Synthesis and 2-Dimensional Modeling of Self-Propagating High-Temperature Synthesis of $La_{0.6}Sr_{0.4}MnO_3$

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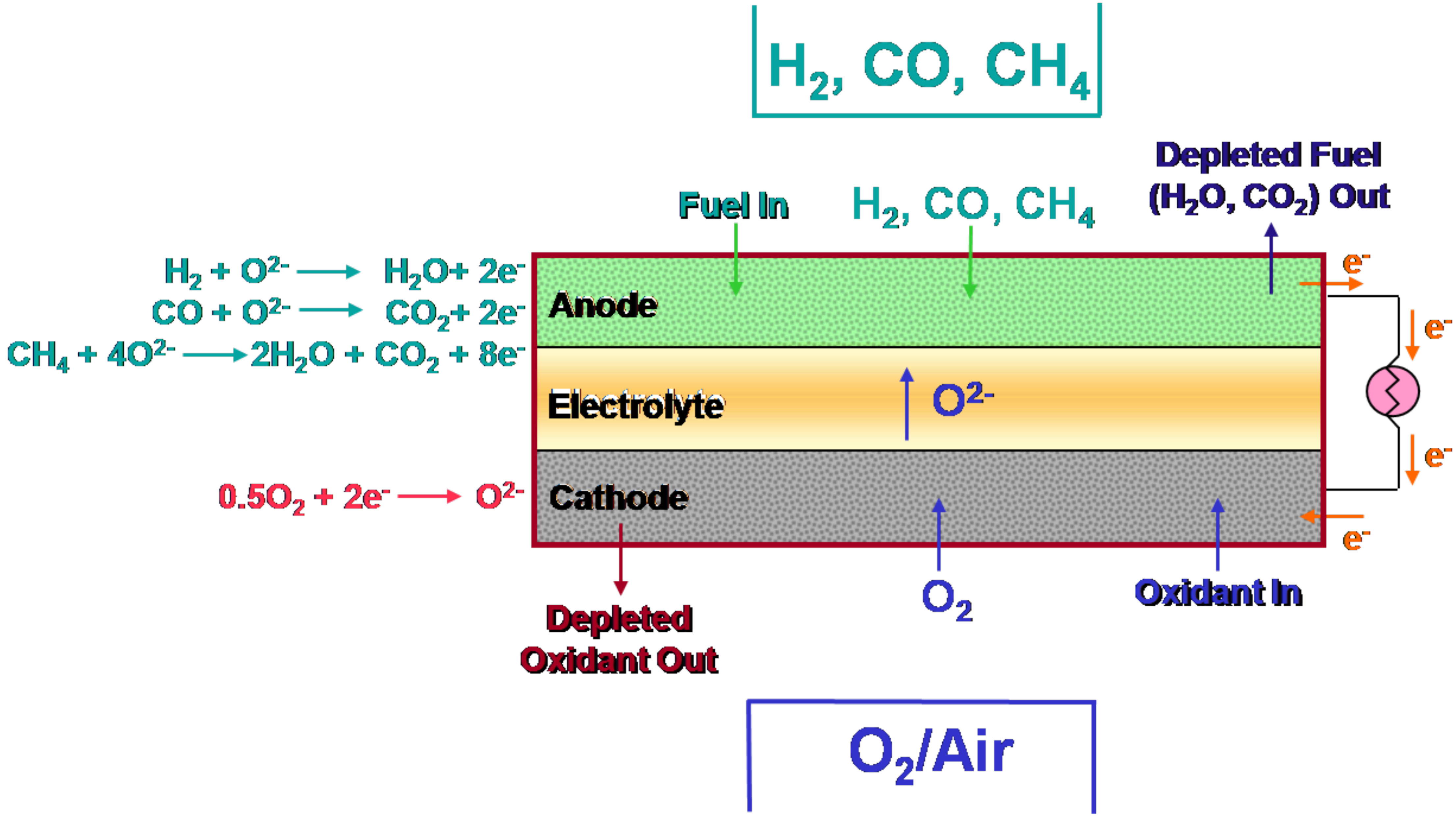
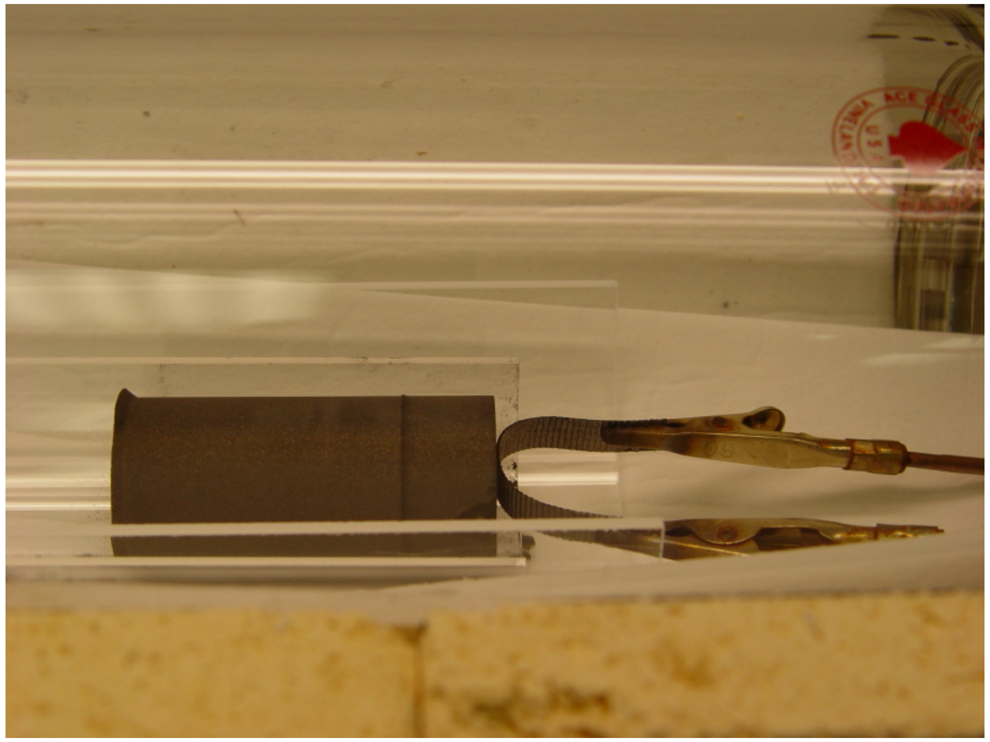
Solid Oxide Fuel Cell

