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Model of Combustion Synthesis of Thermoelectric Calcium Cobaltates

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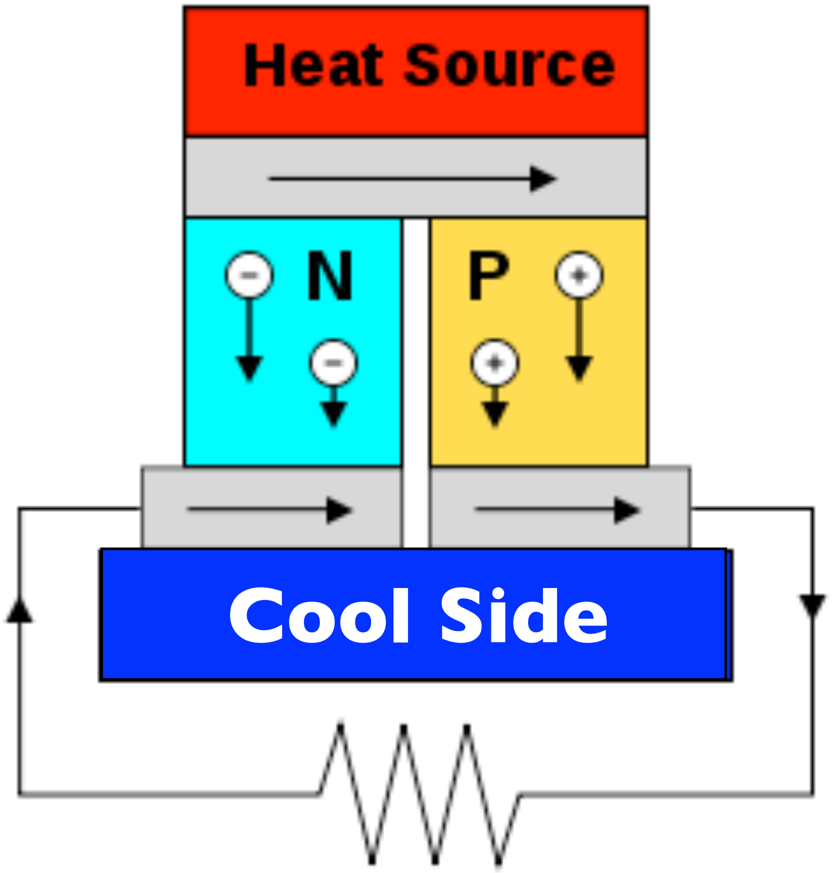
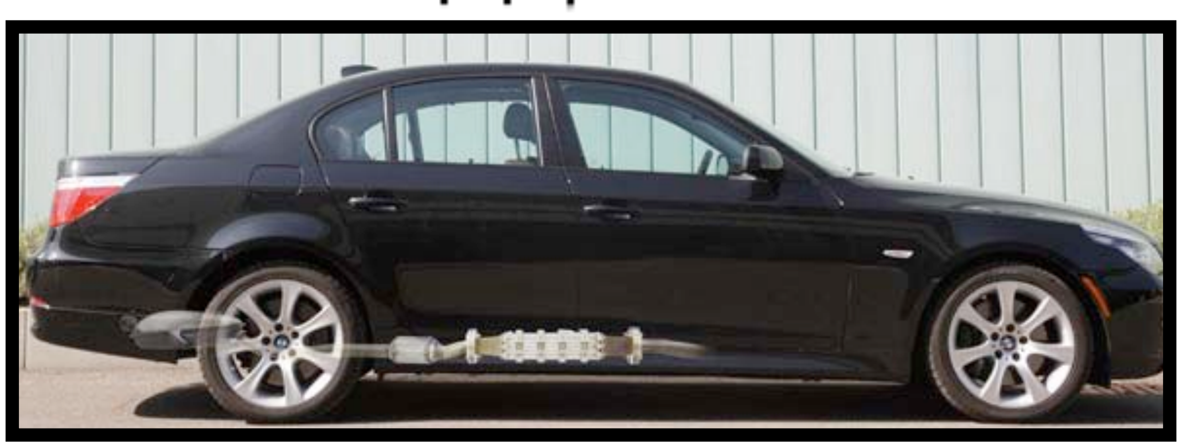
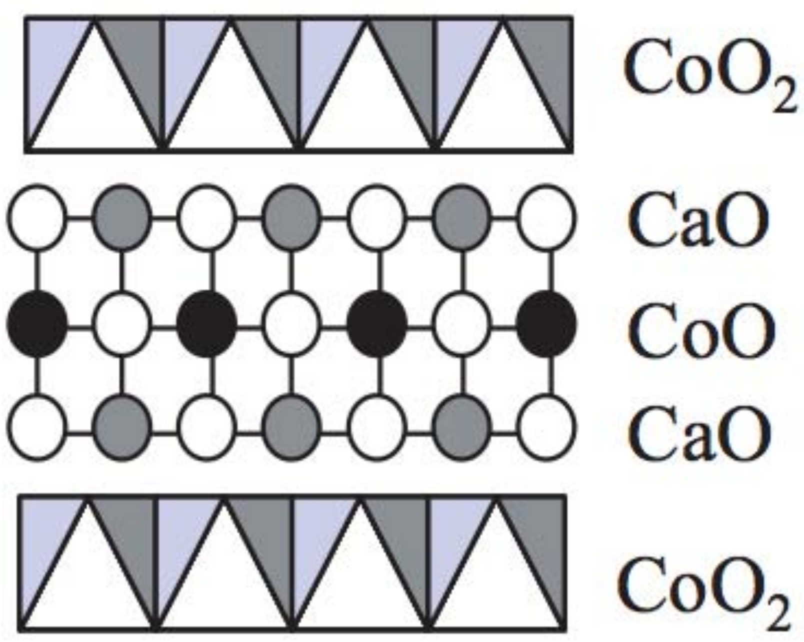
Thermoelectric Materials

