Comprehensive Time Dependent Black Liquor Single Droplet Experiments and Predictions

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Introduction

Black Liquor is a byproduct of the paper production process.

Black Liquor consists of primarily lignin from wood and chemicals (NaOH, NaS, Na_2CO_3) which are used to remove the lignin in wood from the pulp.

Black liquor contains approximately ½ the energy content of the wood which is being converted to paper.

The annual energy content of black liquor produced in the United States is 9×10^{17} J or 1% of the total energy production.

Fundamental information on black liquor combustion and gasification is required to produce more efficient recovery boilers or new gasifier designs which will allow a greater fraction of the energy in black liquor to be recovered and potentially be exported.

Objectives

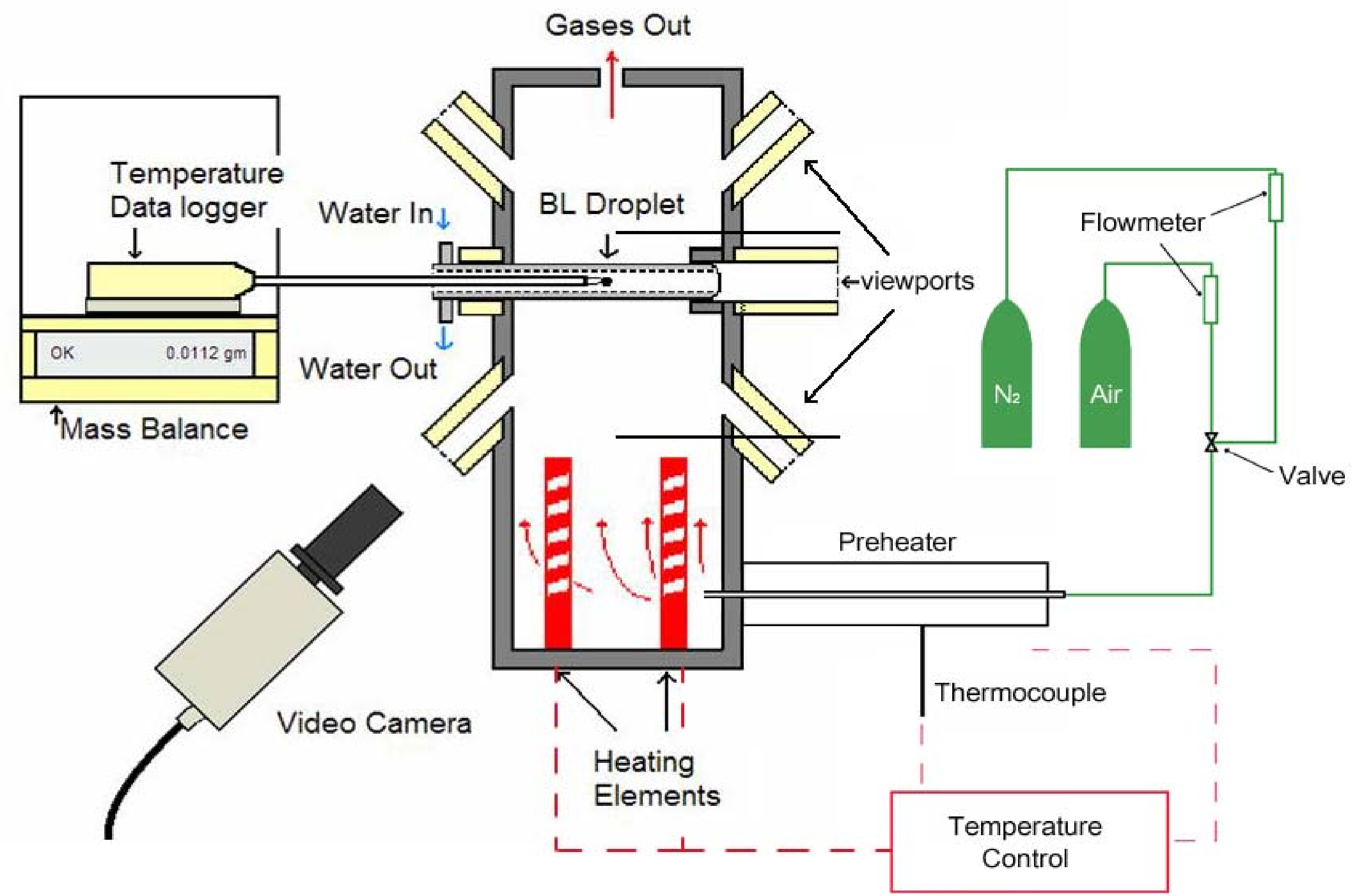
For a single, burning, black liquor droplet, obtain simultaneous measurements of

- Mass loss
- Size and shape
- Temperature (internal and surface)
- Major Gas Species Loss

Compare the experimental results with a 1-D burning droplet model

My presentation will focus on the surface temperature measurements

Method – Droplet Reactor



* The three viewports are in three orthogonal direction

Method – Measurements

Mass: Balance

Interior Temperature: Thermocouple, 250 μm wires

Surface Temperature: 2-Color Thermometry

Diameter: Images, half of widest and narrowest lengths

Product Gas: Molecular Beam Mass Spectrometer (MBMS)

Method – Reactor Conditions

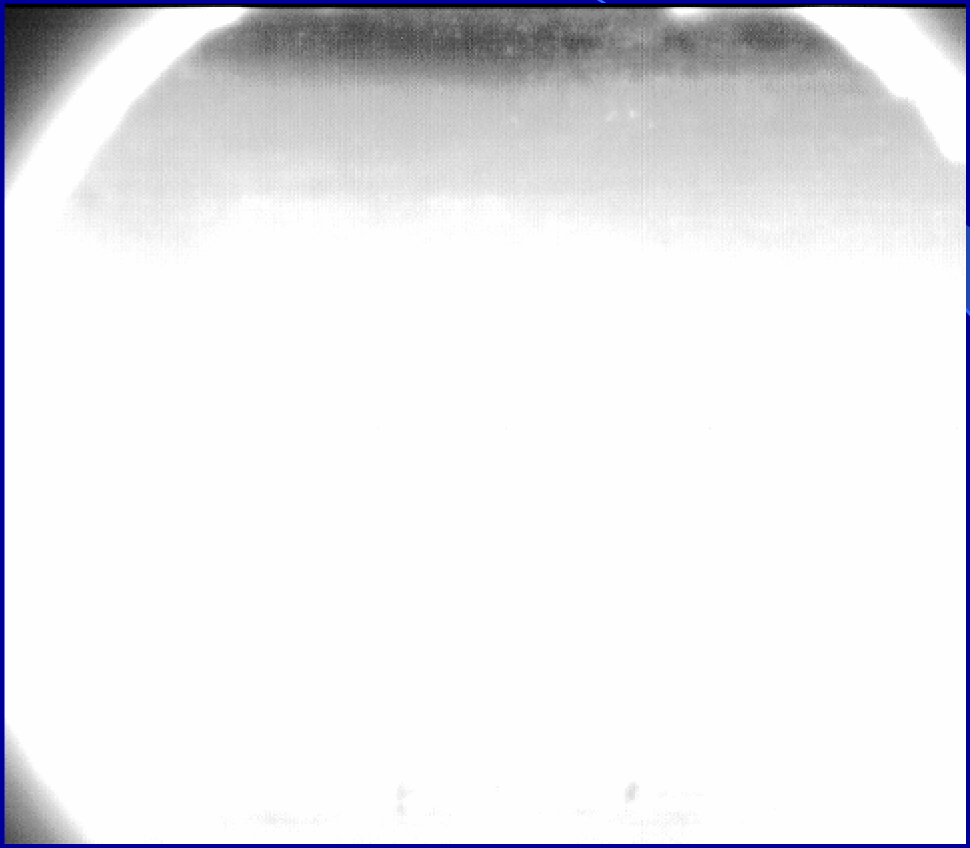
- 1-5 mm droplets
- 5 liquors, mainly 70 % solids contents
- Furnace gases:
  - Air and nitrogen
- Furnace temperatures:
  - 700, 800, and 900 °C
- Data acquisition rates:
  - Cameras: 30 and 60 fps
  - Internal temperature: 100 Hz
  - Surface temperature: 30 fps
  - Mass: 18 Hz
- 3-4 repeats

