Heat Transfer from Condensate Droplets Falling Through an Immiscible Layer of Tributyl Phosphate

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James E. Laurinat
Actinide Technology Section, SRNL

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Background

- "Red oil" explosion in Tomsk, Russia in 1993 initiated a safety review of two-layer TBP/nitric acid solutions in Savannah River Site solvent storage tanks and evaporators. TBP and nitric acid are used in liquid-liquid extraction of actinides.
- Runaway reaction occurs when heat of TBP decomposition reaction exceeds heat losses due to evaporation of condensable gases. Reaction occurs in TBP layer.
- Conditions for runaway reaction depend on extent of mixing of water from aqueous layer to replace water lost by evaporation.
- This study examines mixing and heating due to steam condensate droplets falling through TBP layer.

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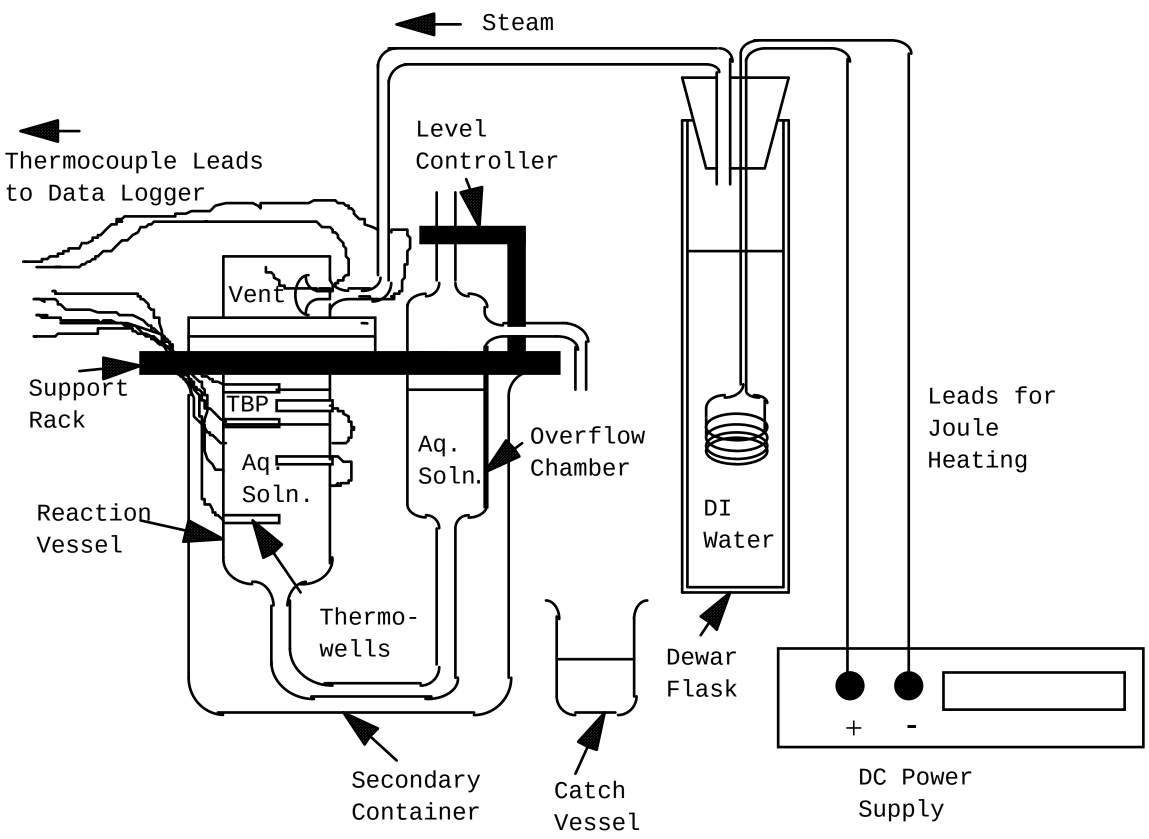
Outline

- Description of experimental apparatus
  - Key feature is overflow chamber to keep liquid level stationary and allow placement of thermocouples at TBP layer surface and TBP/aqueous interface
- Presentation of results
- Model of steady state temperature profile
  - Fit of dispersion coefficient for droplet mixing
- Model of TBP layer surface temperature transient
  - Based on characteristic propagation velocity for droplet flow
- Analysis of surface temperature fluctuations
  - Coupled with Fourier analysis of filtered temperature history