Thermoelectric materials can convert temperature difference to an electric potential (or vice versa)

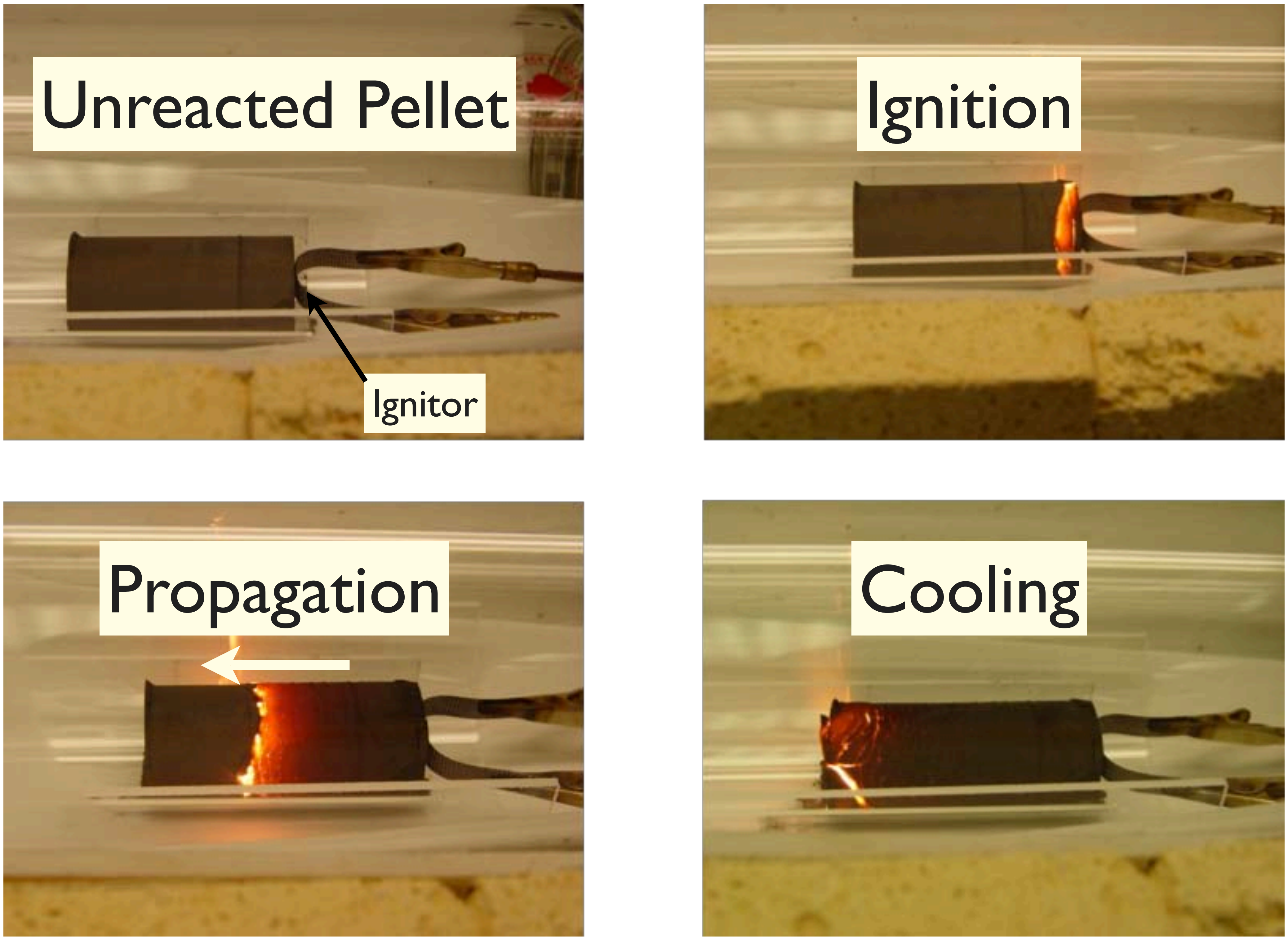




Calcium cobalt oxide ($Ca_{1.24}Co_{1.62}O_{3.86}$) is a promising thermoelectric material for high temperature applications



Self-propagating High-temperature Synthesis (SHS)



Parameters Governing SHS Reactions

- Adiabatic temperature
  - Theoretical maximum temperature reached with no heat loss to the environment
  - At least 1800 K for reaction to happen
- Pellet size
  - Surface heat loss, cooling
- Fuel ratio (amount of metal powder)
- Thermal conductivity

Experimental Background

$$1.24\ CaO_2 + 1.62\ Co \rightarrow Ca_{1.24}Co_{1.62}O_{3.86}$$

- Mixed and pressed in to 7/8" pellet, 3 cm long
- Reacted in oxygen
- Once ignited, reaction propagates at 0.27 mm/s
- Temperature in center of the pellet measured by 2 K-type thermocouples