Method – Liquors Used

	Softwood		Softwood/Hardwood		
	A	B	C	D	E
C	35.6	36.0	39.3	38.6	37.5
H	3.34	3.48	3.64	3.52	3.63
S	4.06	3.49	2.69	3.47	3.92
Na	18.8	22.0	18.4	n.a.	n.a.
K	1.50	1.26	2.20	n.a.	n.a.
Cl	0.10	0.55	0.22	n.a.	n.a.
O	36.6	33.3	33.5	n.a.	n.a.

O – by difference; n.a. – not available

Example - Black Liquor In Air



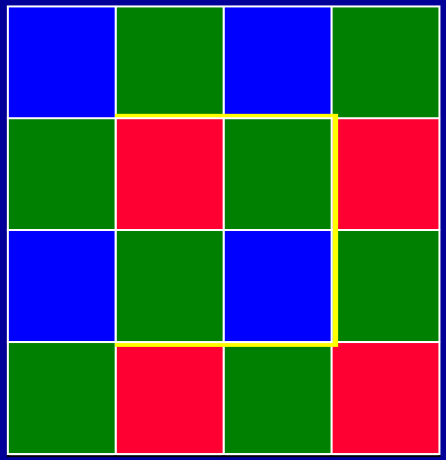
Method – Digital Cameras

Digital Camera collects light on an array of detectors. A 4x4 array is shown below

A mask is placed over the detectors allowing either red, green or blue light through to the detector as shown, known as the Bayer pattern

Each individual detector is called a pixie, a group of four detectors consisting of one red, two green, and one blue is called a pixel

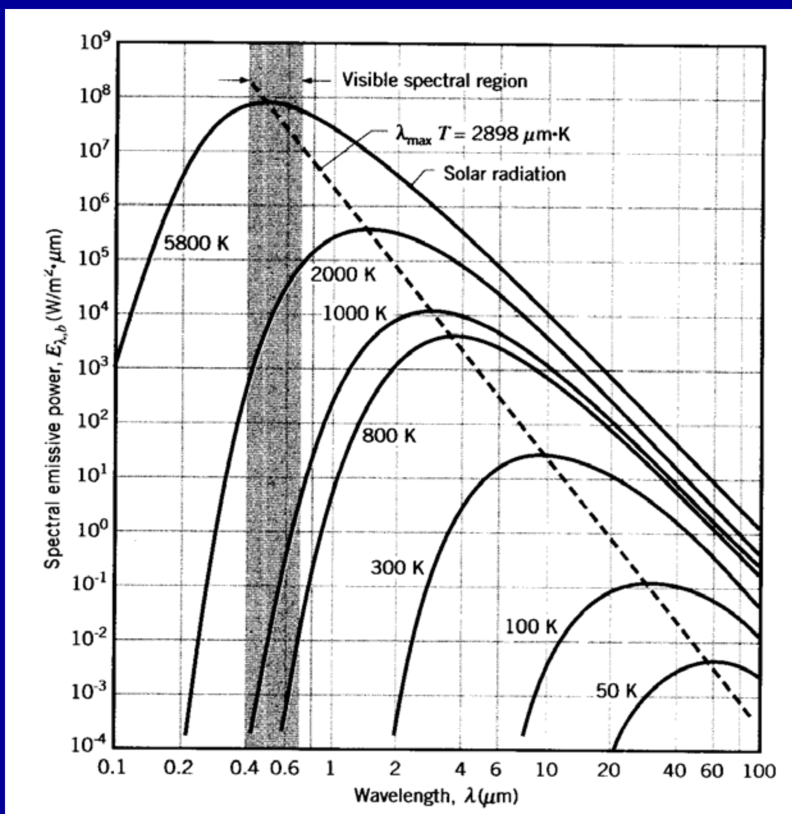
With a little luck and a lot of perseverance you can find a camera manufacturer that sells software that allows the recording of the absolute charge (voltage) collected on each individual pixie



Method – Radiation Thermometry

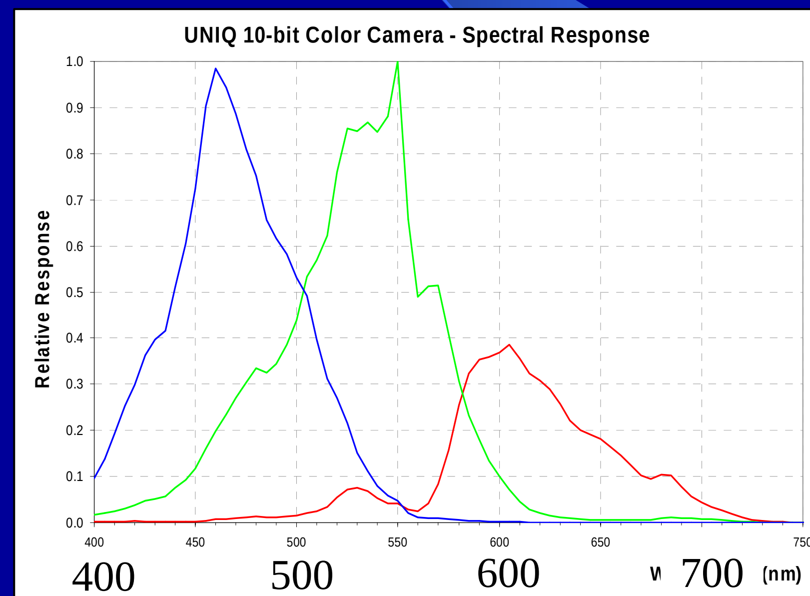
The total intensity and ratio of intensity at different colors can be used to measure temperature