View of Experimental Apparatus, Including Mixing Vessel, Overflow Chamber, Dewar Flask, and Power Source

Vessel diameter = 5.72 cm
TBP layer = 50 mL
Aqueous layer = 225 mL
(50% HNO_3)
Condensate flow = 1.36×10^{-2} g/s
Superficial velocity = 5.2×10^{-4} cm/s
Droplet diameter = 0.3 cm



Note: The Steam line from the Dewar flask to the reaction vessel was insulated with glass wool, and the secondary vessel also contained glass wool insulation. This insulation is not shown.

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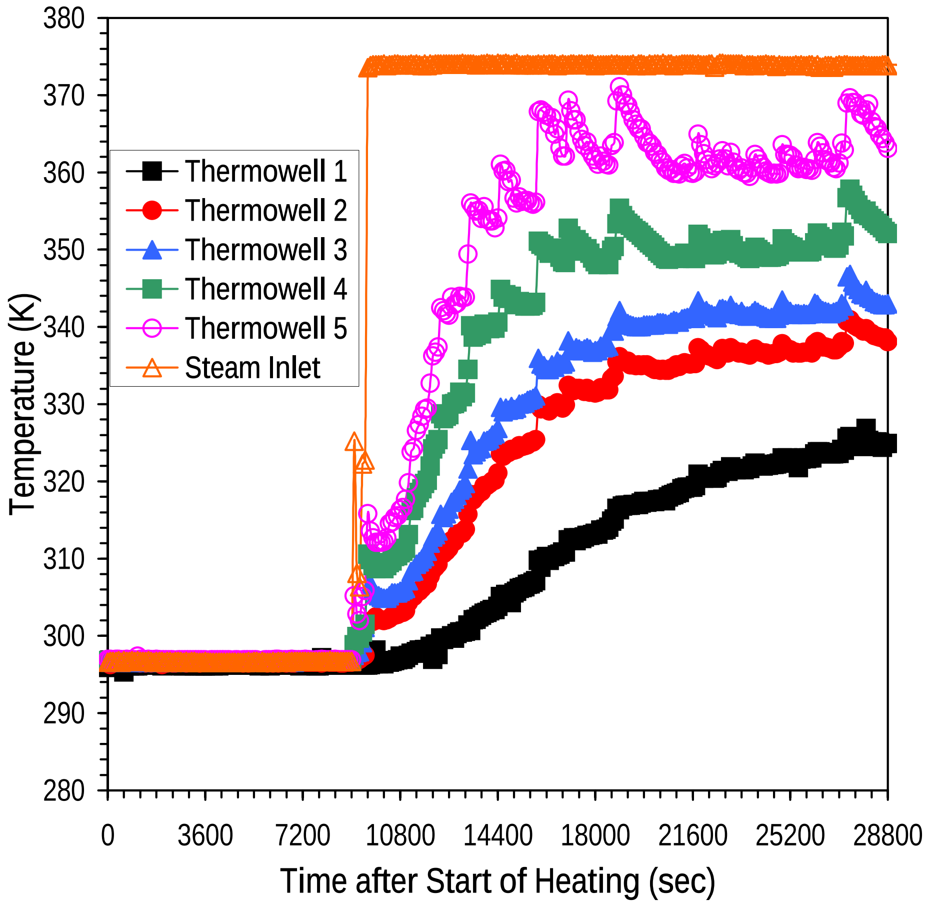
Temperature Transients during Steam Heating Experiment



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Heat Transfer Models for TBP and Aqueous Layers

- Heat transfer within the TBP and aqueous layers is modeled using transient energy balances. Droplet flow is modeled using convection and dispersion.