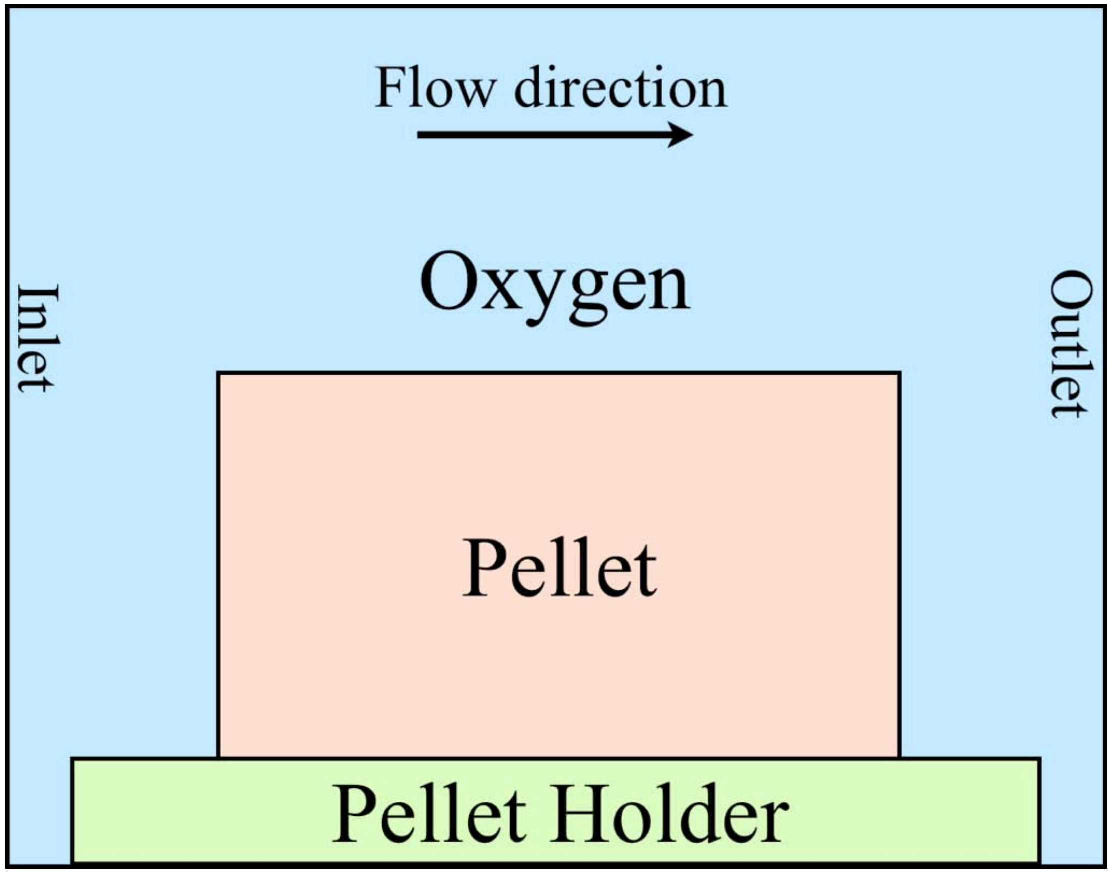
Modeling

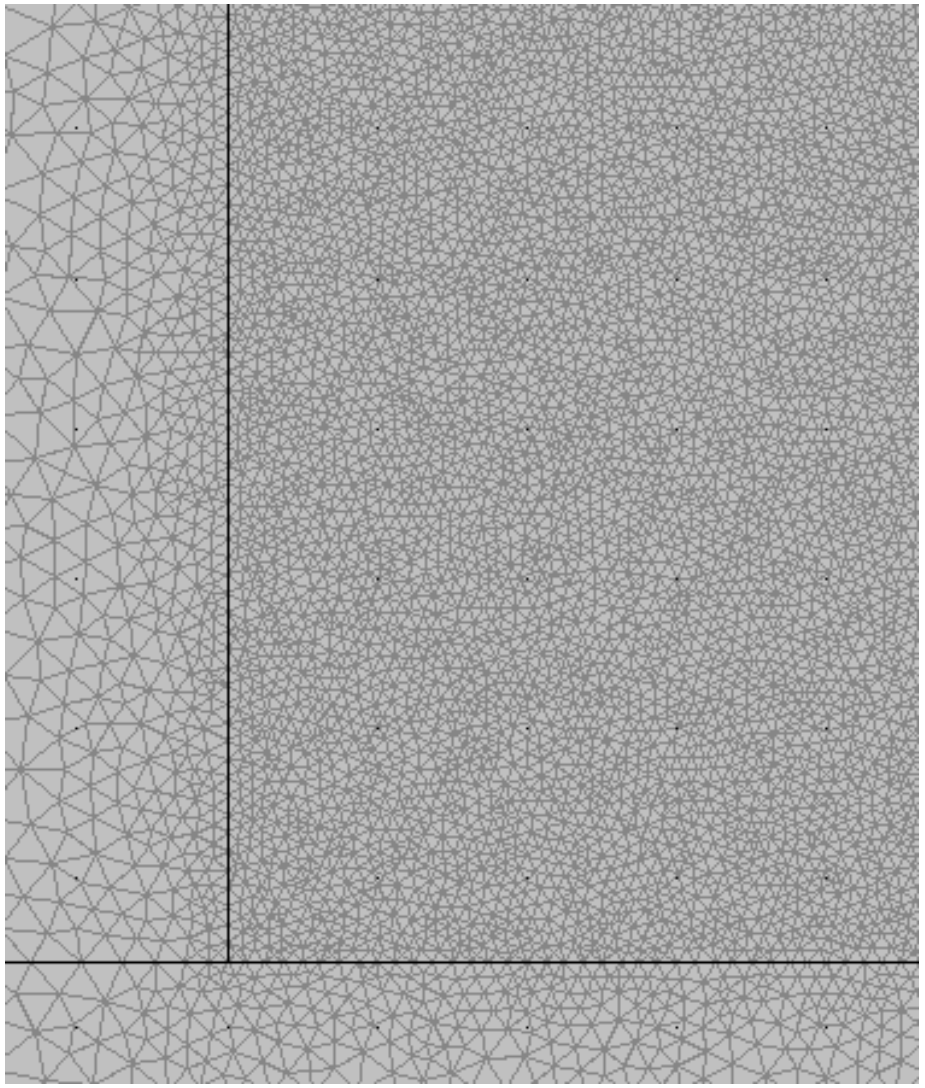
Modeling can help to predict results of experiments
Useful for scale-up