Spectral Emission = $\varepsilon_\lambda E_{b,\lambda}$



Adapted from Incropera and DeWitt

Camera's Response = α_λ



Method – Surface Temperature

$$P_\lambda = S_\lambda \int_{\lambda_1}^{\lambda_2} \varepsilon_\lambda E(T)_\lambda \alpha_\lambda d\lambda$$

$Where:$

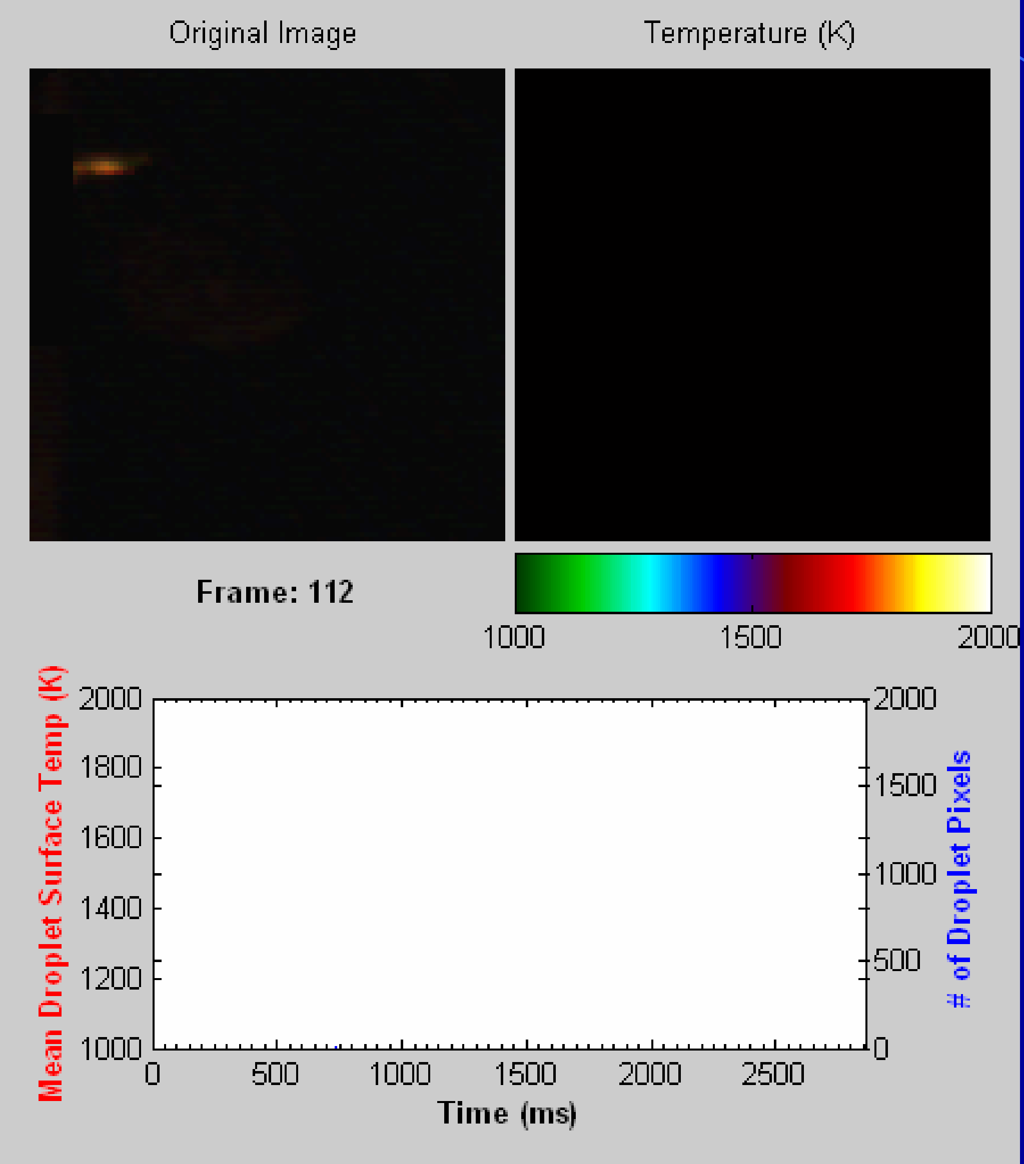
E_λ = Black Body Emissive Power

ε_λ = spectral emissivity

α_λ = spectral response of the detector