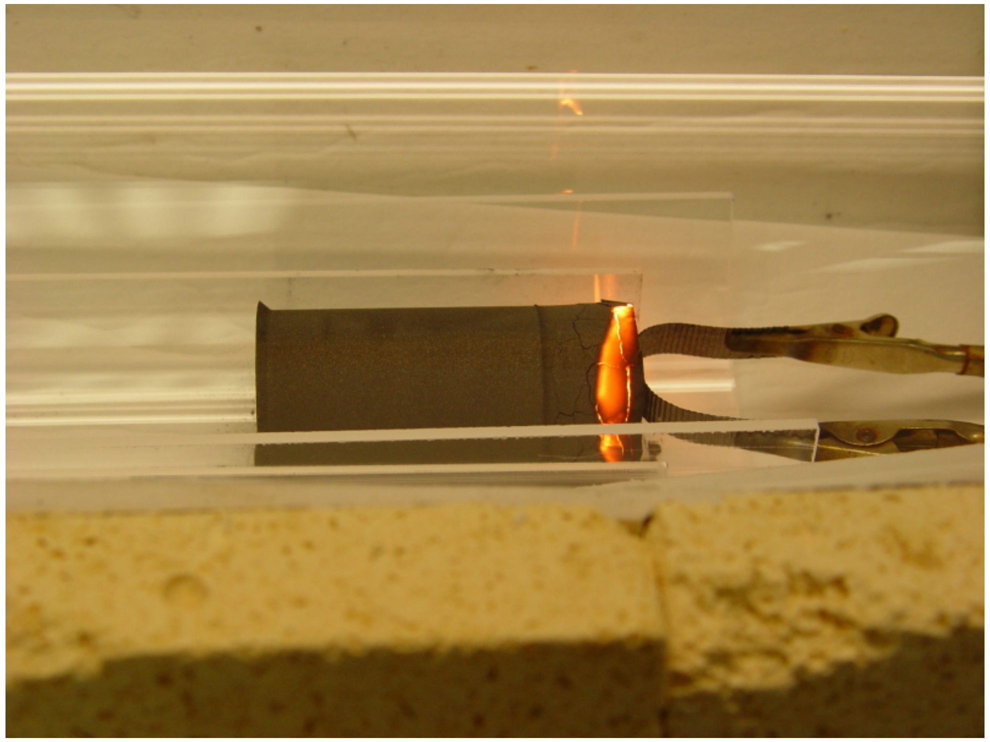


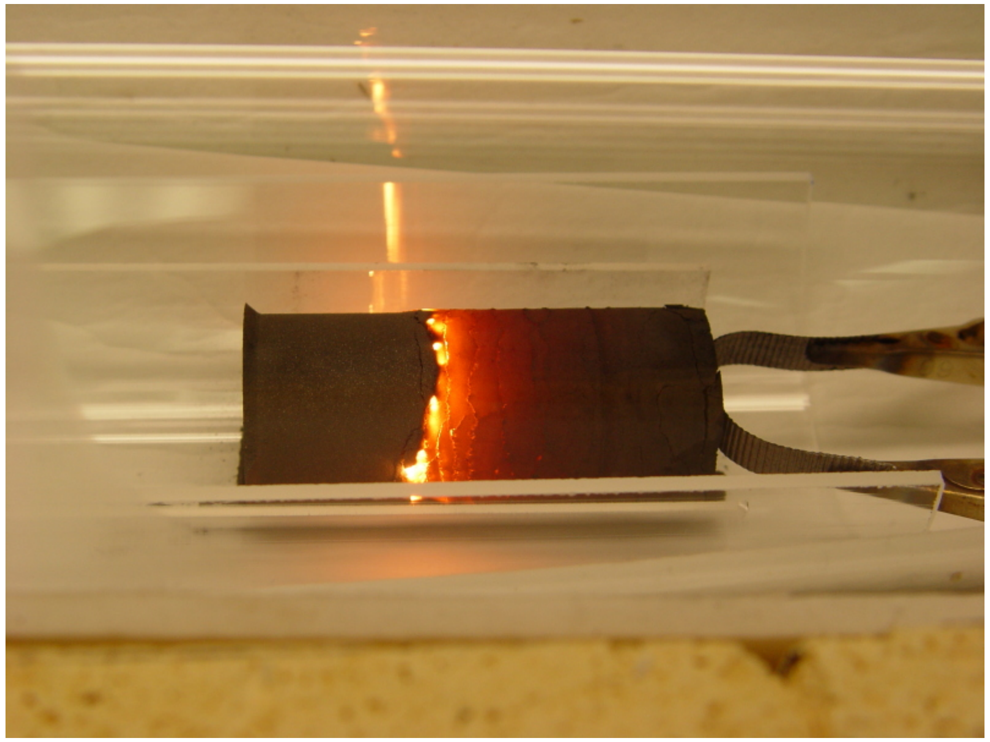
SHS - Fast and Cheap Synthesis

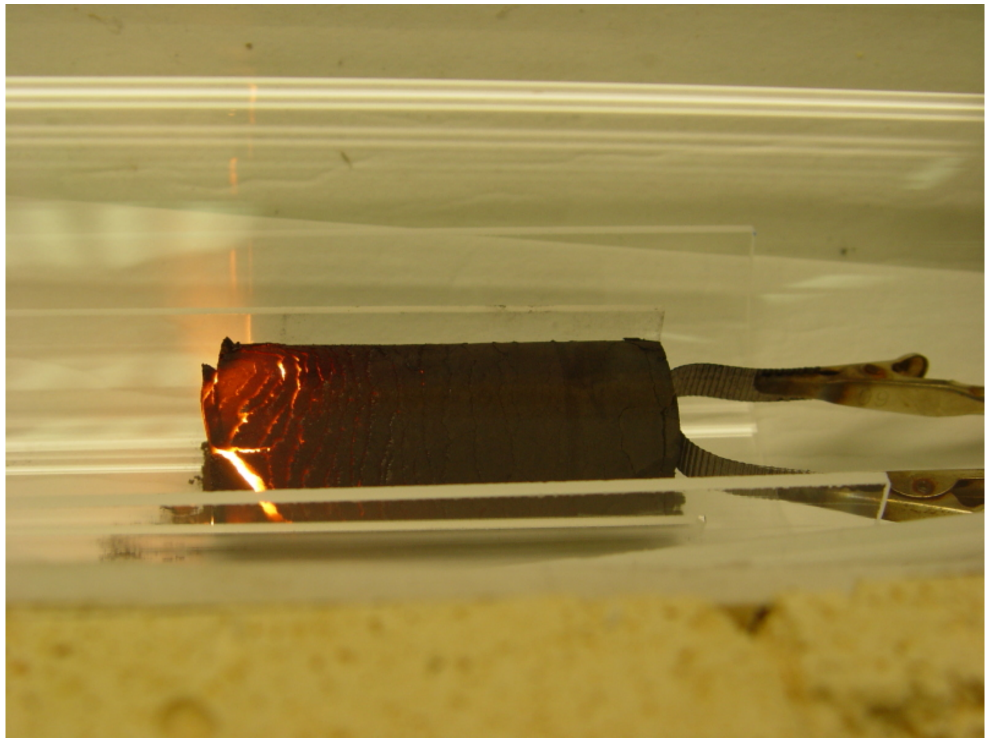
- Low cost (low energy requirements)
  - Cheaper then sintering
- Fast reaction (a few seconds)
- Highly exothermic reaction
- Fine powders
- High purity