- How is larger pellet going to affect temperature?
- What is going to happen if the reactant mixture is modified?
- How is the pellet porosity affecting the reaction?
- What are the effects of sample preheating?
- COMSOL 3.5a with Chemical Engineering Module

Geometry/Mesh

2-D approximation





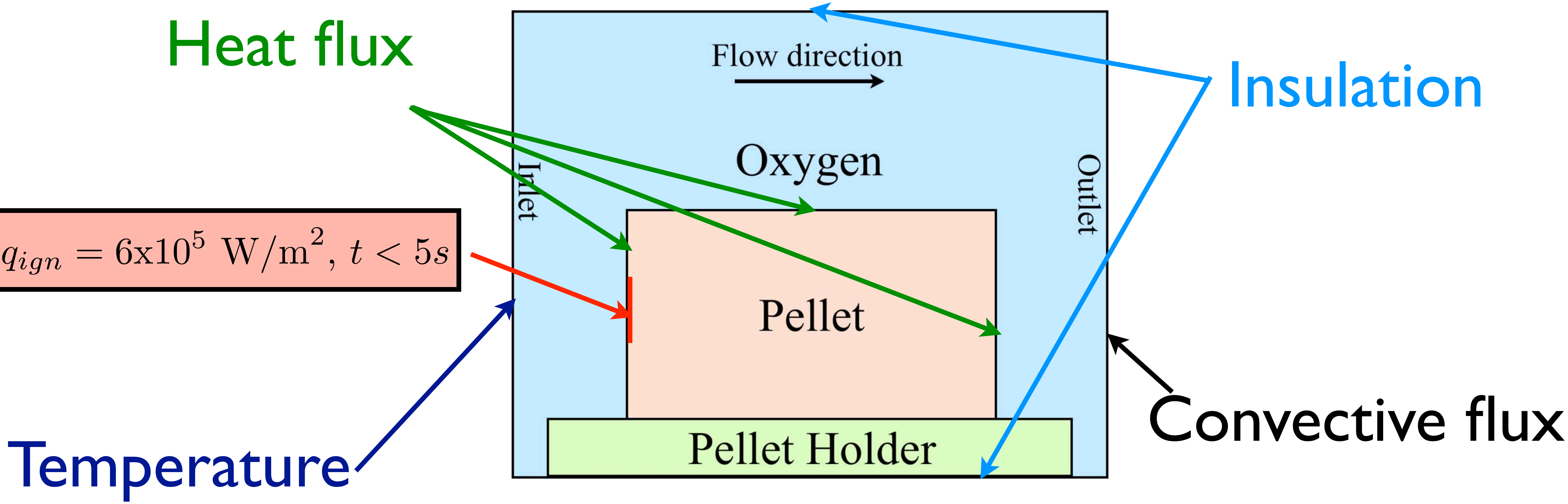
Very fine pellet mesh (larger temperature gradient, fast reaction)
Triangular mesh - 58302 elements (45875 for the pellet)

Energy Balance

$$\rho C_p \left(\frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T \right) = \nabla \cdot (k \nabla T) + Q$$

$$-q_0 = h_c(T - T_\infty) + \epsilon_r \sigma (T^4 - T_\infty^4)$$

$$q_{ign} = 6\text{x}10^5 \ \mathrm{W/m}^2, \ t < 5s$$



Heat transfer in porous solid

$$\rho C_p = \epsilon \rho_{gas} C_{p,gas} + (1-\epsilon)\rho_{solid} C_{p,solid}$$

- Porous pellet - affects heat transfer
  - Can easily study the influence of porosity
  - Modified the built in equations
- Thermal conductivity also a function of porosity

$$k_e = k_f \left(k_s/k_f\right)^{A-0.057log(k_f/k_f)}$$
$$A = 0.280 - 0.7571log(\epsilon)$$

Mass Balance

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i) = \boxed{R_i} - \mathbf{u} \nabla c_i$$

- Assuming reaction is independent of oxygen diffusion
- No oxygen convention inside the pellet

$$\frac{\partial c_{cco}}{\partial t} = R_{cco}$$

- Only for pellet (insulation boundary on pellet, oxygen interface)
- First order reaction