S_λ = Sensitivity Volts produced per unit of energy converted by each pixel

Results – Surface Temperature



Gas Temperature: 700 C

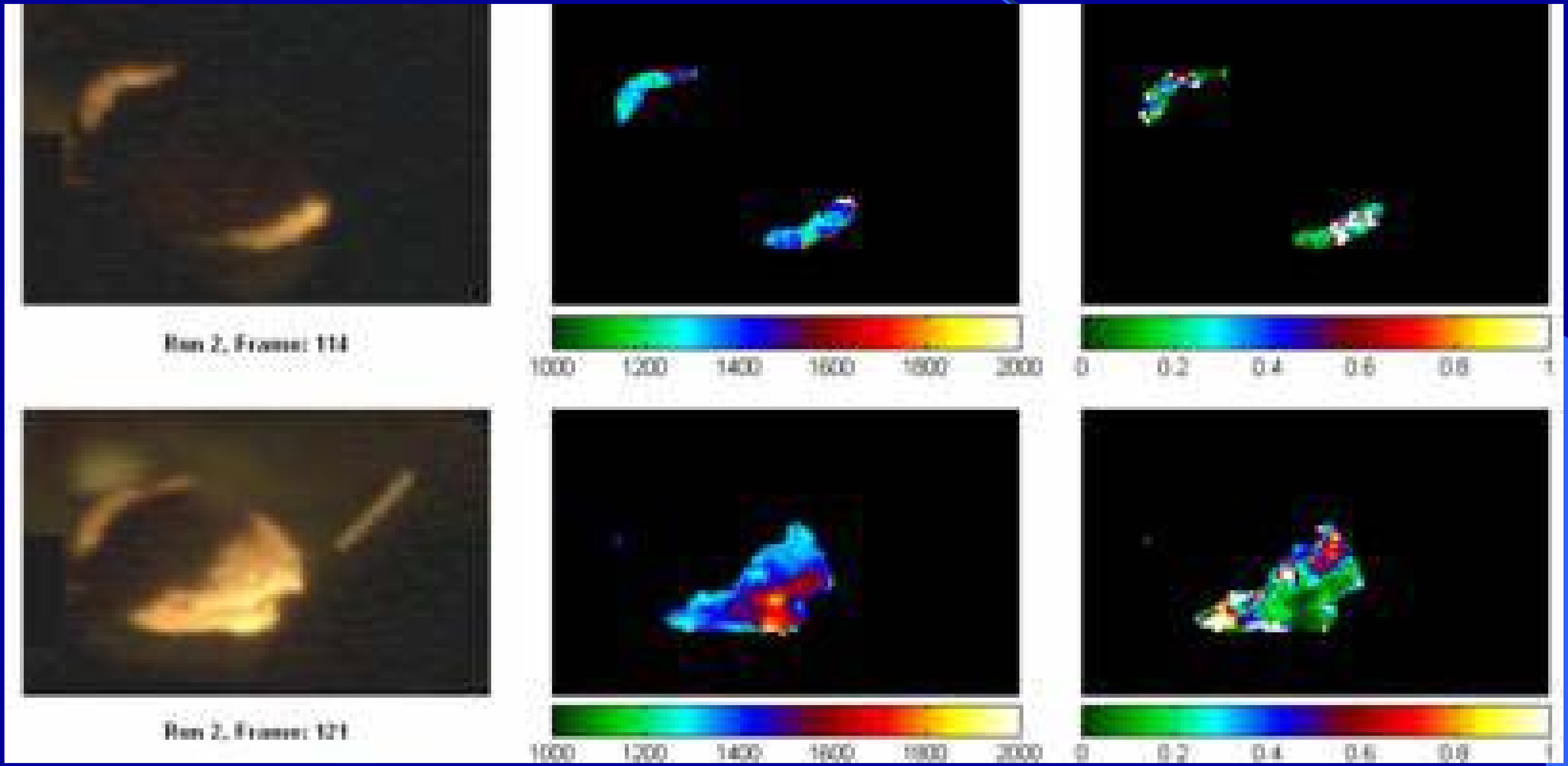
Liquor D

Droplet has been drying

Images start at 750 ms

Method – Surface Temperature

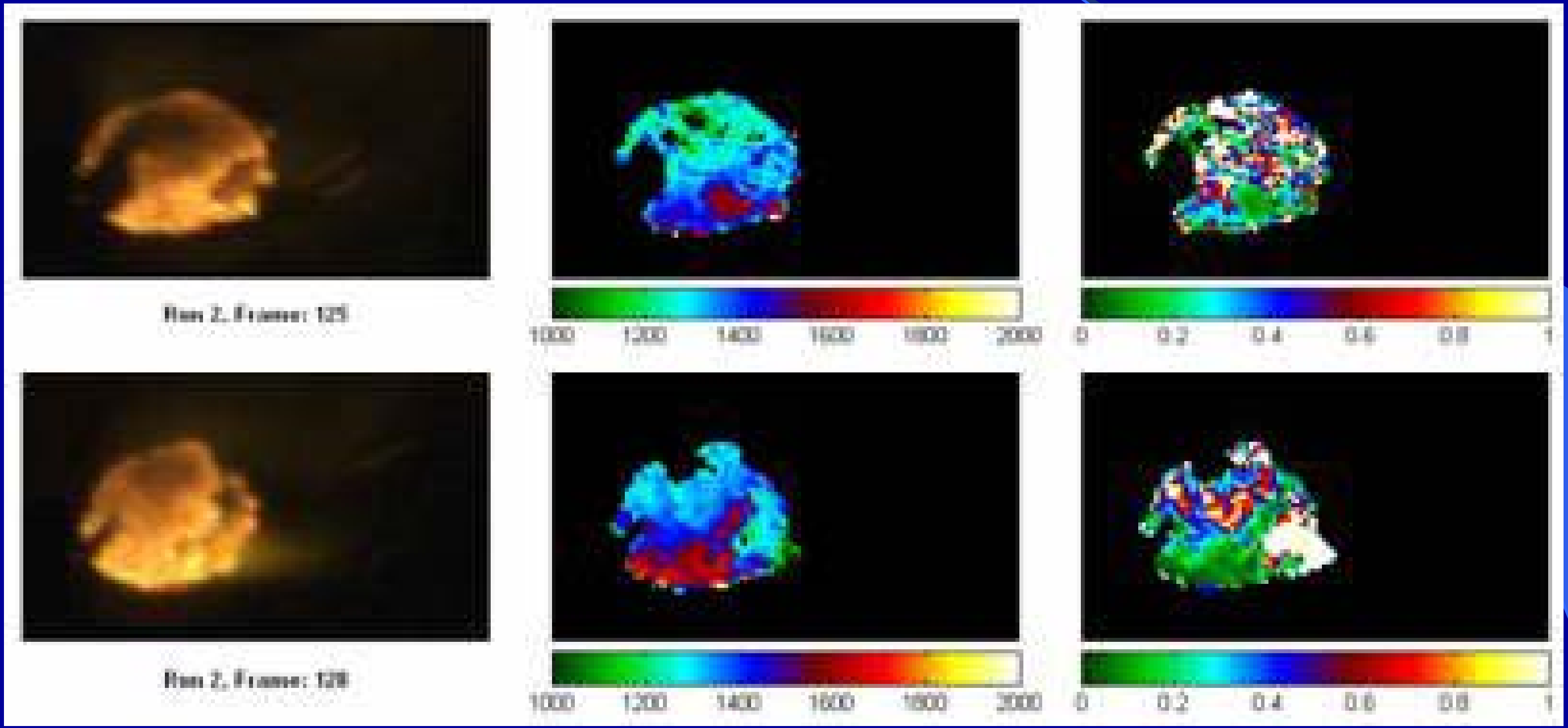
Onset of burning is not uniform across the droplet



Bottom half of droplet burns faster, hotter.
ISP particle is seen leaving the droplet