Self-propagating High-temperature Synthesis of SOFC Cathode Materials









System Description

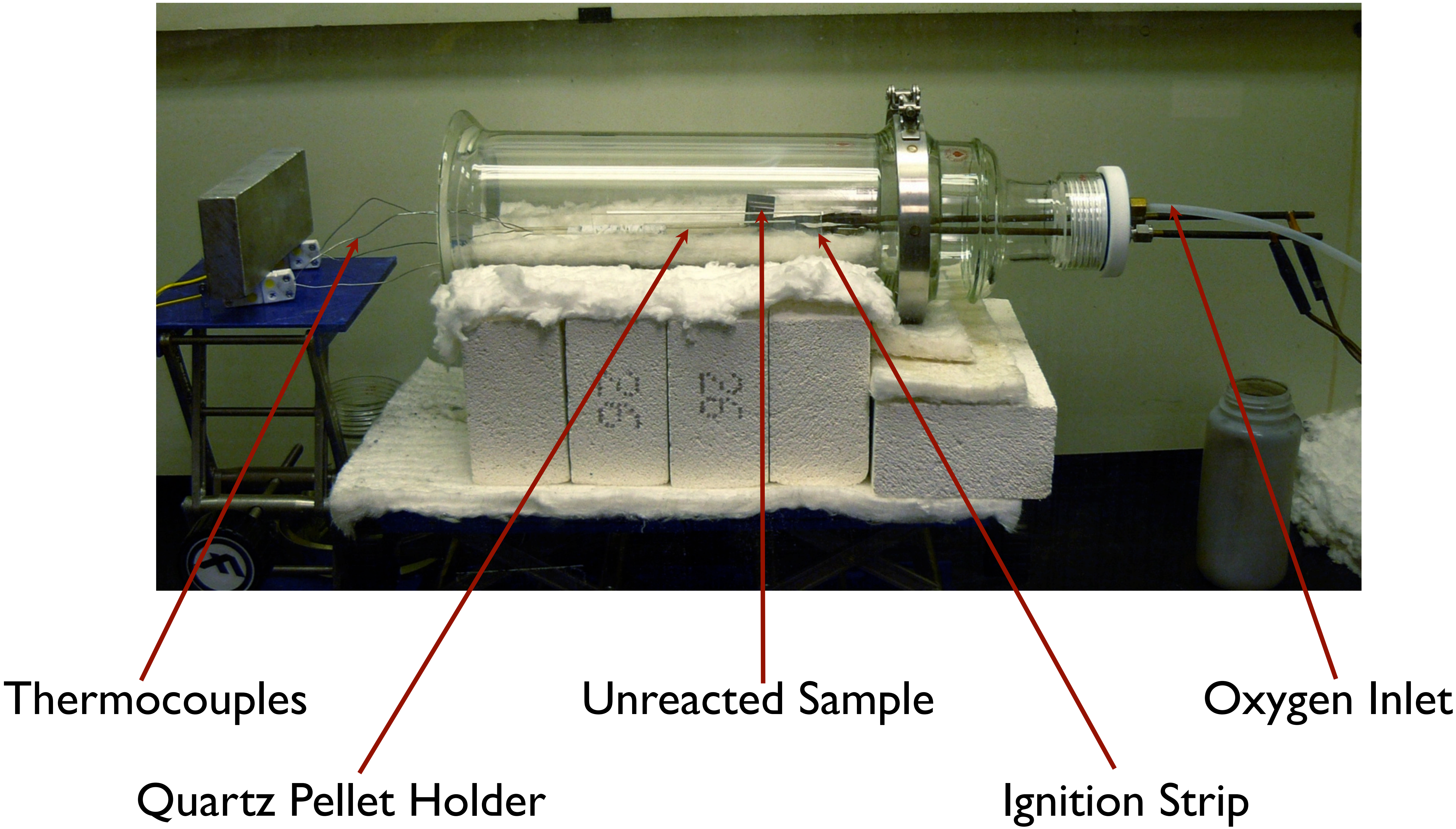
$$0.3\ La_2O_3 + 0.4\ SrO_2 + 0.75\ Mn + 0.125\ Mn_2O_3 + 0.4625\ O_2 \rightarrow La_{0.6}Sr_{0.4}MnO_3$$

- Adiabatic temperature: 3,200K
- Heat of reaction: -436 kJ/mol
- Green mixture is oxygen deficient
- O_2 by diffusion
- Slow but steady propagation

Sample Preparation

- Mixed in stoichiometric ratios
- Mixed in ball mill (with no balls) for 4 hrs
- Pressed into pellets in a hydraulic press
  - 0.75 metric ton, 3 cm long, 7/8” diameter
- Diluted with previously reacted product
  - SHS + 8 hours in furnace at 1,200 °C

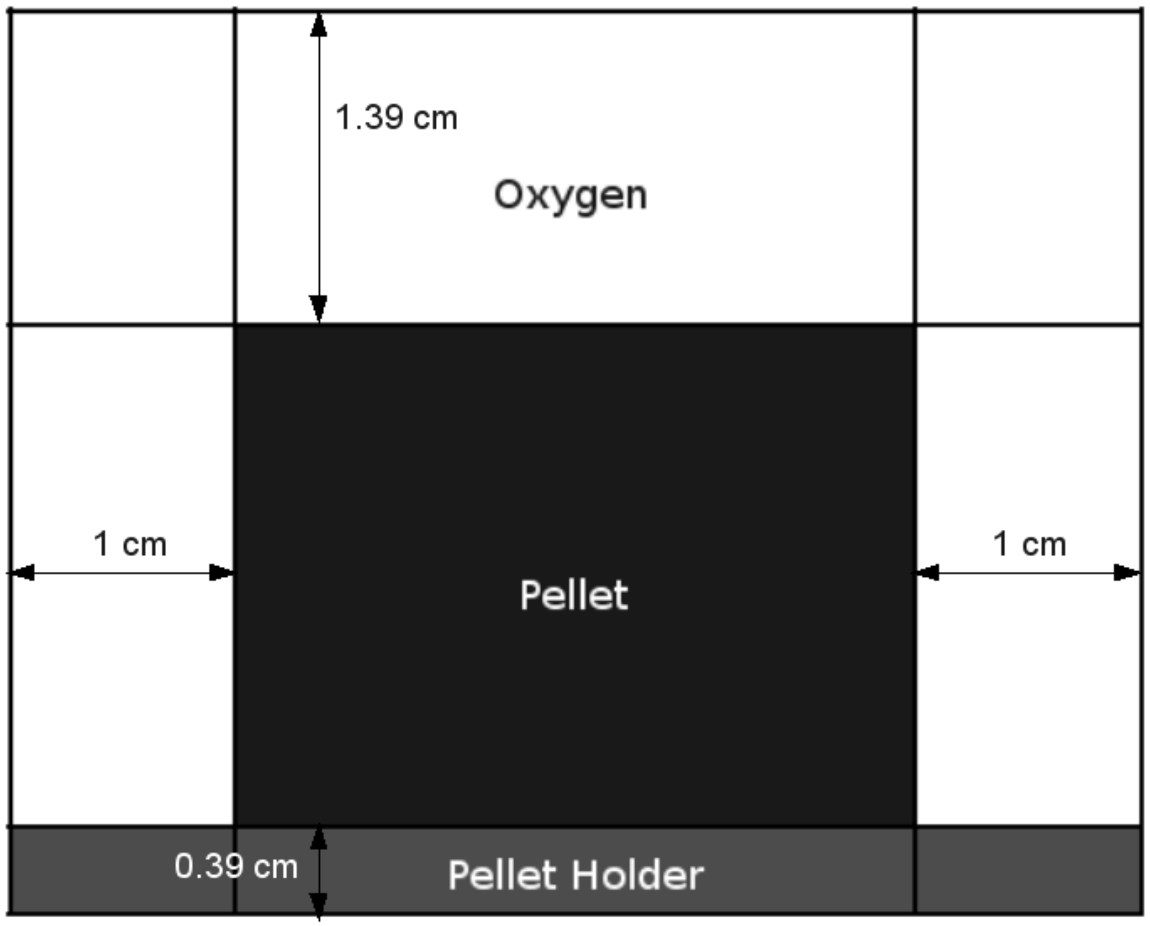
Experimental Setup



Assumptions

- Constant oxygen flow (independent of temperature)
- Constant diffusivity
- Constant densities (LSM and reactants)
- All heat is released during Mn oxidation

Geometry



- Pellet: 3 cm x 7/8 inch, 0.39 cm quartz pellet holder
- 1 cm of oxygen on both sides and 1.39 cm above