- Heat Transfer Equation for TBP Layer

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial z^2}$$

  – At steady state $$\frac{d^2 T}{dz^2} = 0$$

- Heat Transfer Equation for Aqueous Layer

$$\frac{\partial T}{\partial t} = \alpha_{aq} \frac{\partial^2 T}{\partial z^2} - v_{sd} \frac{\partial T}{\partial z}$$

  – At steady state $$0 = \alpha_{aq} \frac{d^2 T}{dz^2} - v_{sd} \frac{dT}{dz}$$

    - T temperature
    - t time
    - z distance from top surface of TBP layer
    - α thermal diffusivity for TBP layer
    - α_{aq} thermal diffusivity for aqueous layer
    - v_{sd} superficial velocity for droplet flow

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Thermal Diffusivity Correlation

- Thermal diffusivity is modeled using a bubble flow correlation for the turbulent dispersion coefficient (J. B. Joshi, “Axial Mixing in Multiphase Contactors – A Unified Correlation,” Trans IChemE, 58, 155-165, 1980).
- A factor of 1.5 is added to account for the added mass of the droplets (C. Darwin, “A Note on Hydrodynamics,” Proc Camb Phil Soc, 49, 342-352, 1953).

$$\alpha = \alpha_m + \alpha_{t,d} \qquad \alpha_{aq} = \alpha_{m,aq} + \alpha_{t,d,aq}$$

$$\alpha_{t,d} = 1.5 c_d d v_{sd} \qquad \alpha_{t,d,aq} = 1.5 c_d d v_{sd}$$

- α_m molecular thermal diffusivity in TBP layer
- $\alpha_{t,d}$ turbulent thermal diffusivity in TBP layer
- $\alpha_{m,aq}$ molecular thermal diffusivity in aqueous layer
- $\alpha_{t,d,aq}$ turbulent thermal diffusivity in aqueous layer
- c_d thermal dispersion coefficient
- d diameter of test vessel

Boundary Conditions for Steady State Solution to Heat Transfer Model

- Surface conditions are $T = T_s$ and $-\dfrac{\alpha}{v_{sd}}\dfrac{dT}{dz} = St\left(T_{sat} - T\right)$ at $z = 0$

  where $St = \dfrac{\rho_c c_{p,c} v_{sd} + h_{rad} + \dfrac{k_{m,v}}{H}}{\rho c_p v_{sd}}$

- Conditions at TBP-aqueous interface are $T = T_i$ and $\alpha_{aq}\left.\dfrac{\partial T}{\partial z}\right|_{aq} = \alpha\left.\dfrac{\partial T}{\partial z}\right|_{TBP}$ at $z = h$

- Condition at bottom of vessel is $T = T_b$ at $z = h_{aq}$

• T_s	top surface temperature	ρ_c	condensate density
• T_i	interface temperature	$c_{p,c}$	condensate heat capacity
• T_b	bottom temperature	ρ	TBP density
• T_{sat}	steam temperature	c_p	TBP heat capacity
• St	Stanton number	h_{rad}	radiation heat transfer coefficient
• h	depth of interface	$k_{m,v}$	gas phase thermal conductivity
• h_{aq}	total liquid depth	H	height of gas space above liquid

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Solution to Steady State Heat Transfer Model

- Steady state solution for TBP phase is $T = T_s - St(T_{sat} - T_s)\frac{v_{sd} z}{\alpha}$

- Steady state solution for aqueous phase is

$$T = \frac{T_i\left(\exp\left(\frac{v_{sd}(z-h)}{\alpha_{aq}}\right) - \exp\left(\frac{v_{sd}(h_{aq}-h)}{\alpha_{aq}}\right)\right) + T_b\left(1-\exp\left(\frac{v_{sd}(z-h)}{\alpha_{aq}}\right)\right)}{1-\exp\left(\frac{v_{sd}(h_{aq}-h)}{\alpha_{aq}}\right)}$$

- At the interface, $T_i = T_b + St(T_{sat} - T_s)\left(\exp\left(\frac{v_{sd}(h_{aq}-h)}{\alpha_{aq}}\right) - 1\right)$

- The steady state solution was fit using a calculated Stanton number of 3.80 and a dispersion coefficient (c_d) of 0.329. The value for the dispersion coefficient agrees with values of 0.29 to 0.33 obtained by Joshi for bubble mixing data.