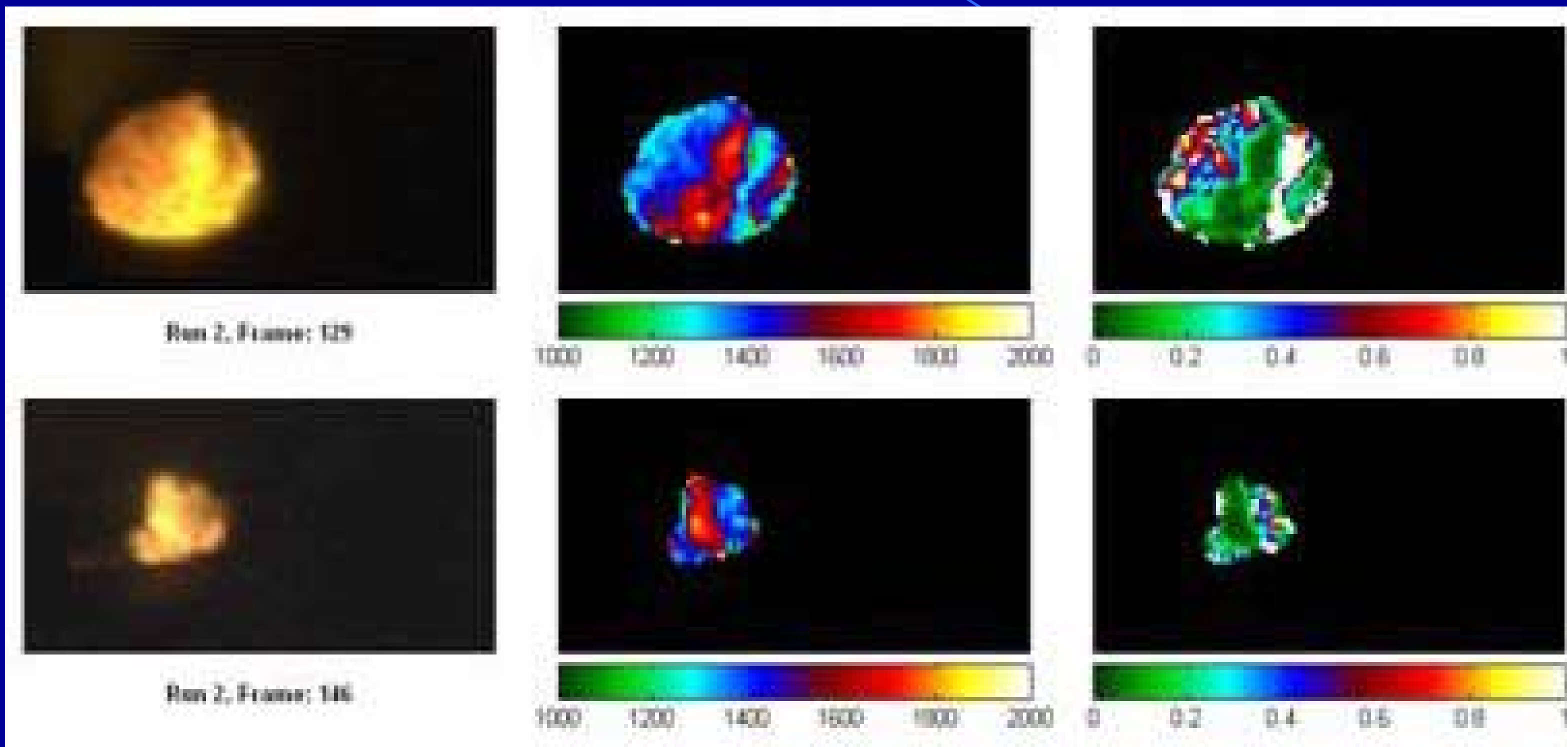
Method – Surface Temperature

Bottom half of the droplet remains the hottest



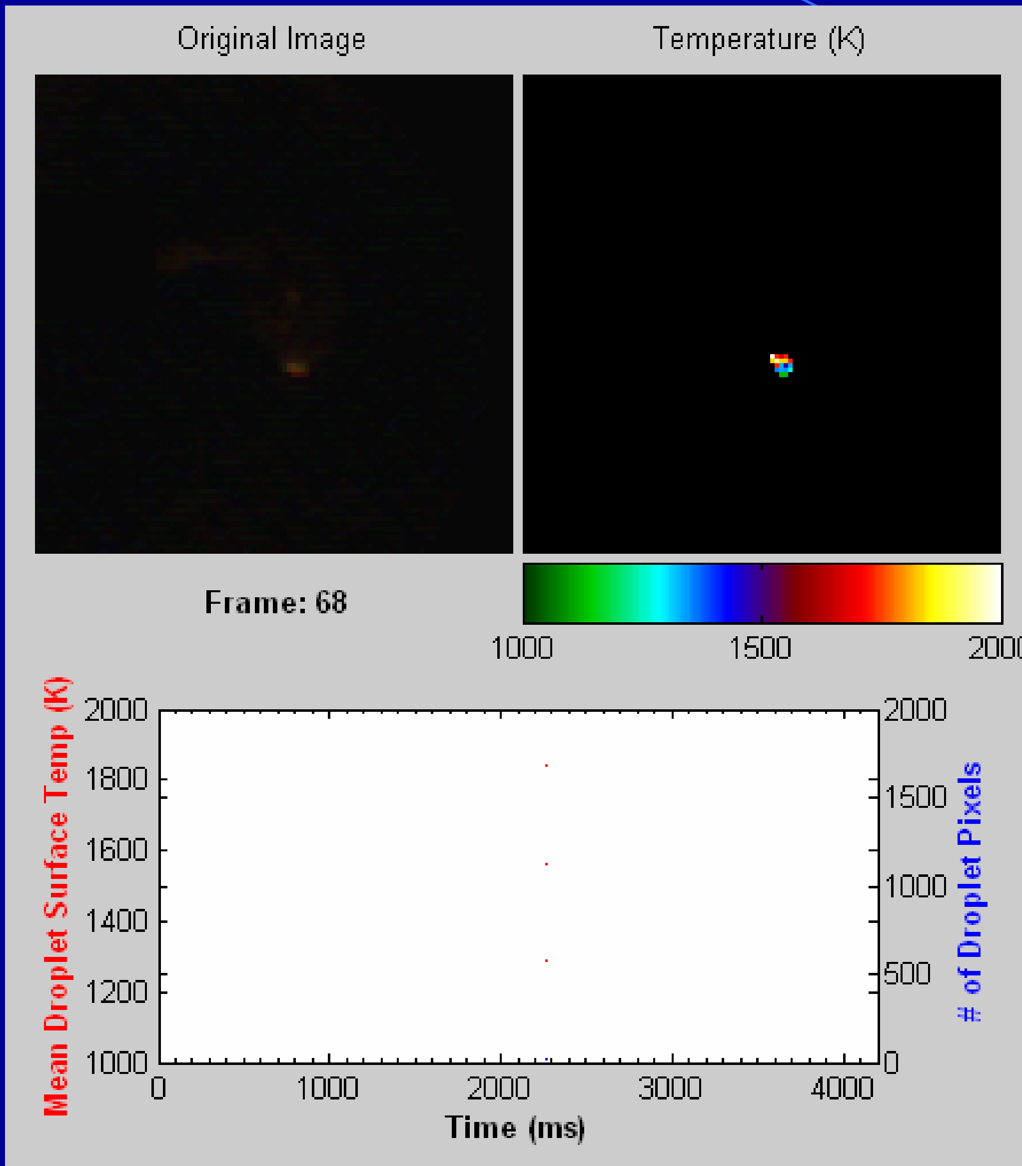
Large temperature variations are observed from one side of the droplet to the other 1700 K vs below 1000 K

Method – Surface Temperature



Initially the particle swells but eventually, the diameter decreases, and the temperature becomes more uniform.

