Thermo-Kinetic Model of Pyrolysis (ThermoKin)

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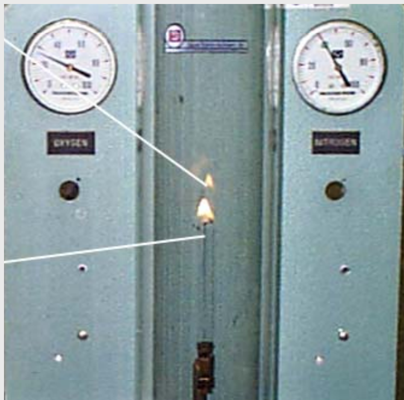
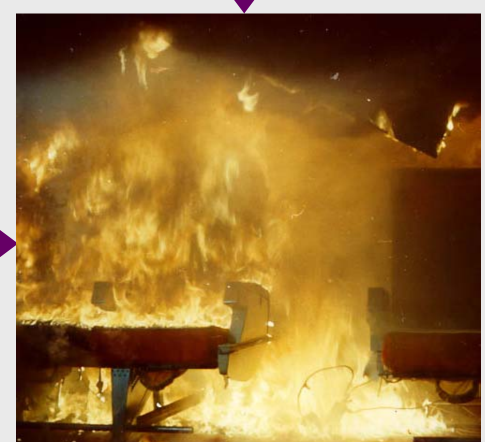
The Main Question

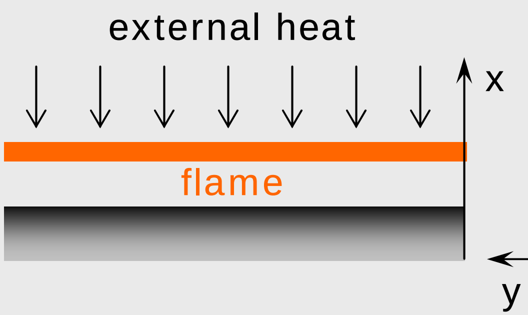


How are these tests related?

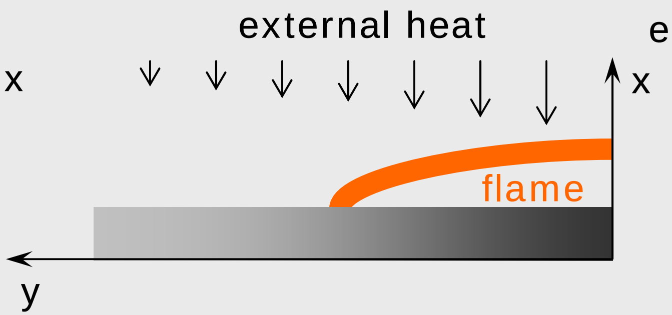


Model Geometries

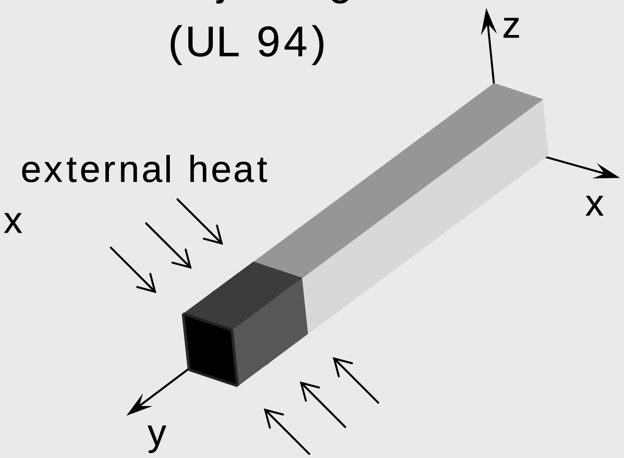
Heat Production Response (Cone Calorimeter)



Flame Spread (LIFT)



Small Object Ignition (UL 94)



Material Is Represented by a Mixture of Components

Components are characterized by:
- mass density
- heat capacity
- thermal conductivity
- gas transfer coefficient
- radiation absorption coefficient
- surface emissivity