Reaction rate and heat of reaction

Coupling the energy and mass balance

$$\frac{d\eta}{dt} = (1-\eta)^n \, k e^{\left(\frac{-E}{RT}\right)}$$

First order reaction can be written in terms of concentration

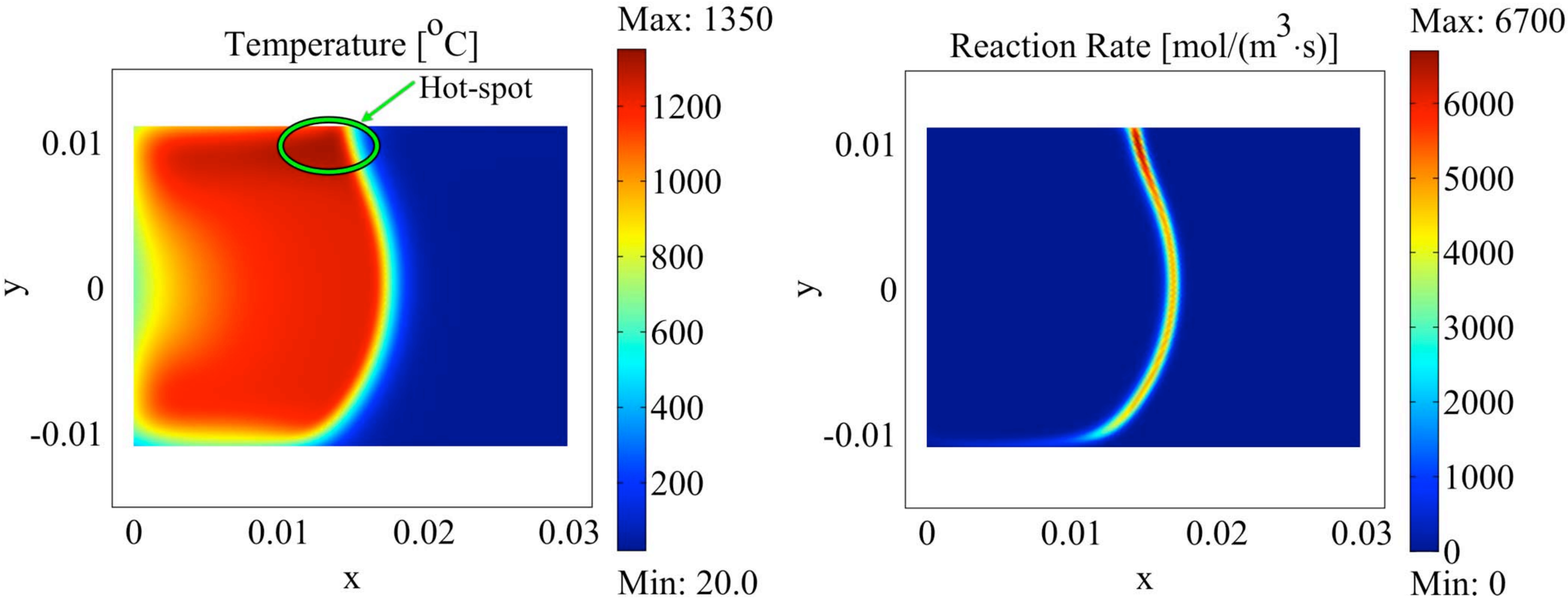