Results – Surface Temperature



Gas Temperature: 800 C

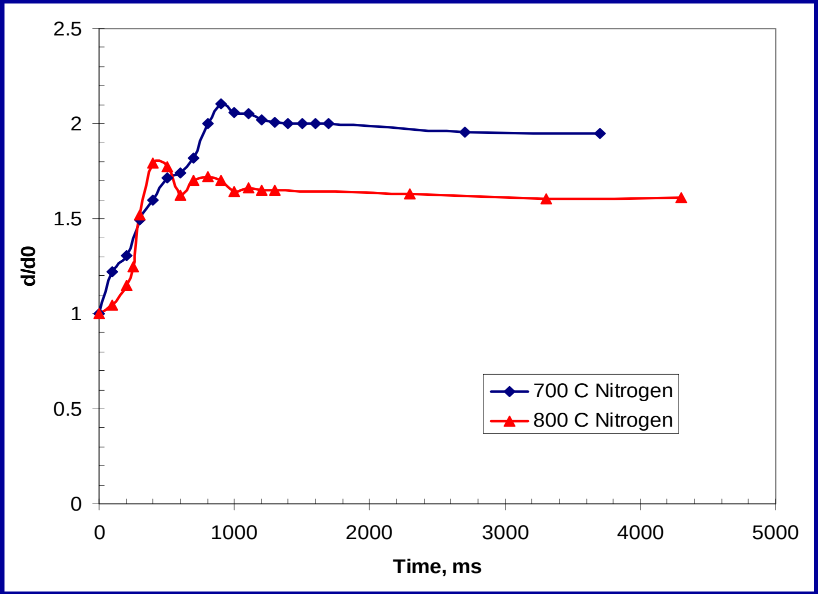
Liquor D

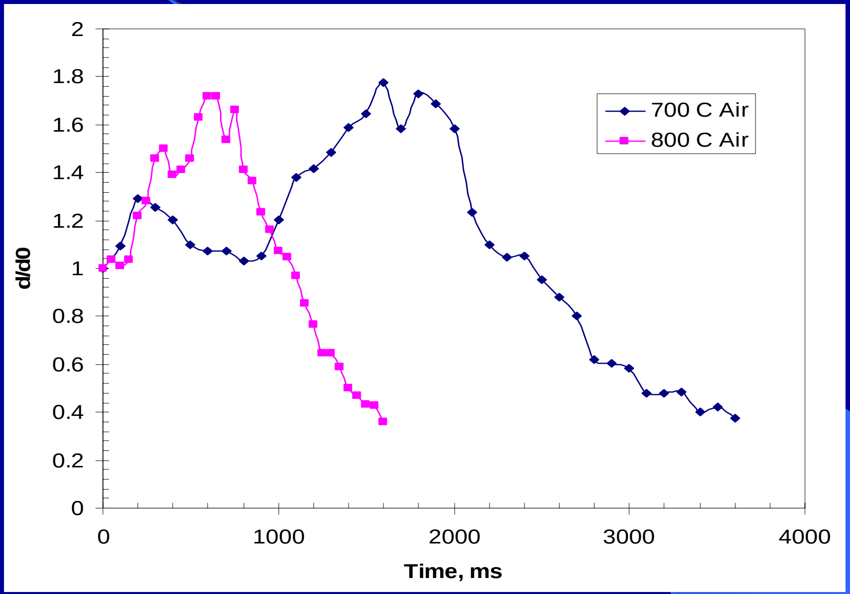
Droplet has been drying

Images start at 2.2 s

Gas emitted produces sooting flame.
The sooting flame is a lower temperature than the char

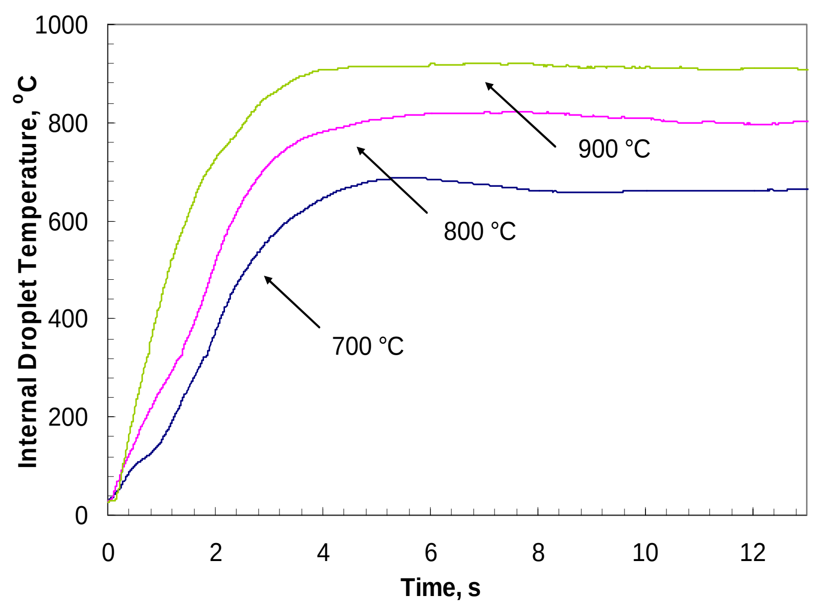
Results
Gas Composition Effects on Swelling

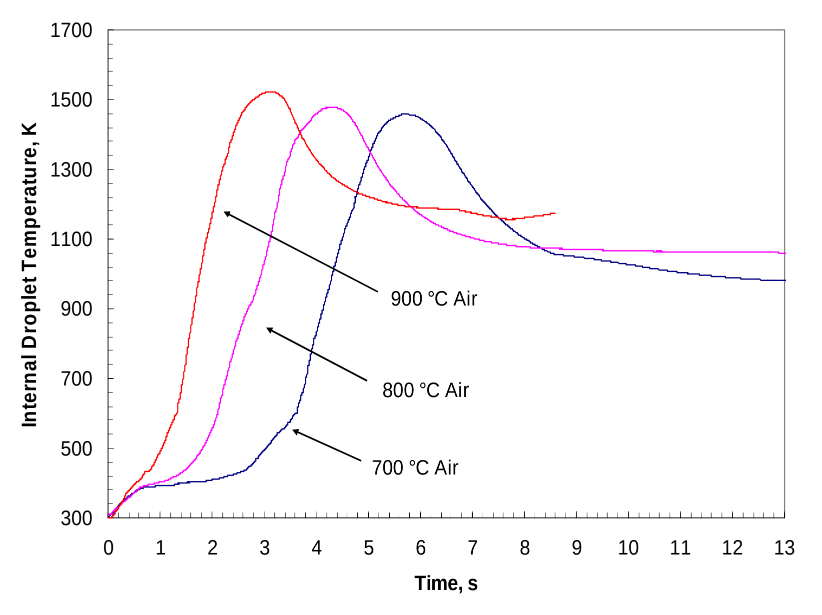




- Swelling reaches maximum and stabilizes in nitrogen
- Droplets shrink due to oxidation in air
- Low temperatures swell more than high tempeartures