Model Description

Energy Balance

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

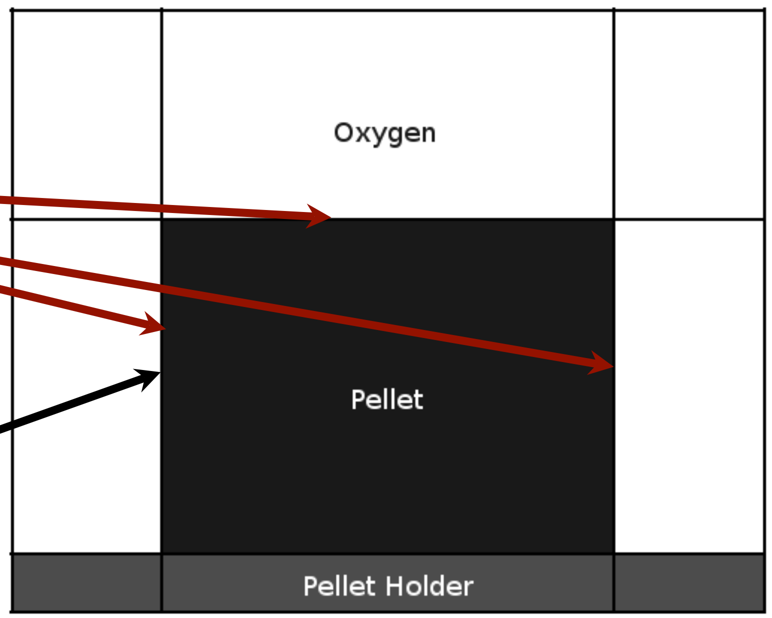
$$\mathbf{n} \cdot \left[\left(k_1 T_1 - \rho_1 C_{p1} T_1 \mathbf{u}_1 \right) - \left(k_2 T_2 - \rho_2 C_{p2} T_2 \mathbf{u}_2 \right) \right] = q_0$$

$$q_0 = q_r + q_{nc} + q_{iq}$$

$$q_r = \varepsilon \sigma \left(T^4 - T_\infty^4 \right)$$

$$q_{nc} = h_{nc} \left(T_f - T_\infty \right)$$

$$q_{iq} = 3 \times 10^6 (W / m^3); \; (t > 1.5 \; s)$$



Model Description

Mass Balance

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

$$\frac{\partial C_{SrO_2}}{\partial t} = -k_{SrO_2} C_{SrO_2}$$

$$\frac{\partial C_{O_2}}{\partial t} = k_{SrO_2} C_{SrO_2} - \frac{\partial \eta}{\partial t} 0.75 \eta C_{Mn_0}$$

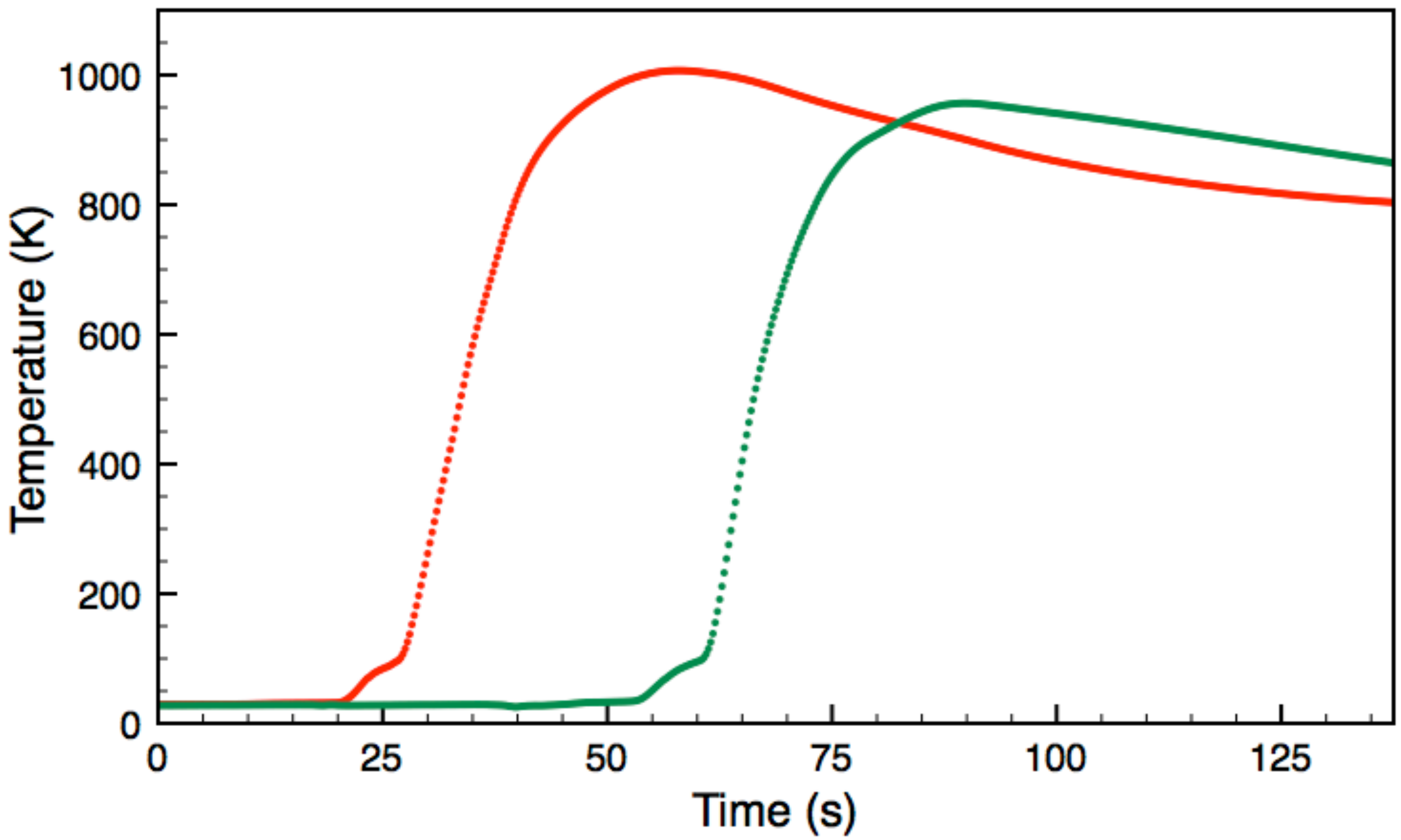
$$D_s = D\frac{\varepsilon}{\tau}$$

Kinetics (Mn Balance)

$$-\Delta H_r = \frac{\partial \eta_r}{\partial t} \rho \int C_p \, dT$$

$$\frac{\partial \eta_r}{\partial t} = \left(1 - \eta_r\right)^n k_r e^{\frac{-E_0}{RT}}$$