$$\eta = \frac{c_{cco}}{c_{cco,f}}$$

$$R_{cco} = \left(c_{cco,f} - c_{cco}\right) k e^{\left(\frac{-E}{RT}\right)}$$

Heat source is a product of enthalpy of reaction with reaction rate

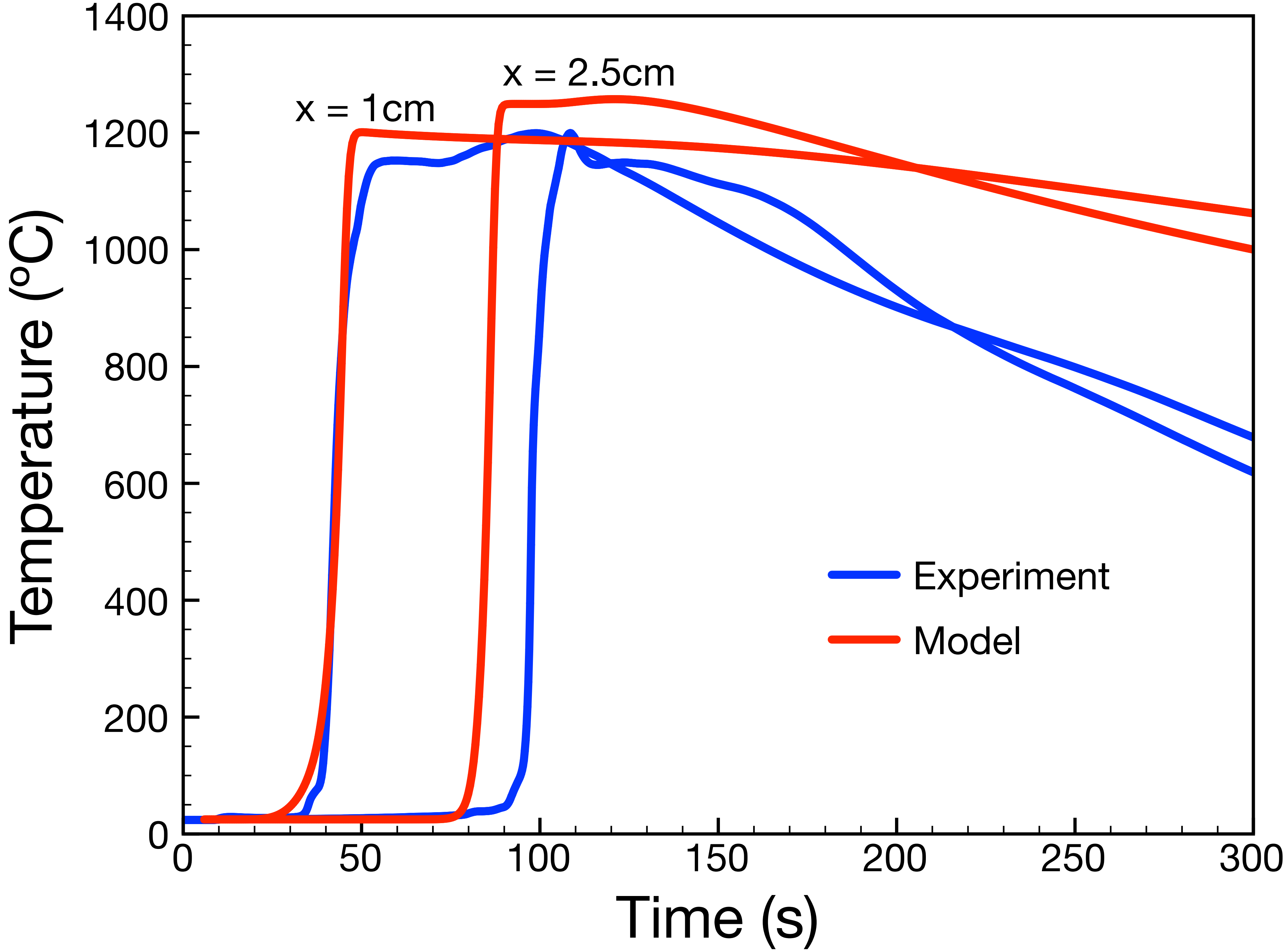