The properties depend on temperature: $property = p_0 + p_1 T + p_n T^n$

Components are classified as:
- solid
- liquid
- gaseous

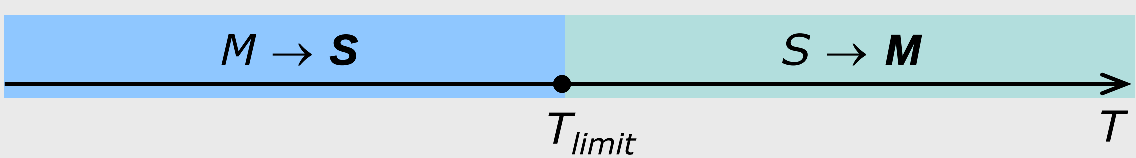
Components May Undergo Reactions

$$\theta_B \text{ COMP } B \;+\; \theta_C \text{ COMP } C \;\rightarrow\; \theta_D \text{ COMP } D \;+\; \theta_F \text{ COMP } F \;+\; heat$$

$$rate = A\exp\left(-\frac{E}{RT}\right)\left[\frac{m_B}{V}\right]\left[\frac{m_C}{V}\right]$$

$$heat = h_0 + h_1 T + h_n T^n$$

Reactions are used to simulate temperature transitions:



Volumetric Expansion

$$V = \sum^{solids} \frac{m_s}{\rho_s} + \sum^{liquids} \frac{m_l}{\rho_l} + \gamma \sum^{gases} \frac{m_g}{\rho_g}$$

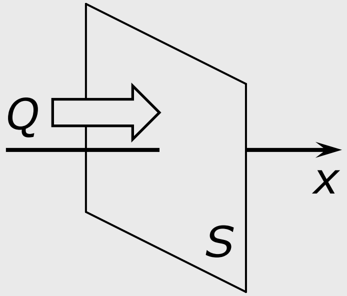
$\gamma = 0$: solids & liquids + gases = material

$\gamma = 1$: solids & liquids + gases = material

$$\gamma = \frac{\gamma_s \sum^{solids} \frac{m_s}{\rho_s} + \gamma_l \sum^{liquids} \frac{m_l}{\rho_l} + \tau \sum^{gases} \frac{m_g}{\rho_g}}{\sum^{solids} \frac{m_s}{\rho_s} + \sum^{liquids} \frac{m_l}{\rho_l} + \tau \sum^{gases} \frac{m_g}{\rho_g}}$$

Heat Transfer

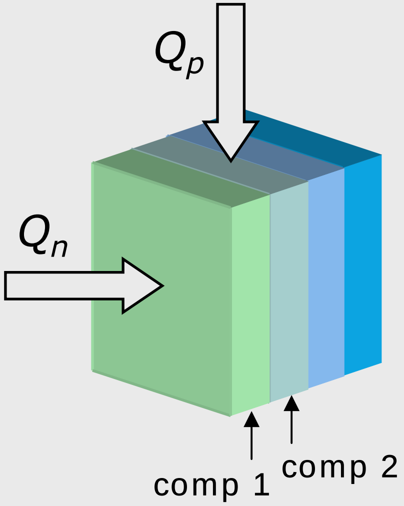
The rate of transfer $Q = -kS\frac{\partial T}{\partial x}$



Material conductivity $k = \beta k_p + (1-\beta)k_n$

$$k_p = \frac{1}{V}\sum^{comps} k_c V_c$$

$$k_n = \frac{V}{\sum^{comps} \frac{V_c}{k_c}}$$



Gas Transfer

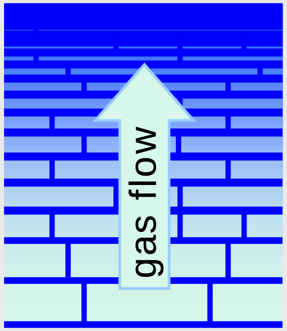
The rate of transfer of gas g, $J_g = -\lambda \rho_g S \dfrac{\partial \left(\dfrac{m_g/\rho_g}{V} \right)}{\partial x}$

volume fraction of material occupied by gases

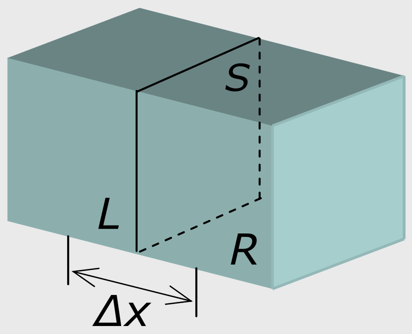
According to Boyle's law, $J_g = -\lambda \rho_g S \dfrac{\partial \left(\dfrac{\alpha (m_g/\rho_g)}{\alpha V} \right)}{\partial x} = -\dfrac{\lambda \rho_g S}{P^{def}} \dfrac{\partial (\alpha P_g)}{\partial x}$