Results - Internal Temperature

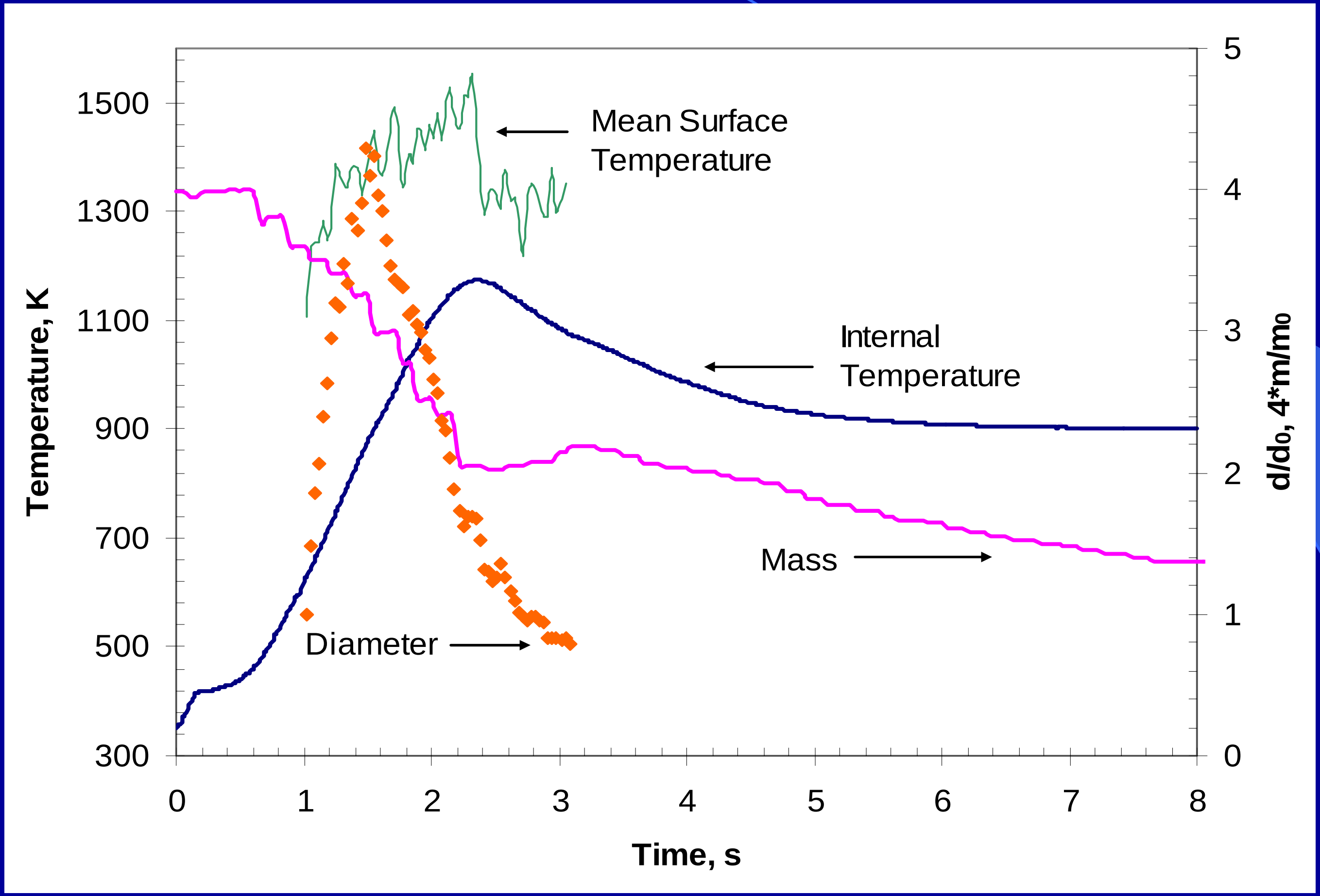




- Moisture vaporizes near boiling point of water
- High furnace temperature increases reaction rate
- Droplet temperature reaches a maximum in air
- Increased furnace temperature increases the maximum droplet internal temperature

Results - Simultaneous Data

Furnace Temp. = 700 C, Liquor D, In Air



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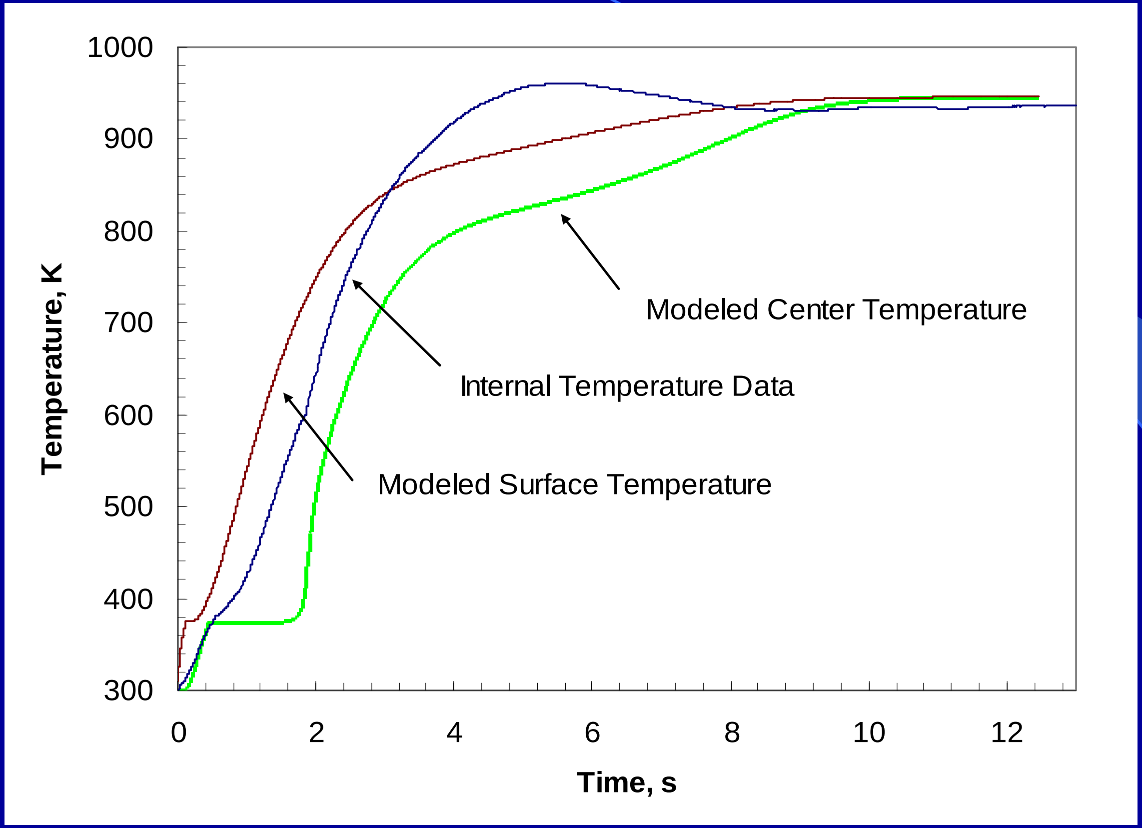
Droplet Burning Model