$$Q = \Delta H_r R_{cco}$$

Temperature and Reaction Profile

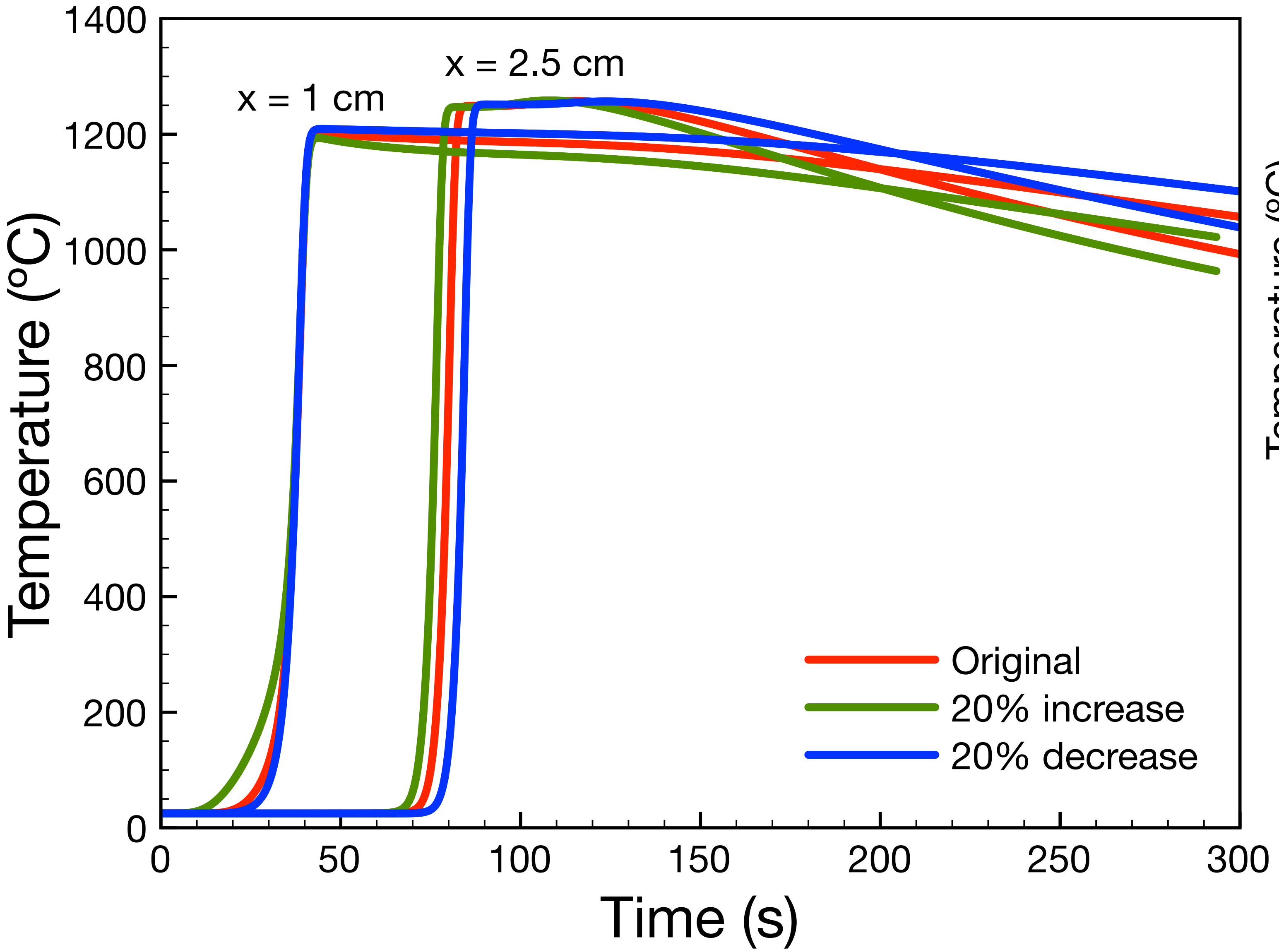


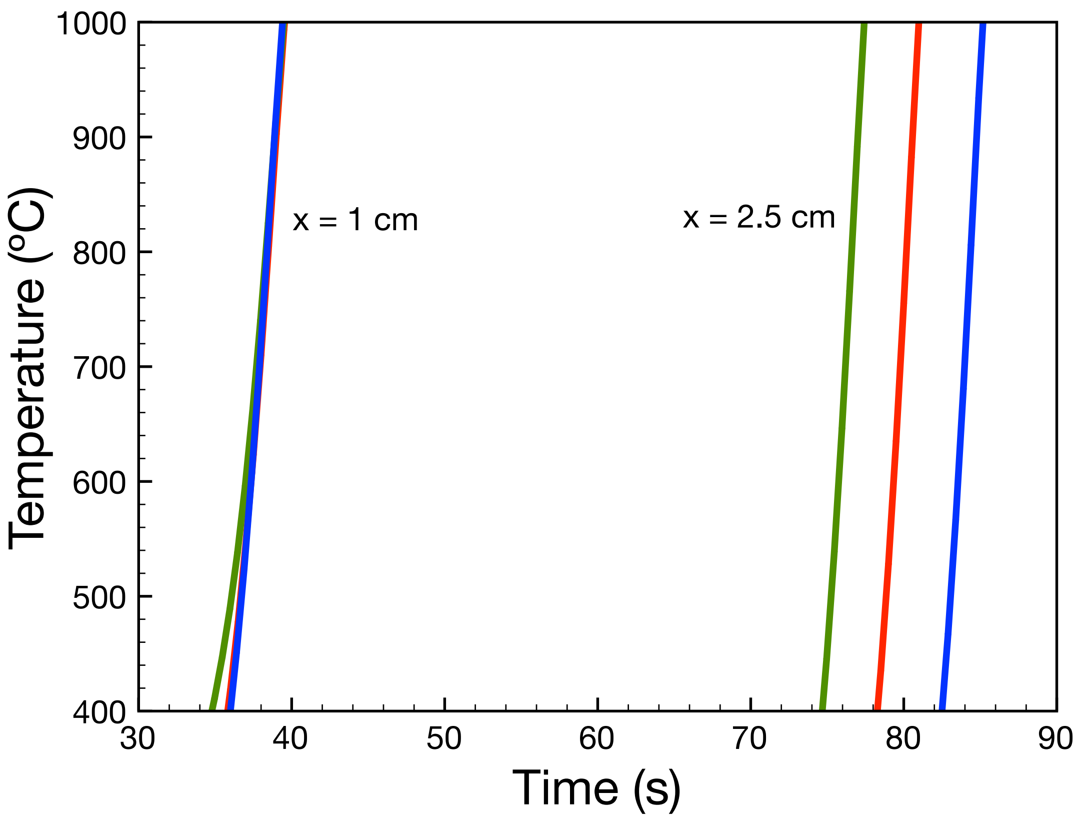
Large temperature gradient and narrow reaction zone are typical for SHS reactions