$\gamma = 0$: $\alpha = const$ $\Longrightarrow$ $J_g = -\dfrac{\lambda \rho_g S \alpha}{P^{def}} \dfrac{\partial P_g}{\partial x}$

$\gamma > 0$: $P = const$ $\Longrightarrow$ $J_g = -\lambda \rho_g S \dfrac{P}{P^{def}} \dfrac{\partial \alpha_g}{\partial x}$



Conservation Equations Are Formulated using Finite Elements

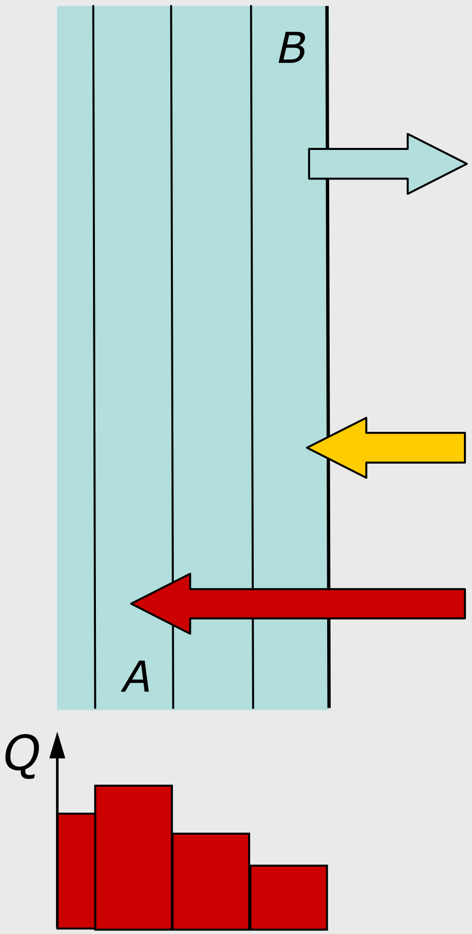


- Elements have rectangular shape.
- Elements are defined by component masses and temperature.

$$\frac{\Delta m_g^R}{\Delta t} = V^R \sum^{rxns} \theta_r^g rate_r^R + \lambda^{LR} \rho_g^{LR} S \frac{\frac{m_g^L}{\rho_g^L V^L} - \frac{m_g^R}{\rho_g^R V^R}}{\Delta x}$$

$$m^R c^R \frac{\Delta T^R}{\Delta t} = V^R \sum^{rxns} heat_r^R rate_r^R + k^{LR} S \frac{T^L - T^R}{\Delta x} + \frac{1}{2} \sum^{gases} c_g^{LR} (T^L - T^R) J_g^{LR}$$

Boundary Conditions for 1-Dimensional Model



Beer-Lambert absorption

$$J_c^B = \begin{cases} j_0^c \left(\dfrac{m_c^B}{V^B} - j_1^c \rho_c^B \right) \\ j_0^c \exp\left(-\dfrac{j_1^c}{RT^B} \right) \end{cases}$$

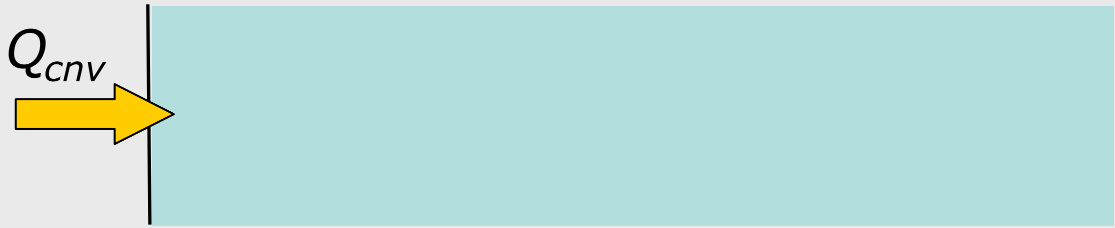
$$Q_{cnv}^B = h_{env}\left[T_{env}(t) - T^B \right]$$