Temperature Data



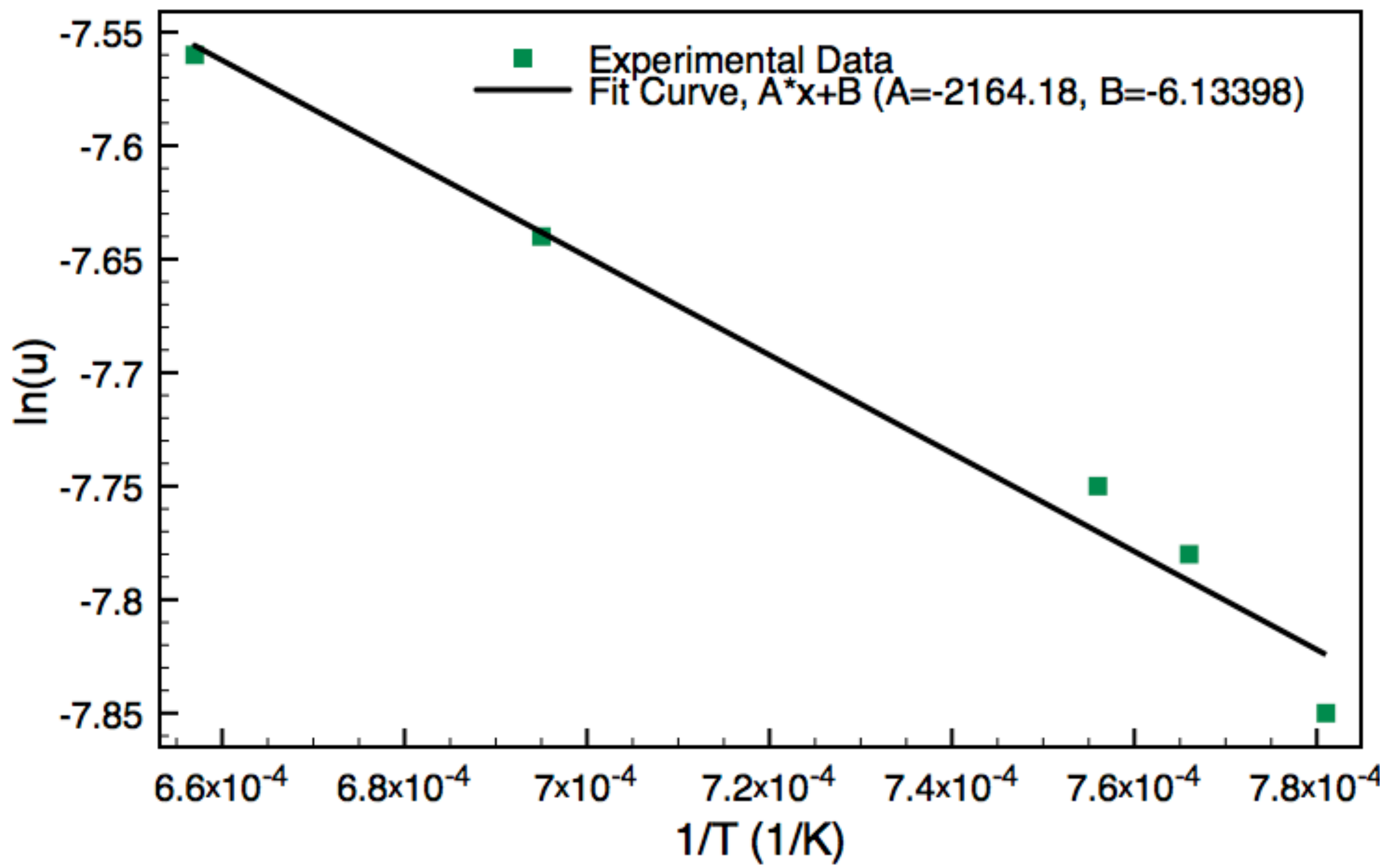
Sample recorded temperature data (5% wt dilution)

- Data points were collected at 4/s
- Used to estimate velocity (difference between the two peaks)
- Combustion front movement velocity = 0.44 mm/s