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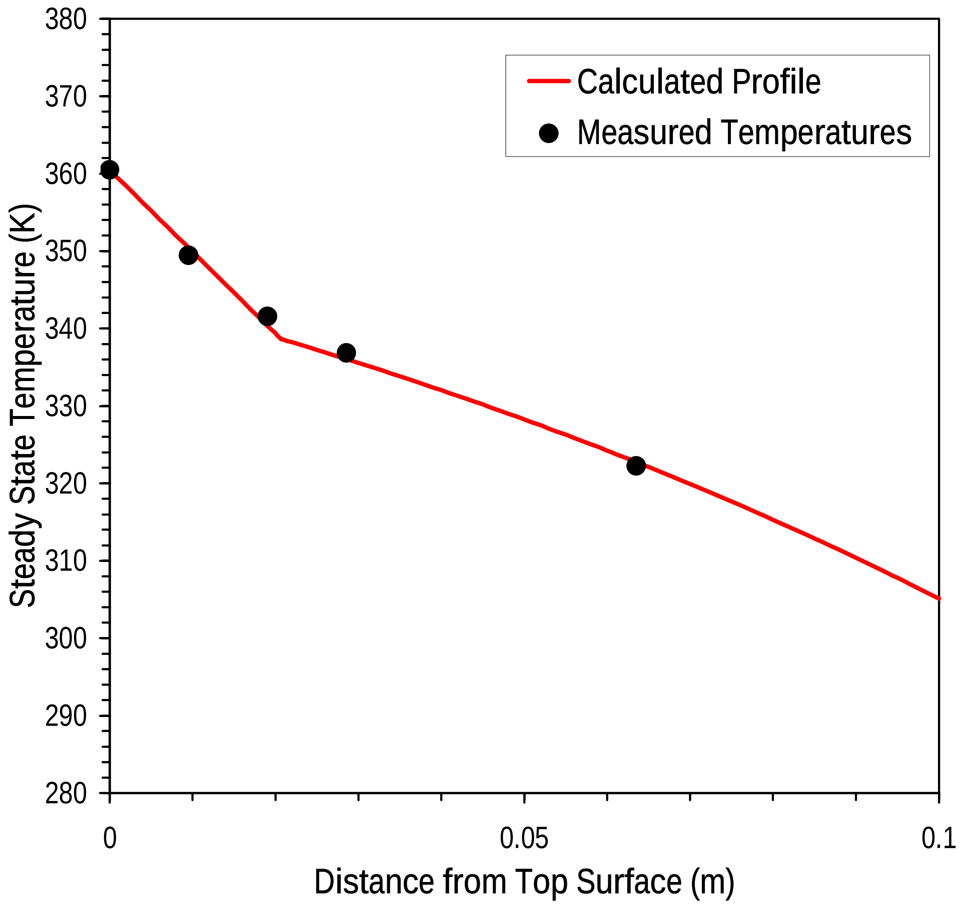
Comparison of Measured and Calculated Steady State Temperatures for Steam Heating Experiment



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Model for Transient Component of Heat Transfer at TBP Surface

- The transient component of the heat transfer at the TBP surface is modeled using a characteristic propagation velocity, v_c. In terms of this velocity, the transient energy balance at the surface can be written:

$$\frac{\partial T}{\partial t} = v_c \left(\frac{\partial T}{\partial z} + \frac{v_{sd}}{\alpha} St \left(T_{sat} - T \right) \right)$$

- The transient solution is defined in terms of the steady state temperature, $\bar{T}$, and a deviation from this temperature, $\hat{T}$, such that $T = \bar{T} + \hat{T}$

- In terms of this temperature deviation, the original form of the energy balance and the form using the propagation velocity become:

$$\frac{\partial \hat{T}}{\partial t} = \alpha \frac{\partial^2 \hat{T}}{\partial z^2} \quad \text{and} \quad \frac{\partial \hat{T}}{\partial t} = v_c \left(\frac{\partial \hat{T}}{\partial z} - \frac{v_{sd}}{\alpha} St \hat{T} \right)$$

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Solution to Model for Transient Component of Heat Transfer at TBP Surface