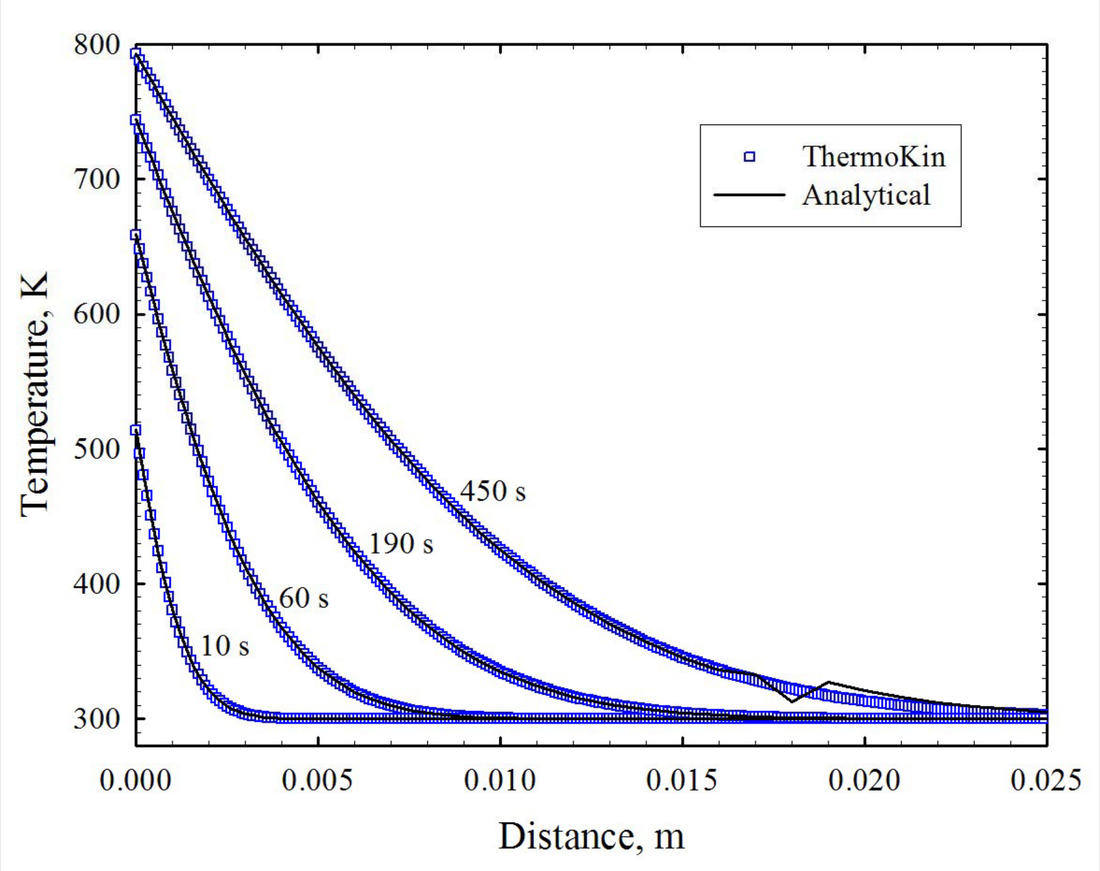
$$Q_{rad} = \varepsilon^A \left[q_{rad}(t) - \sigma \left(T^A \right)^4 \right]$$

Surface flame:

$$\sum^{comps} \frac{J_c^B}{J_{flm}^c} > 1 \Rightarrow q_{rad}(t) = q_{rad}(t) + q_{flm}, \quad h_{env} = h_{flm}, T_{env}(t) = T_{flm}$$