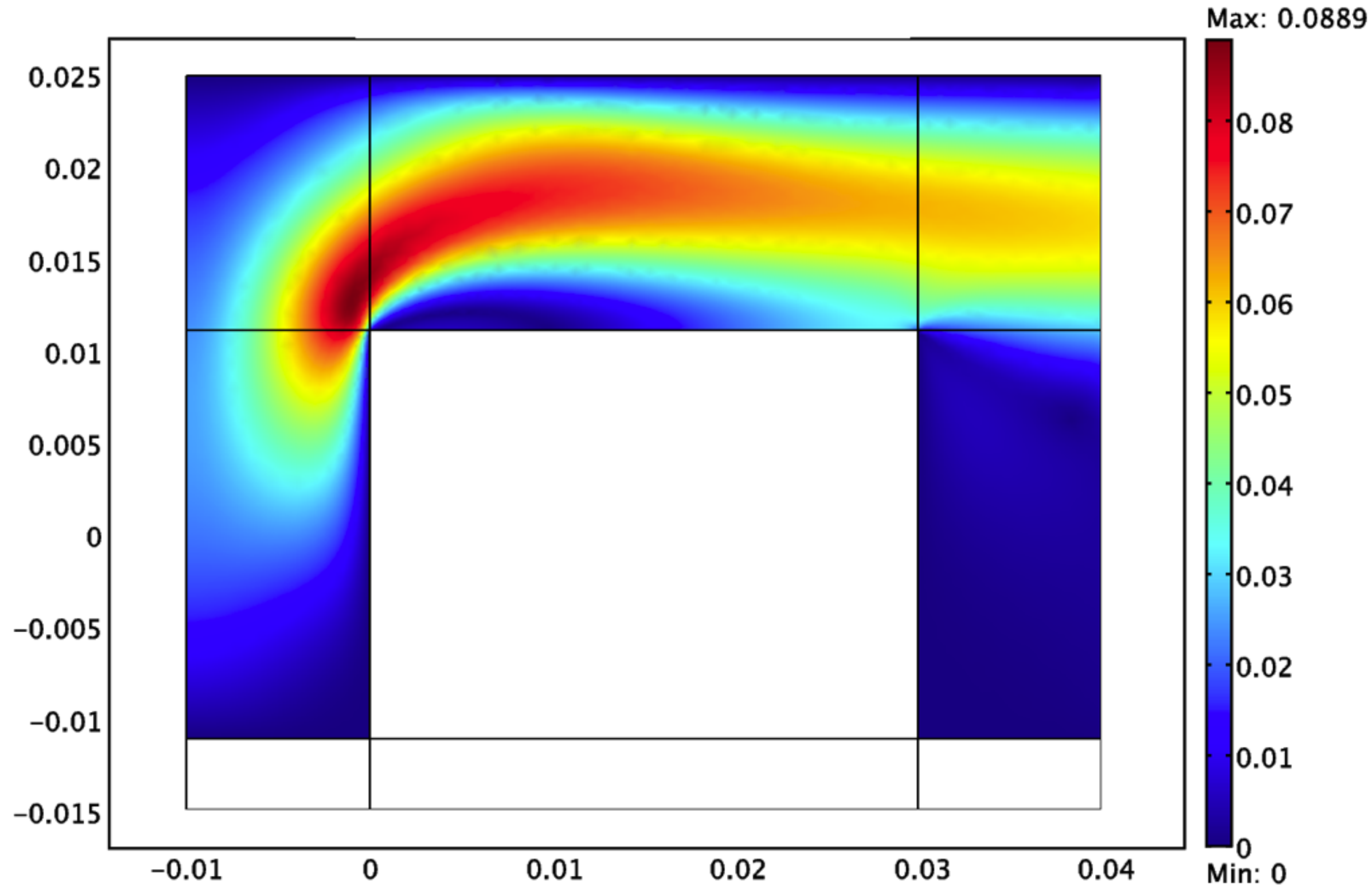
Activation Energy

Calculated from experimental data: 35kJ/mol

$$u_p = e^{\left(\frac{-E}{2RT_m}\right)}$$



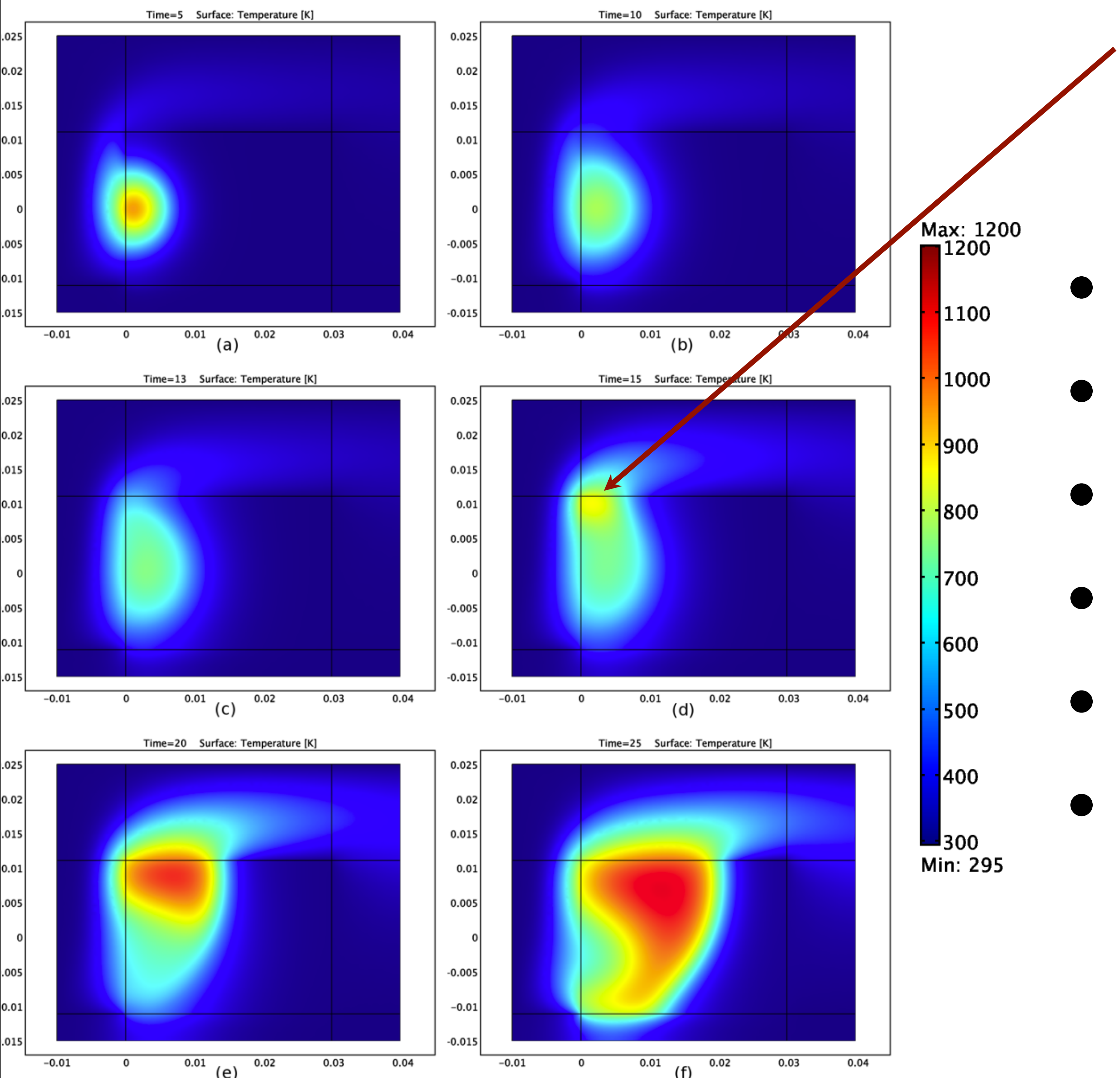
Flow Profile



Flow profile in the reactor

Parabolic profile at inlet (mean x-velocity is 0.02 m/s)
Maximum velocity is at the upper left corner (0.0889 m/s)