- The two forms of the transient energy balance are combined to eliminate the time-dependent term: $$\alpha \frac{\partial^2 \hat{T}}{\partial z^2} = v_c \left(\frac{\partial \hat{T}}{\partial z} - \frac{v_{sd}}{\alpha} St \hat{T} \right)$$
- Factoring of this ordinary differential equation yields $\frac{\partial \hat{T}}{\partial z} = \left(\frac{v_c}{2\alpha} \pm i \frac{v_c}{2\alpha} \sqrt{4St \frac{v_{sd}}{v_c} - 1} \right) \hat{T}$
- Substitution of this factored expression in the original energy balance then gives $$\frac{d\hat{T}}{dt} = \left(\frac{v_c^2}{2\alpha} \left(1 - 2St \frac{v_{sd}}{v_c} \right) \pm i \frac{v_c^2}{2\alpha} \sqrt{4St \frac{v_{sd}}{v_c} - 1} \right) \hat{T}$$
- The general solution to this ordinary time-dependent equation is

$$\hat{T} = C_1 (\cos(\theta) + i \sin(\theta)) \exp\left(\frac{v_c^2 t}{2\alpha} \left(1 - 2St \frac{v_{sd}}{v_c} \right) \right) \left(\cos\left(\frac{v_c^2 t}{2\alpha} \sqrt{4St \frac{v_{sd}}{v_c} - 1} \right) \pm i \sin\left(\frac{v_c^2 t}{2\alpha} \sqrt{4St \frac{v_{sd}}{v_c} - 1} \right) \right)$$

- θ phase angle
- C_1 undetermined coefficient

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Solution to Model for Transient Component of Heat Transfer at TBP Surface (continued)

- Terms that must be evaluated to close the solution to the transient heat transfer equation include C_1, θ, and v_c.
  - The initial deviation from the steady state temperature is $C_1 \cos(\theta)$. Therefore, $C_1 \cos(\theta) = T_i - T_\infty$, where T_∞ represents the steady state surface temperature.
  - The initial surface temperature is determined by the relative ability of the TBP phase to transmit sensible heat from the condensate plus thermal radiation and laminar convection from the top surface of the heating vessel. In other words, the initial temperature rise should equal the difference between the saturation temperature and the initial temperature of the solution prior to heating, T_0, divided by the Stanton number:

$$\frac{T_i - T_0}{T_{sat} - T_0} = \frac{1}{St} \quad \text{or} \quad T_i = T_0 + \frac{T_{sat} - T_0}{St}$$

  - Only a fraction of the thermal flux from the condensate propagates through the TBP layer due to the lower thermal capacity of the TBP. This fraction is proportional to the relative thermal capacity, i.e., the product of the density and heat capacity, of the two phases. This apparent contradiction can be resolved by making the real component of the phase angle, the cosine, equal to the ratio of the thermal capacities of the phases. Thus,

$$\cos(\theta) = \frac{\rho c_p}{\rho_c c_{p,c}} \quad \text{and} \quad \sin(\theta) = \pm\sqrt{1 - \left(\frac{\rho c_p}{\rho_c c_{p,c}}\right)^2}$$

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Solution to Model for Transient Component of Heat Transfer at TBP Surface (continued)

– Finally, the characteristic propagation velocity is bounded by the thermal convection velocities in the condensate and TBP phases. The thermal convection velocity in the TBP phase is just the superficial droplet velocity. The thermal convection velocity in the condensate is equal to the droplet velocity, multiplied by the ratio of thermal capacities of the two phases. An intermediate value equal to the geometric mean of these two phase velocities gave the best fit to the data:

$$v_c = \sqrt{\frac{\rho_c c_{p,c}}{\rho c_p}} v_{sd}$$

- With these constants, the transient solution takes the form

$$T = T_\infty - \left(T_\infty - T_0 - \frac{T_{sat} - T_0}{St} \right) \exp\left(\frac{\rho_c c_{p,c} v_{sd}^2 t}{2 \rho c_p \alpha} \left(1 - 2St \sqrt{\frac{\rho c_p}{\rho_c c_{p,c}}} \right) \right)$$

$$\left(\cos\left(\frac{\rho_c c_{p,c} v_{sd}^2 t}{2 \rho c_p \alpha} \sqrt{4St \sqrt{\frac{\rho c_p}{\rho_c c_{p,c}}} - 1} \right) + \frac{\rho_c c_{p,c}}{\rho c_p} \sqrt{1 - \left(\frac{\rho c_p}{\rho_c c_{p,c}} \right)^2} \sin\left(\frac{\rho_c c_{p,c} v_{sd}^2 t}{2 \rho c_p \alpha} \sqrt{4St \sqrt{\frac{\rho c_p}{\rho_c c_{p,c}}} - 1} \right) \right)$$