Conduction in Semi-Infinite Solid





Chemical Reactions

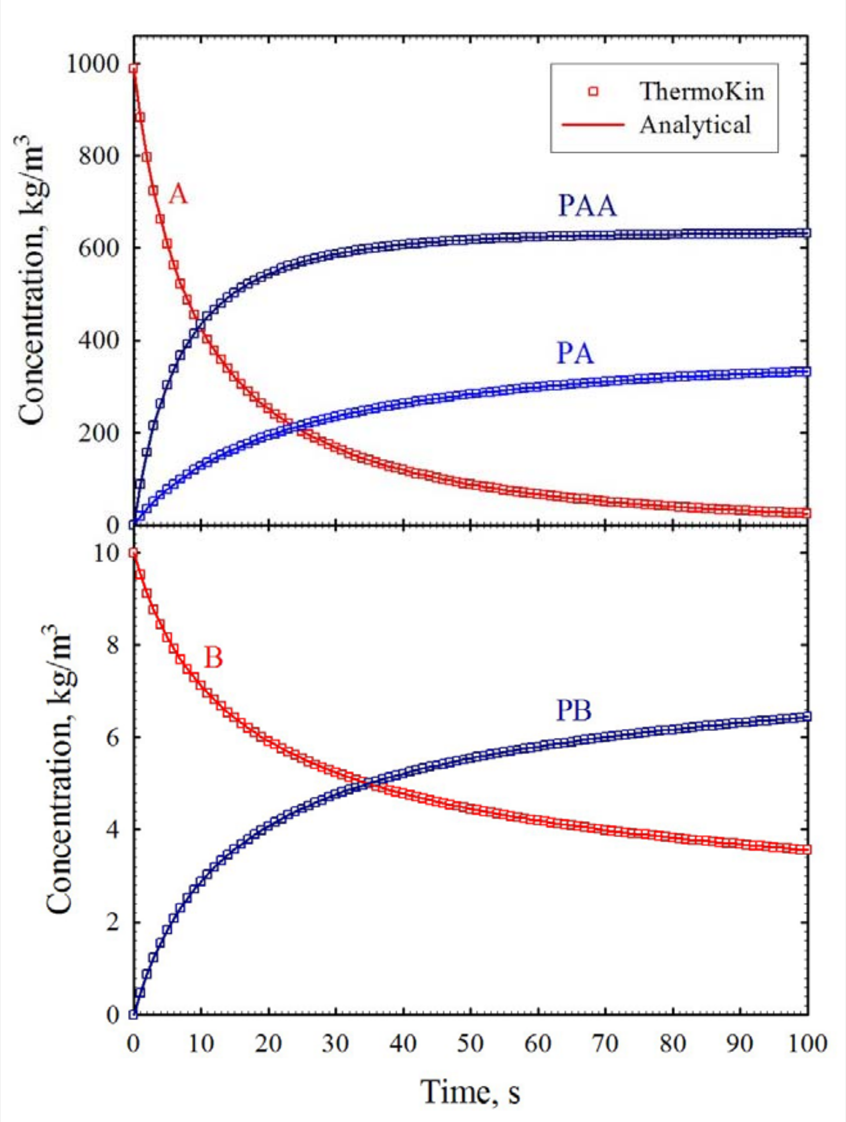
A $\rightarrow$ PA

A + A $\rightarrow$ PAA

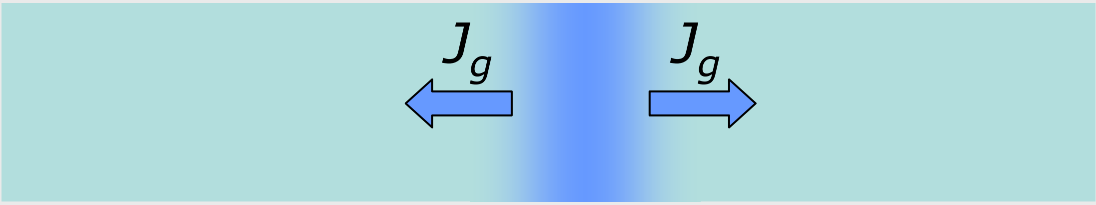
B $\rightarrow$ PB

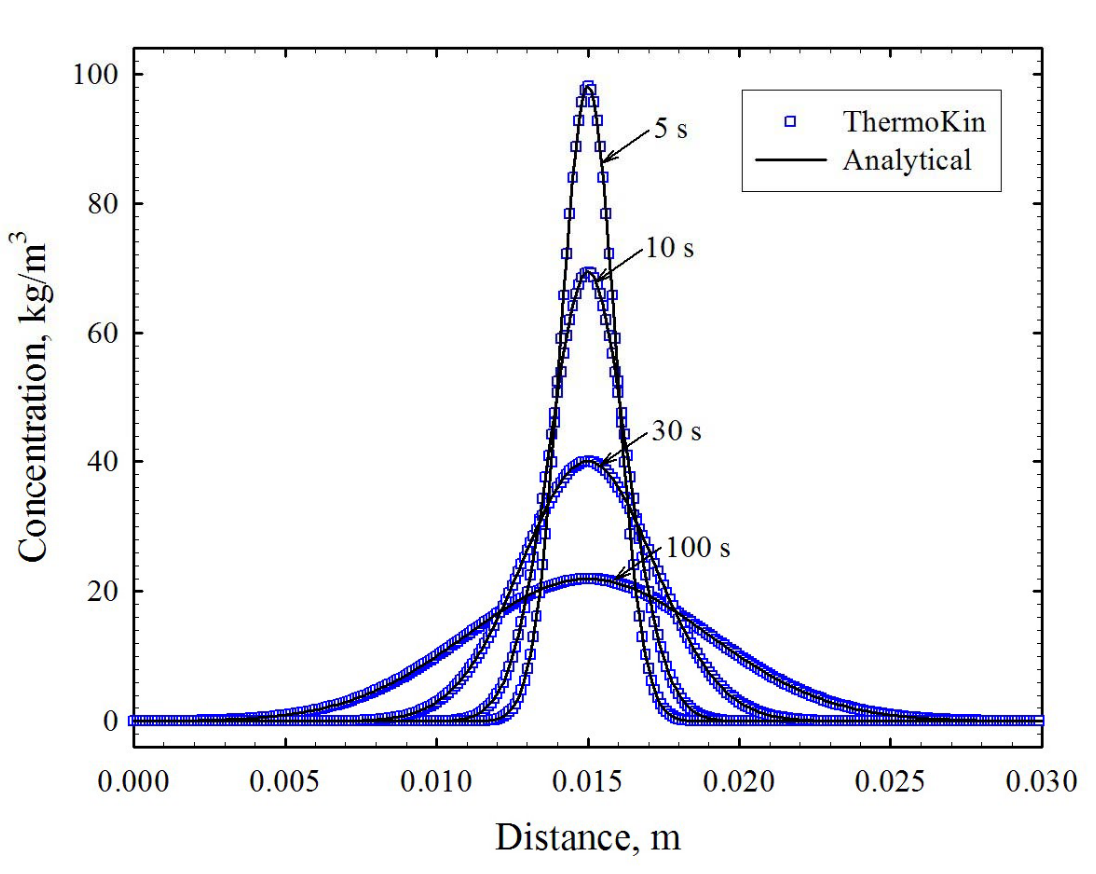
B + A $\rightarrow$ PB

$[A]_0 >> [B]_0$



Diffusion from Thin Layer



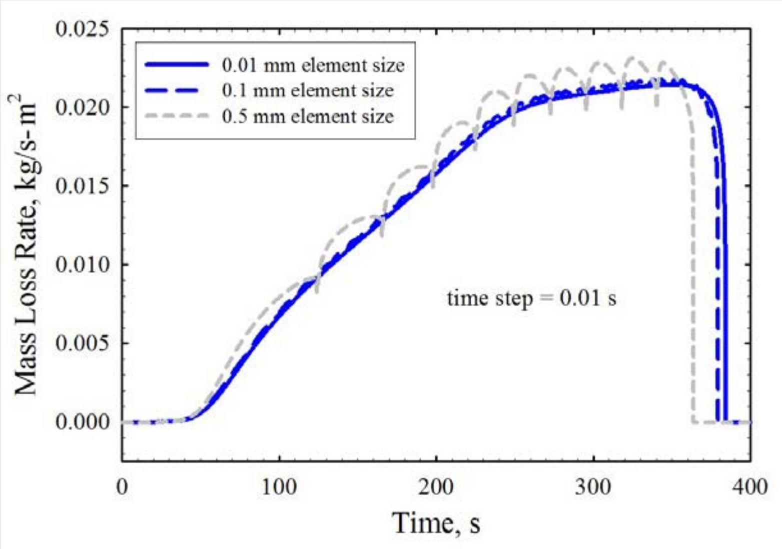


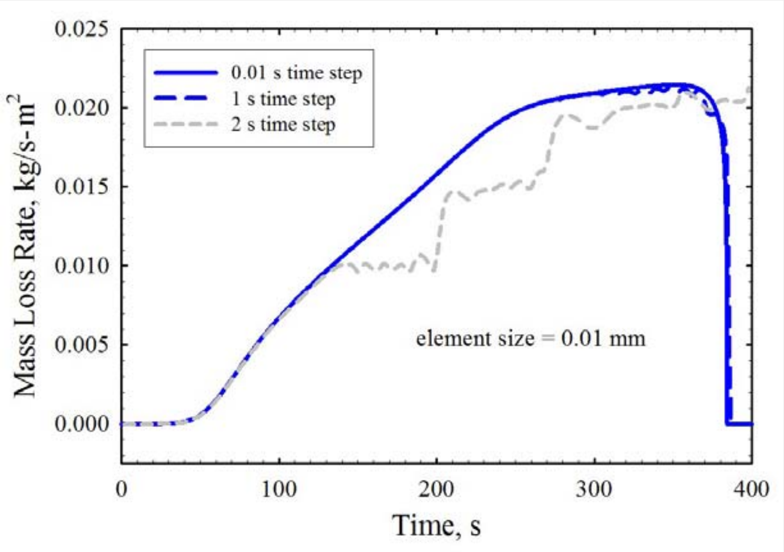
Integration Parameters