Experimental data and model



Effect of thermal conductivity



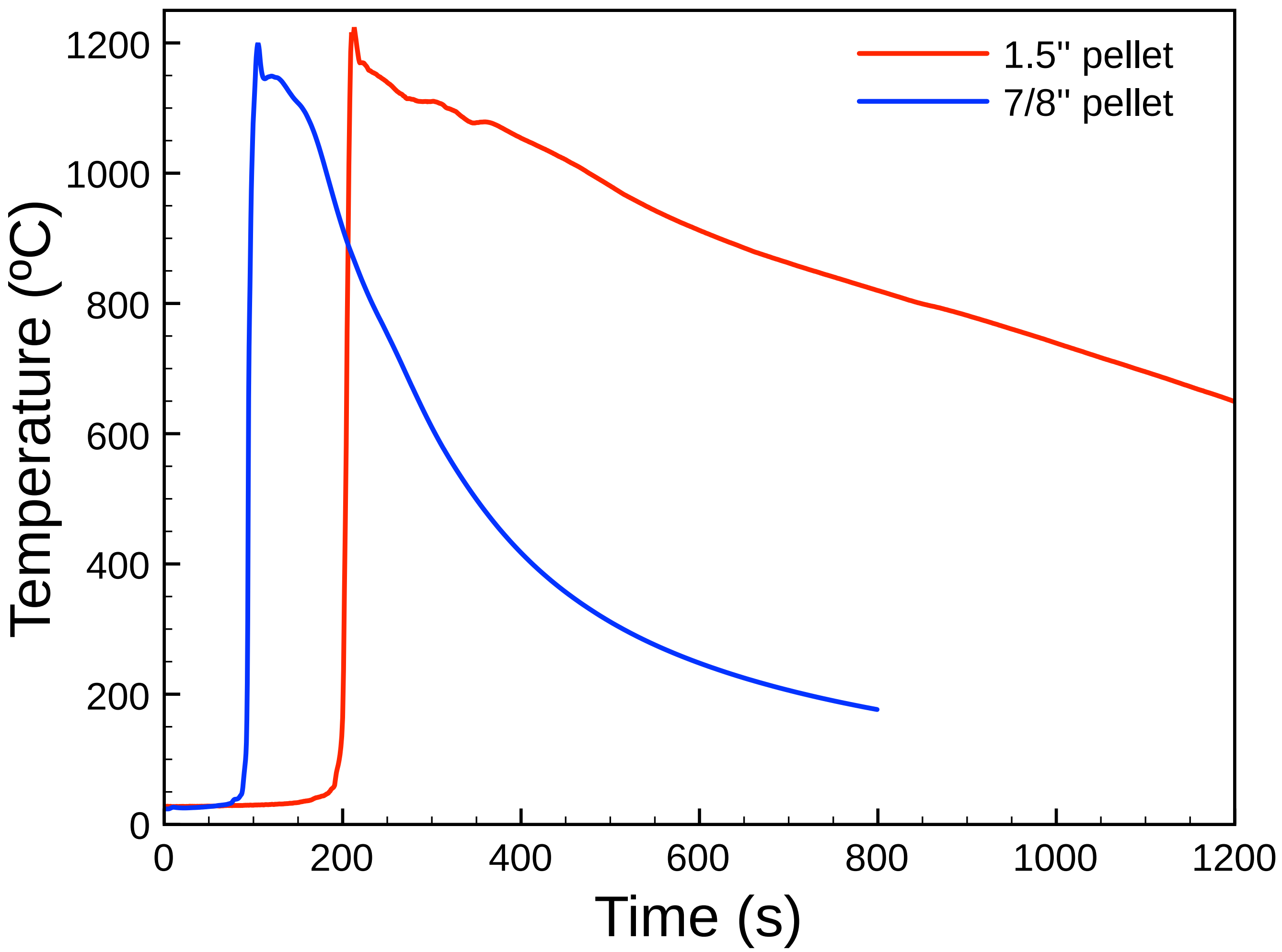


k at 25 °C (W/m K)	u (mm/s)
0.22	0.33
0.27	0.36
0.32	0.40

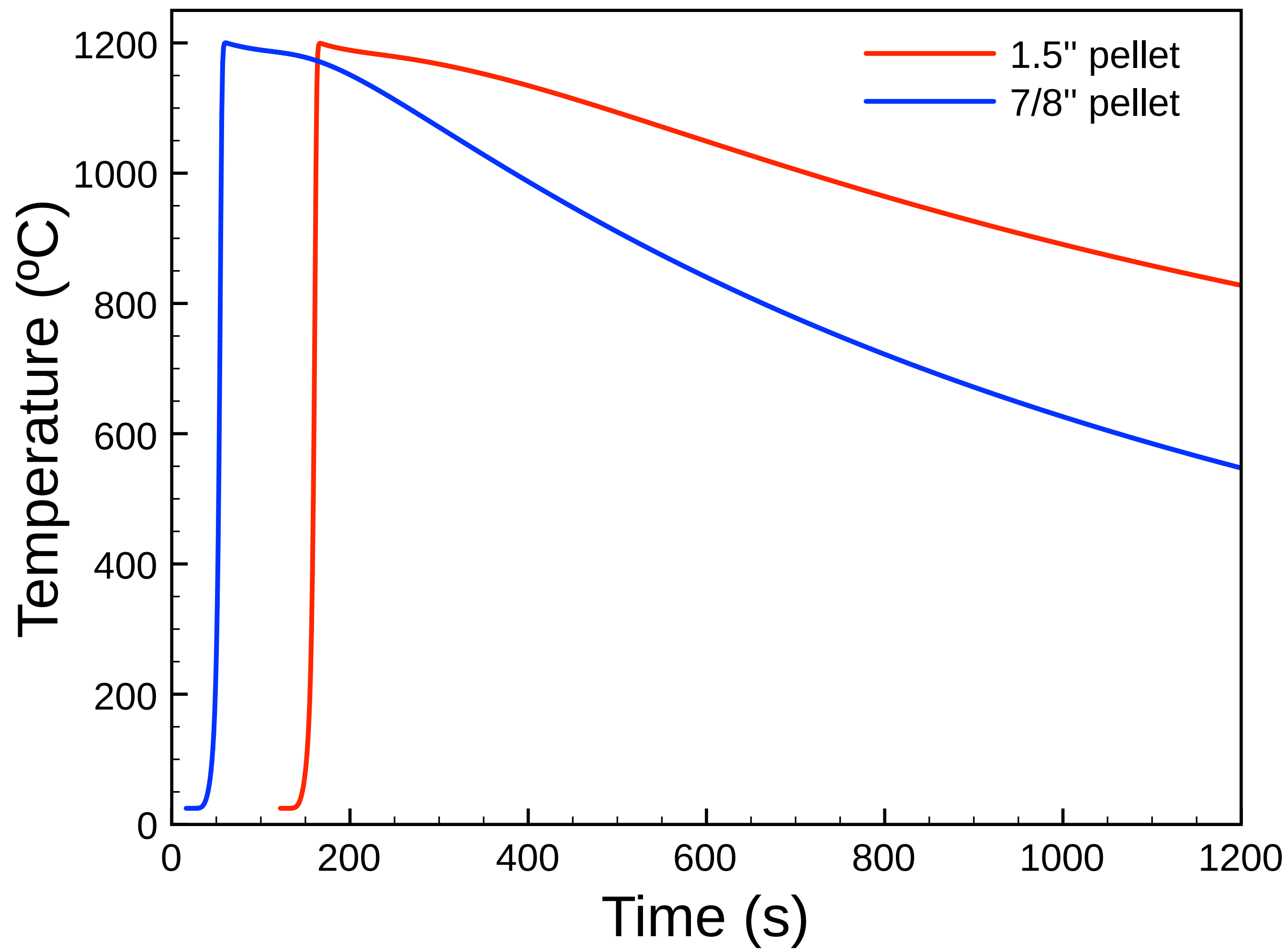
Propagation speed is very sensitive to thermal conductivity

Pellet size

Increased from 7/8” to 1.5”
All equations are the same, only geometry and mesh are modified



Experimental data



Model results

Conclusions

- COMSOL Multiphysics can be used to model SHS reaction
- SHS reactions are very sensitive to thermal conductivity
  - Reaction front movement
- Model predicts that large pellet diameter results in slower cooling rate
- Things to add: O_2 diffusion, pellet expansion