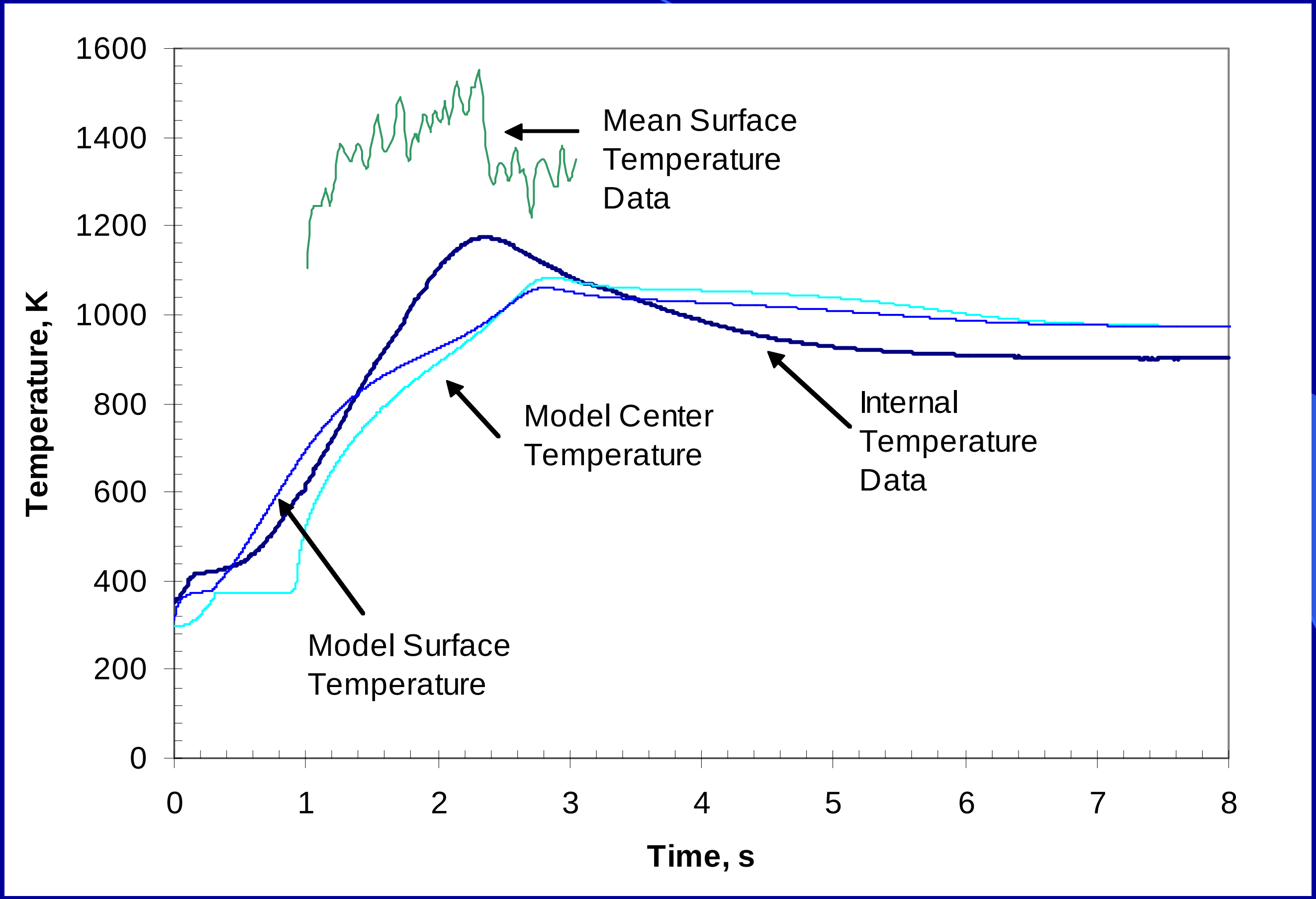
- 1-D Transient
- Simultaneous
  - Drying: internal and external moisture vaporization
  - Devolatilization: wood pyrolysis kinetics
  - Char oxidation/gasification: surface and pores
- Droplet
  - 1.5 mm in diameter, spherical
  - 70% solids content, 35% ash
- Assumptions
  - Constant volume and shape
  - No volatile combustion
  - No inorganic reactions
- Grid and time step
  - Grid independence test
  - 0.001ms time step

Model – Data Comparison- In Nitrogen



- Data within the two extremes of predictions
- Measured temperature overshoot – oxidation
- Predicted temperatures slow down – endothermic

Model – Data Comparison- In Air



- Devolatilization – changed to be exothermic
- Surface ash/carbon ratio consideration
- No flame, no swelling models were added

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Summary and Conclusions

- Simultaneous measurement of mass, size, internal and surface temperature and major gas species have been obtained for 1-5 mm black liquor droplets burning at 700, 800 and 900 °C.
- A 1-D model heat, mass, and species transfer including devolitilization and char oxidation has been completed and compared to the data.
- Droplets swell 2.8 – 3.8 times in nitrogen and 2.4 – 3.5 times during oxidation and more at lower temperature than at higher temperature
- Droplet internal temperatures follow trends expected and predicted by the model.
- Surface temperatures can be as much as 300 C higher than interior temperature and gradients on the surface can differ by as much as 300 C

Summary and Conclusions

- Combustion begins at various locations around the droplet.
- A flame forms around the droplet which is influenced by buoyancy and convective gas velocities. This flame produces soot radiating heat to the droplet and surroundings.
- The up-wind side of the droplet/particle burns the hottest due to oxygen availability.
- Holes or cavities appear on the surface of the char indicating areas where oxygen is temporarily unable to reach the surface.
- Temperature profiles are not one-dimensional in the radial direction.
- Modeling results suggest devolitilization reactions are exothermic
- Including ash fraction in the carbon to reduce reactive carbon surface area has a significant impact in predicted particle surface temperature