Material:
ρ=1000 kg/m^3
c=500+3T J/kg-K
k=0.2 W/m-K
ε=0.95

Decomposition:
A=5×10^{15} 1/s
E=250 kJ/mol
heat=-1000 J/g

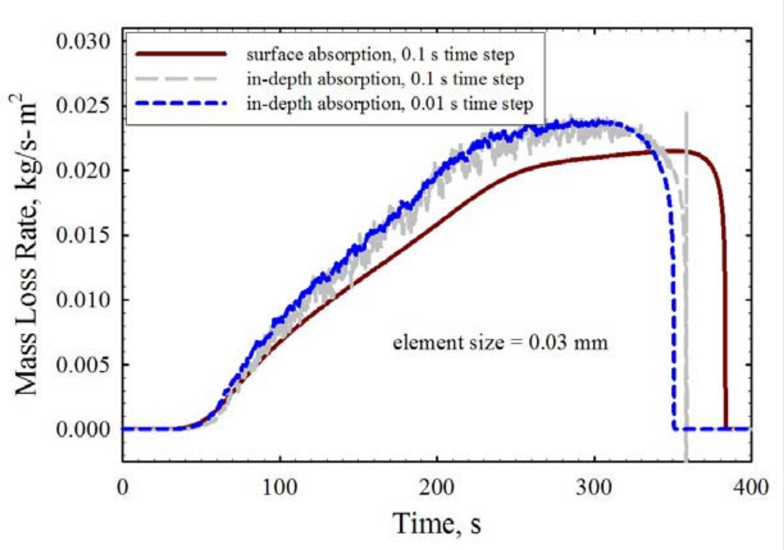
Conditions:
T_{init}=300 K
q_{rad}=50 kW/m^2
thickness=5 mm





Effects of In-Depth Absorption and Charring

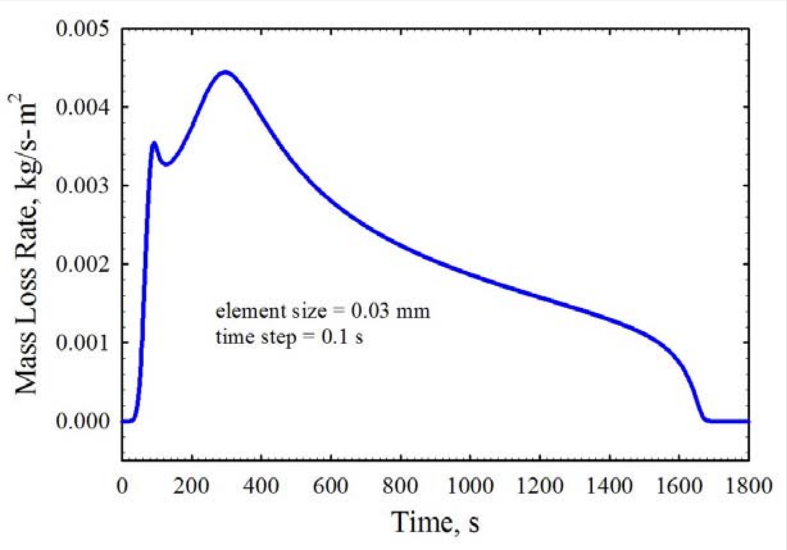
absorption coeff.=3 mm^{-1}



1 Material $\rightarrow$ 0.25 Char

ρ_{char}=50 kg/m^3

thickness: 5 $\rightarrow$ 25 mm



Conclusions

- A versatile framework for numerical simulation of the pyrolysis and combustion of polymeric materials has been formulated.

- The 1-dimensional model has been implemented and tested by comparing the results of numerical calculations with analytical solutions.

- This model will be used to develop parametric descriptions that provide accurate prediction of materials behavior in fires.