A Thermo-Kinetic Model of Pyrolysis

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Research Objectives

- Develop a computational tool that is capable of predicting fuel and heat generation by polymeric materials subjected to fire conditions.

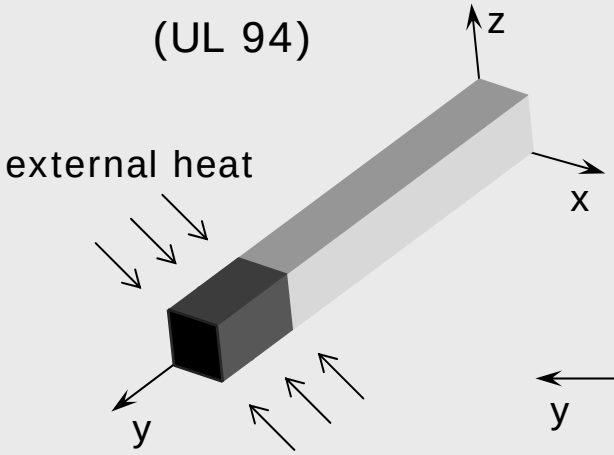
- Identify parameters that are <u>necessary</u> for an accurate description of the materials behavior.

- Classify materials in terms of their parametric descriptions and create a database of these descriptions.

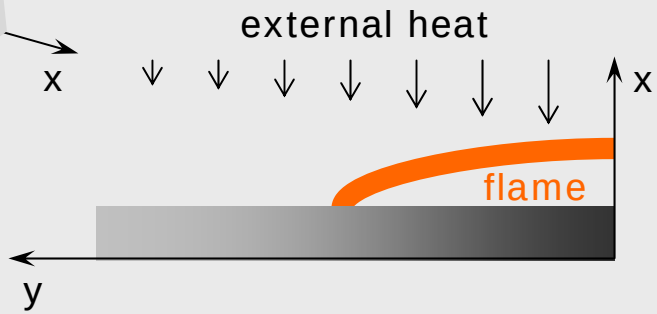
- Establish quantitative relations between materials fire properties and molecular structure.

Model Geometries

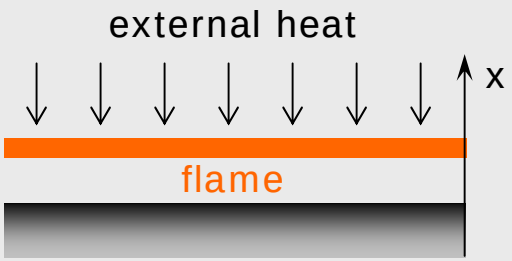
Small Object Ignition
(UL 94)



Flame Spread
(LIFT)



Heat Production Response
(Cone Calorimeter)



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

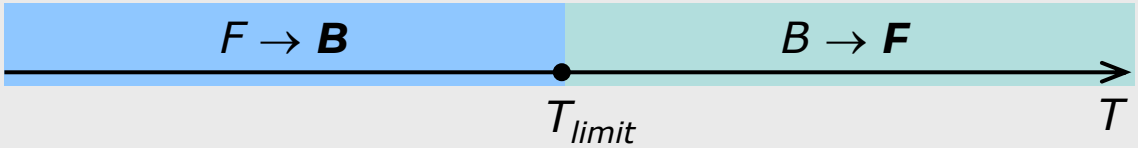
Components May Undergo Reactions

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

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

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

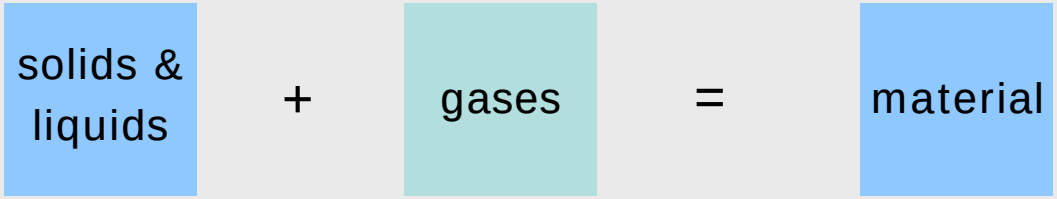
Reactions are used to simulate temperature transitions:



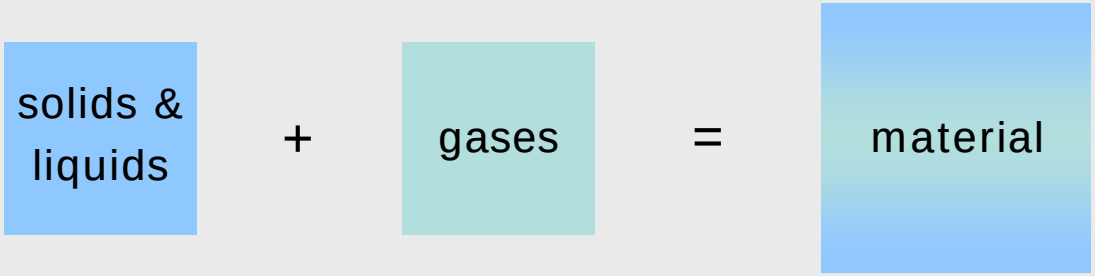
Volumetric Expansion

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

$\gamma = 0$:



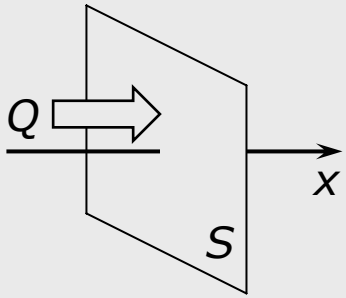
$\gamma = 1$:



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

Heat Transfer

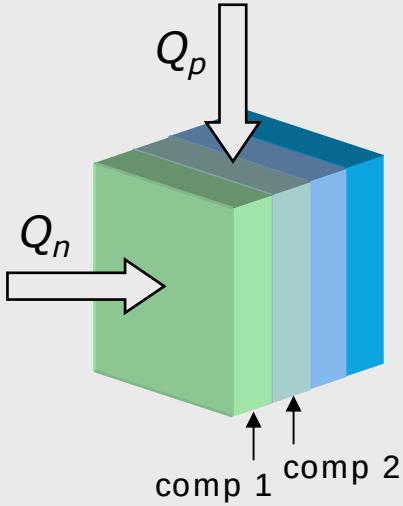
The rate of transfer $Q = -kS\dfrac{\partial T}{\partial x}$



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

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

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



Gas Transfer

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

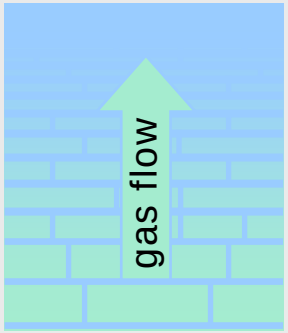
volume fraction of material occupied by gases

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

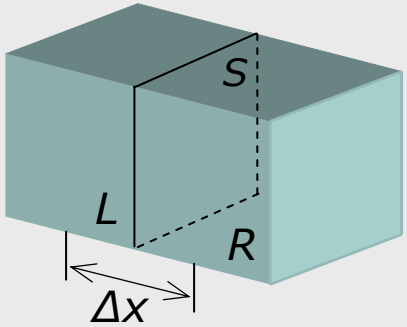
$\gamma = 0 : \quad \alpha = const \quad \Longrightarrow \quad J_g = -\dfrac{\lambda \rho_g S \alpha}{P^{def}} \dfrac{\partial P_g}{\partial x}$

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

$= \dfrac{1}{\gamma}$



Conservation Equations Are Formulated using Finite Elements

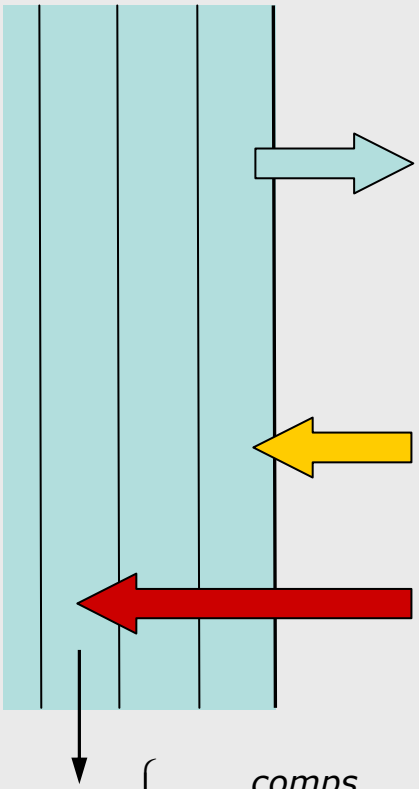


- Elements have rectangular shape.
- Elements are defined by component masses and temperature.

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

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

Boundary Conditions for 1-Dimensional Model



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

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

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

$$max\left\{Q_{rad} \sum^{comps} \varphi_c m_c\right\}$$

Surface flame:

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

$$h_{env} = h_{flm}, T_{env}(t) = T_{flm}$$

Concluding Remarks

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

- ANSI/ISO C++ implementation of the 1-dimensional model has been completed. The program, called ThermoKin, is currently being tested.