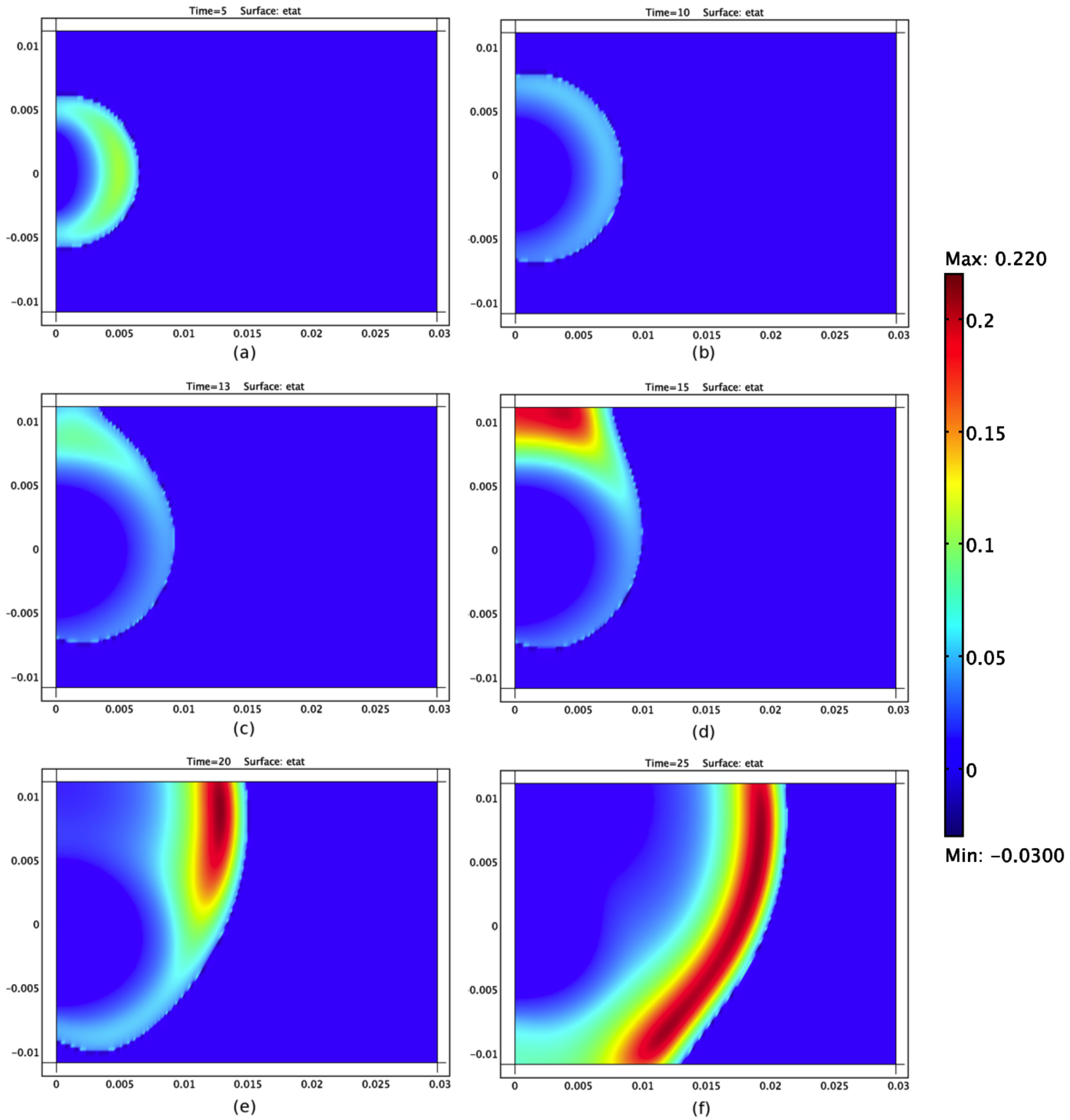
Temperature Profile



Hotspot

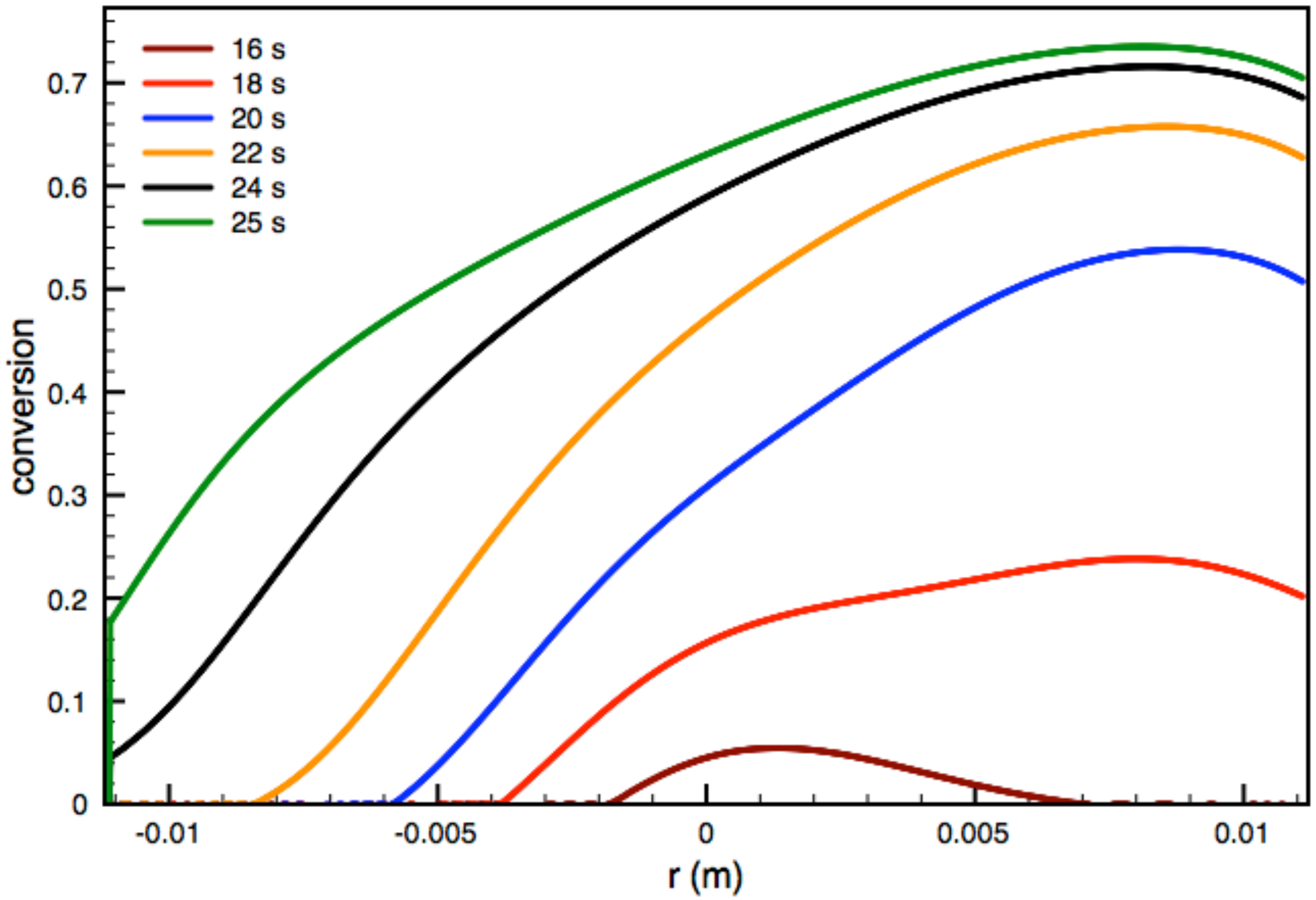
- Unsteady propagation
- Initial heating - ignition
- Hotspot - heat accumulation
- Lower T near pellet holder
- Heat loss to the holder
- Close to experimental data

Reaction Rate



- Unsteady reaction
- Starts slowly then increases
- Reaction is slower near the bottom
- Constant maximum rate

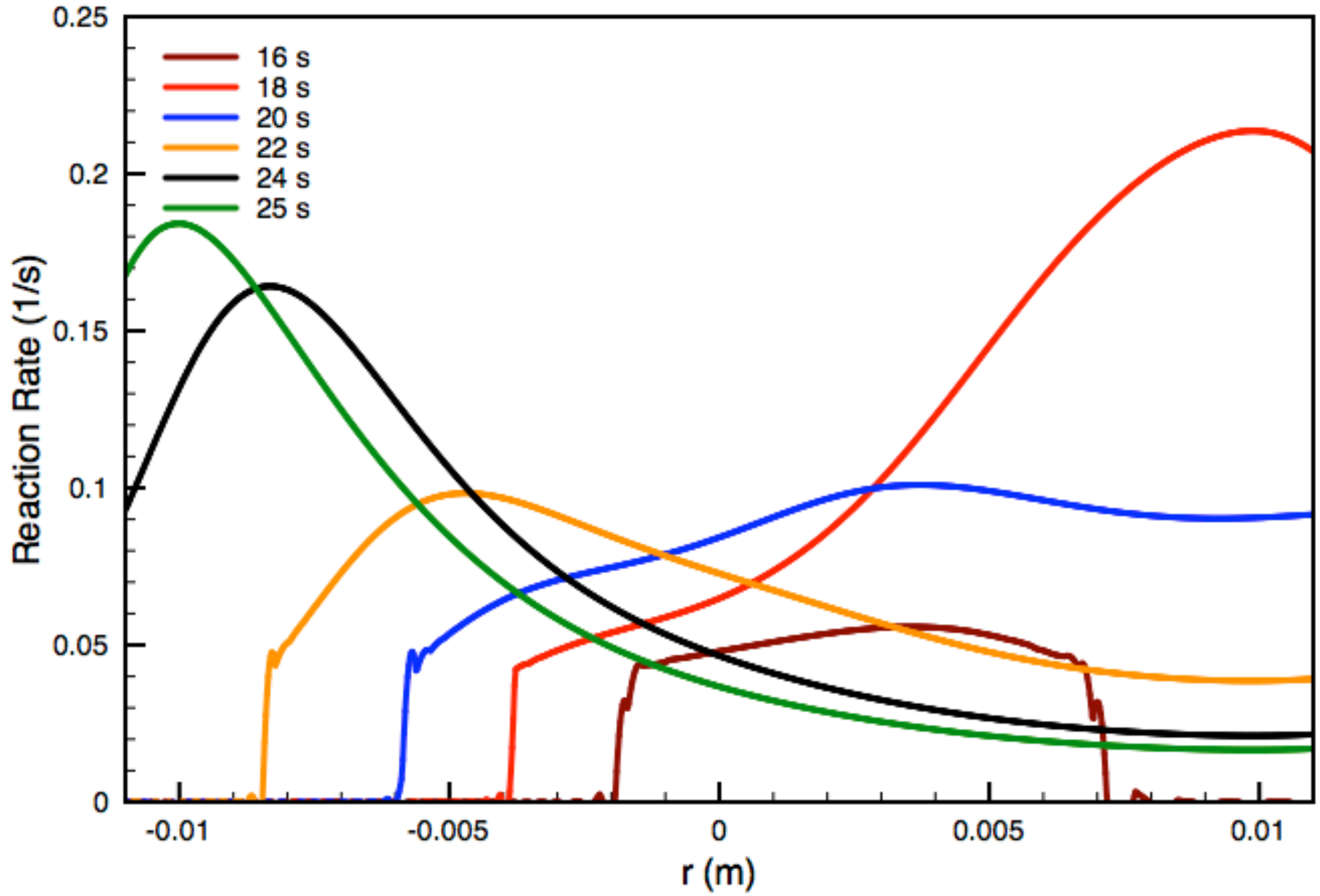
Conversion



Conversion at 1cm as a function of radial position

- Upper half (r > 0) reacts first due to higher reaction rate
- Eventually levels off, only regions near the pellet remain unreacted

