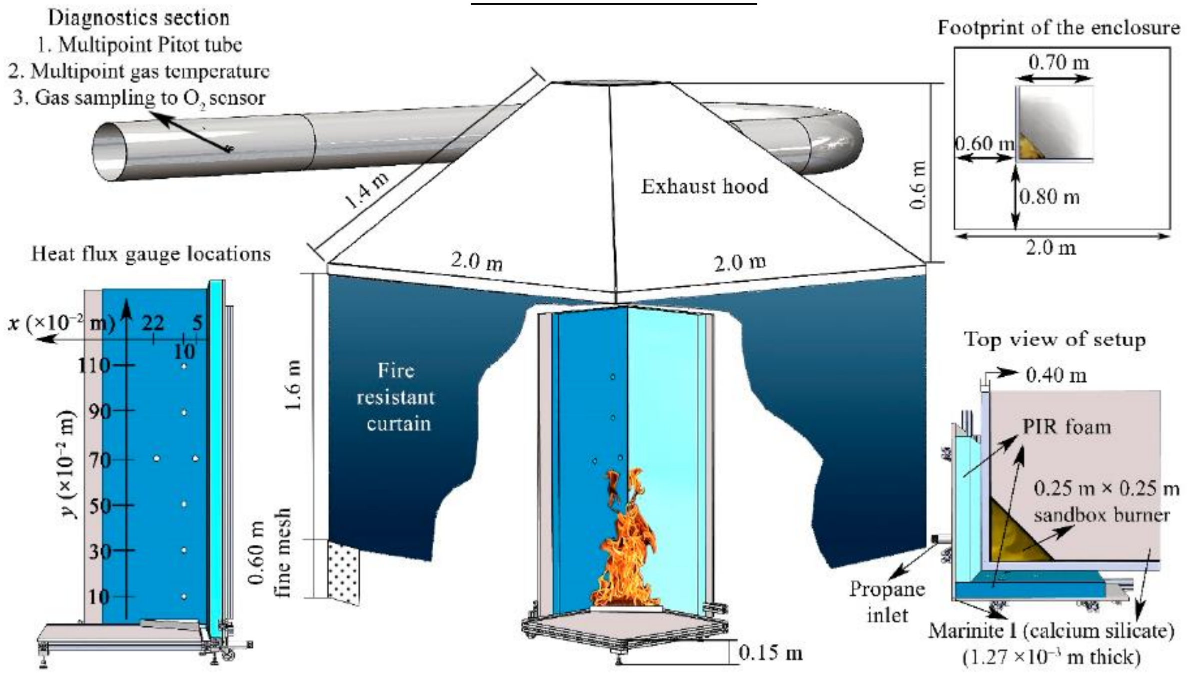
Complications in Material Behavior Observed at Larger Scale

PIR Foam

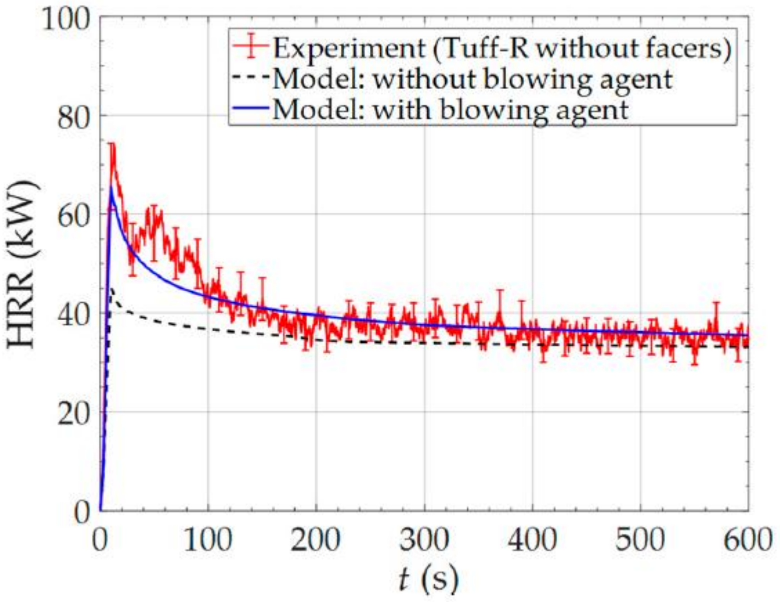


Tuff-R™ foam

Corner-wall Test



Modeling results:



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Concluding Remarks

- Development and application of comprehensive pyrolysis models significantly enhanced our ability to model fire growth.
- The accuracy of the measurements based on which these models are parameterized requires further improvement.
- Current comprehensive pyrolysis models do not account for the global mechanical deformation, delamination, buckling or melt flow. Inclusion of these mechanical effects is the next major challenge that must be addressed to achieve a qualitative improvement in our ability to predict fire dynamics.