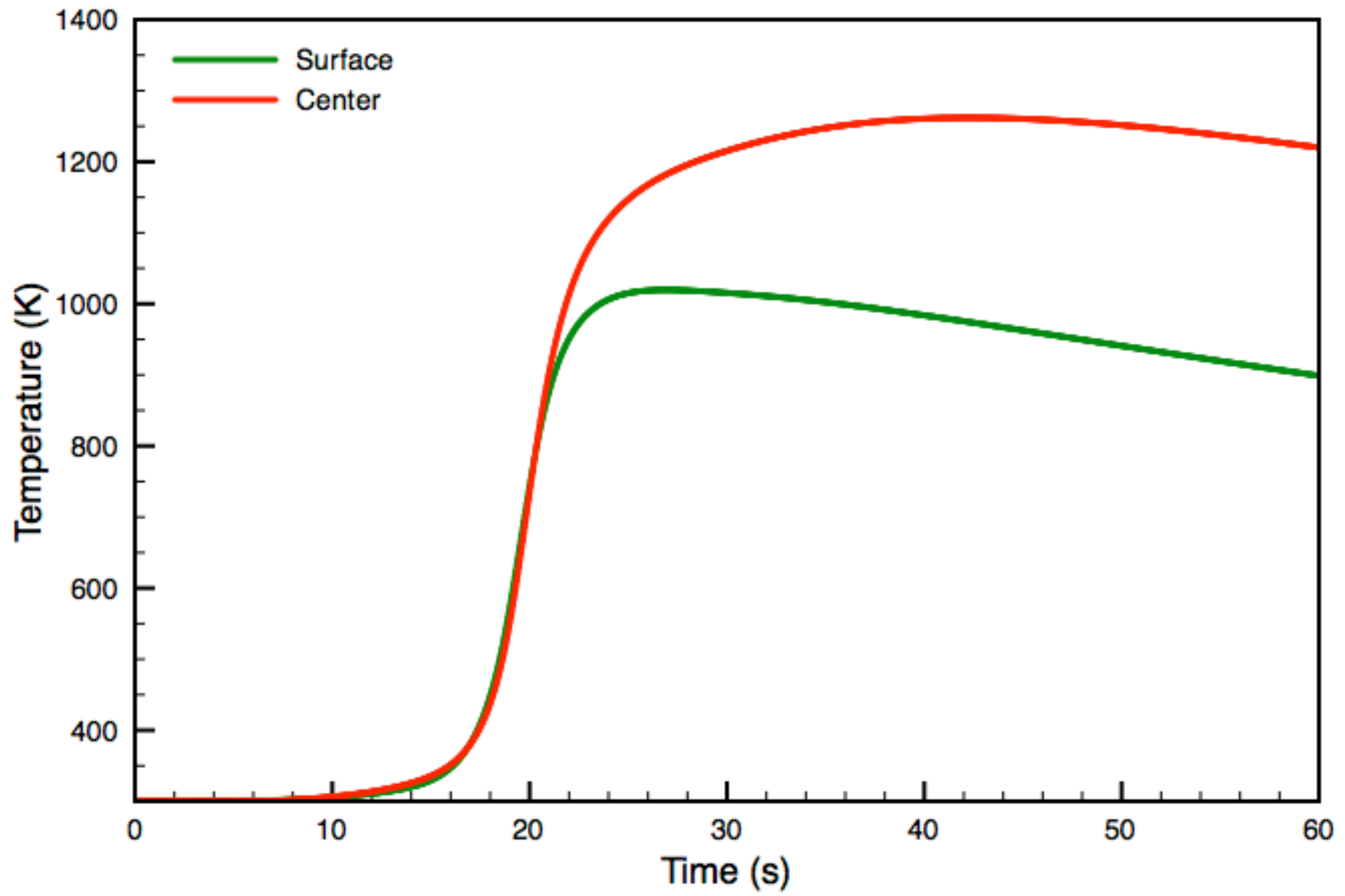
Reaction Rate



Reaction rate at 1cm as a function radial position

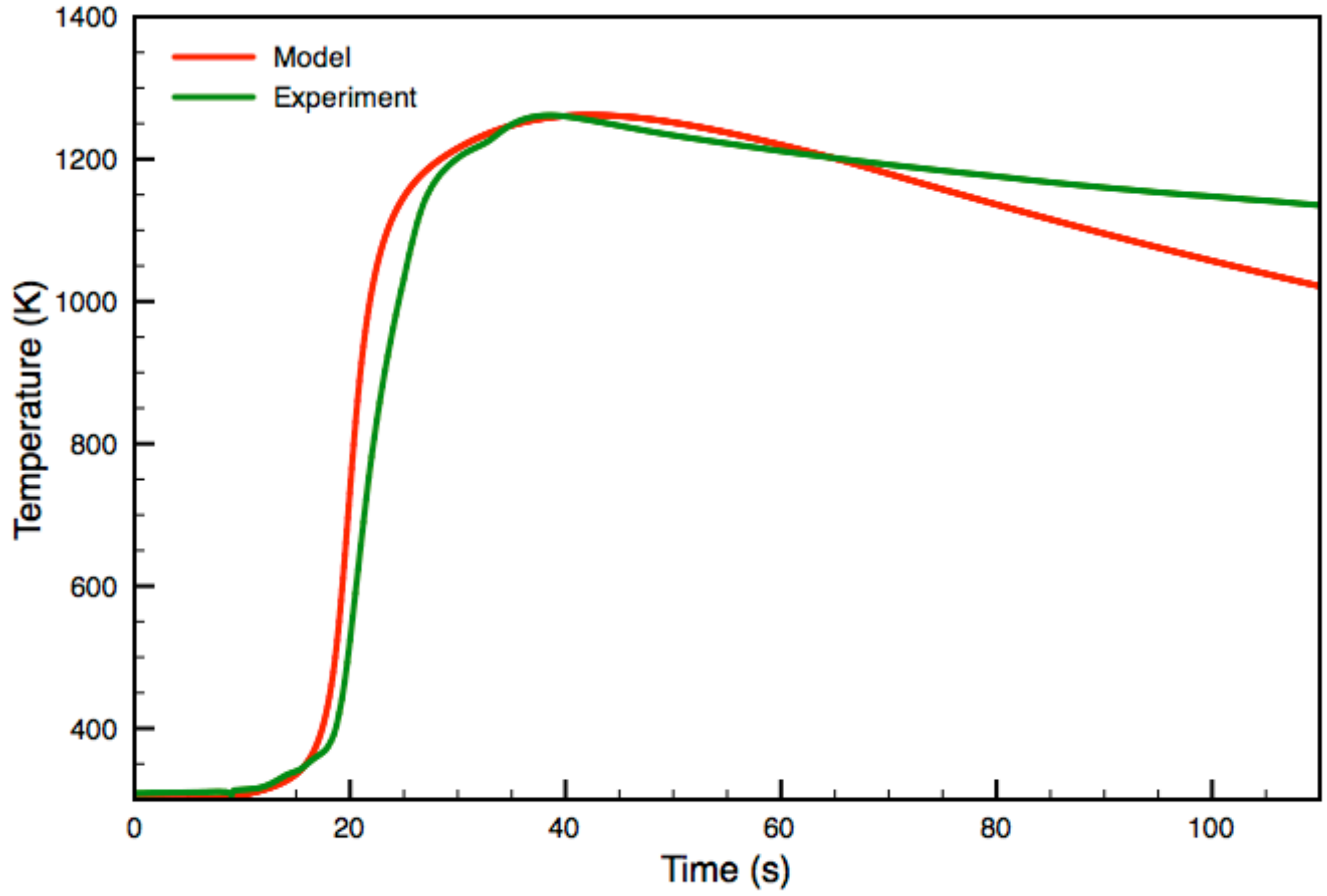
- Reaction propagates first in the upper half
- Reaction shifts from top to bottom

Center and Surface Temperatures



- Surface temperature significantly lower
- Surface cools at faster rate, center stays at maximum temperature longer

Comparison of Experimental Data with Model



- Similar heating trend
- Model cools down at a faster rate

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