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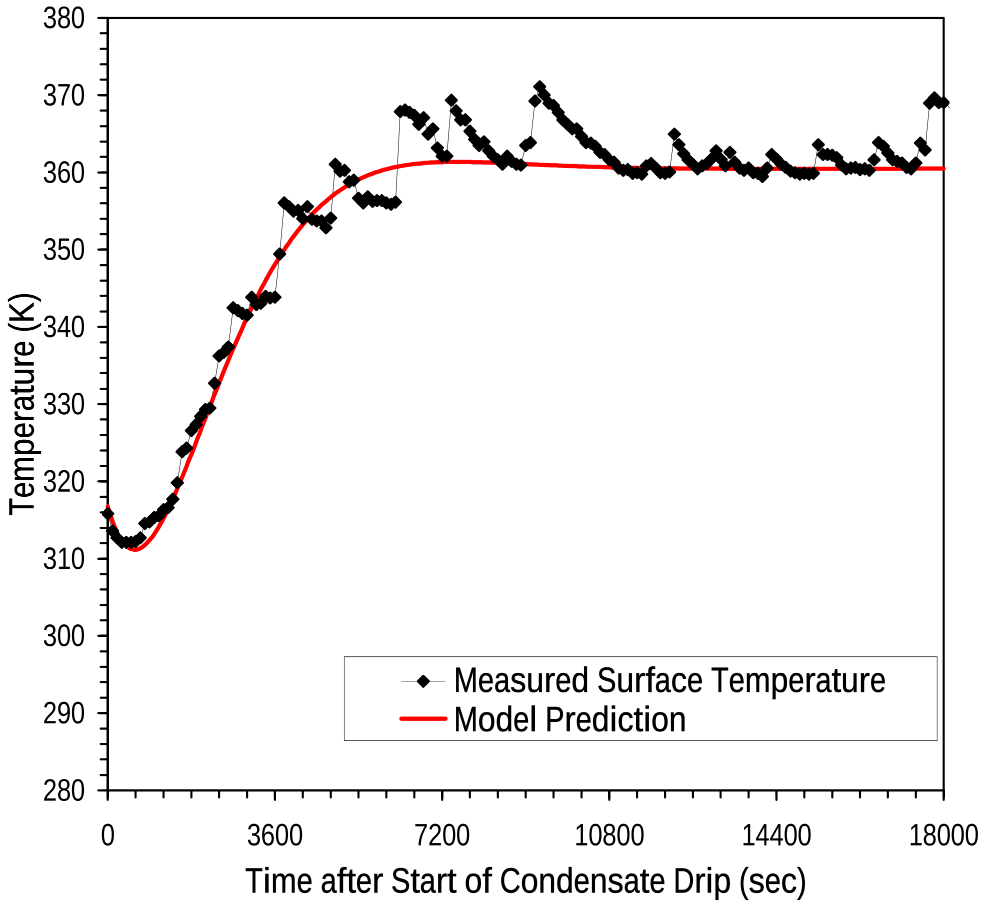
Comparison of Measured and Predicted Temperatures at Top Surface of TBP Layer for Steam Heating Experiment



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Analysis of Surface Temperature Fluctuations

- From surface temperature solution, the wave number β for temperature fluctuations is

$$\beta = \frac{v_c^2}{2\alpha}\sqrt{4St\frac{v_{sd}}{v_c} - 1}$$

- Differentiation of this wave number with respect to the propagation velocity v_c yields a characteristic propagation velocity $v_{c,max}$ and wave number β_{max} at which fluctuations will grow fastest:

$$\frac{\partial \beta}{\partial v_c} = 0 \quad \text{at} \quad v_{c,max}, \beta_{max}$$

- The resulting characteristic propagation velocity and wave number are:

$$v_{c,max} = 3 v_{sd} St \quad \text{and} \quad \beta_{max} = \frac{3\sqrt{3} St^2 v_{sd}^2}{2\alpha}$$

- The corresponding minimum frequency at which fluctuations appear is:

$$\tau_{min} = \frac{2\pi}{\beta_{max}}$$

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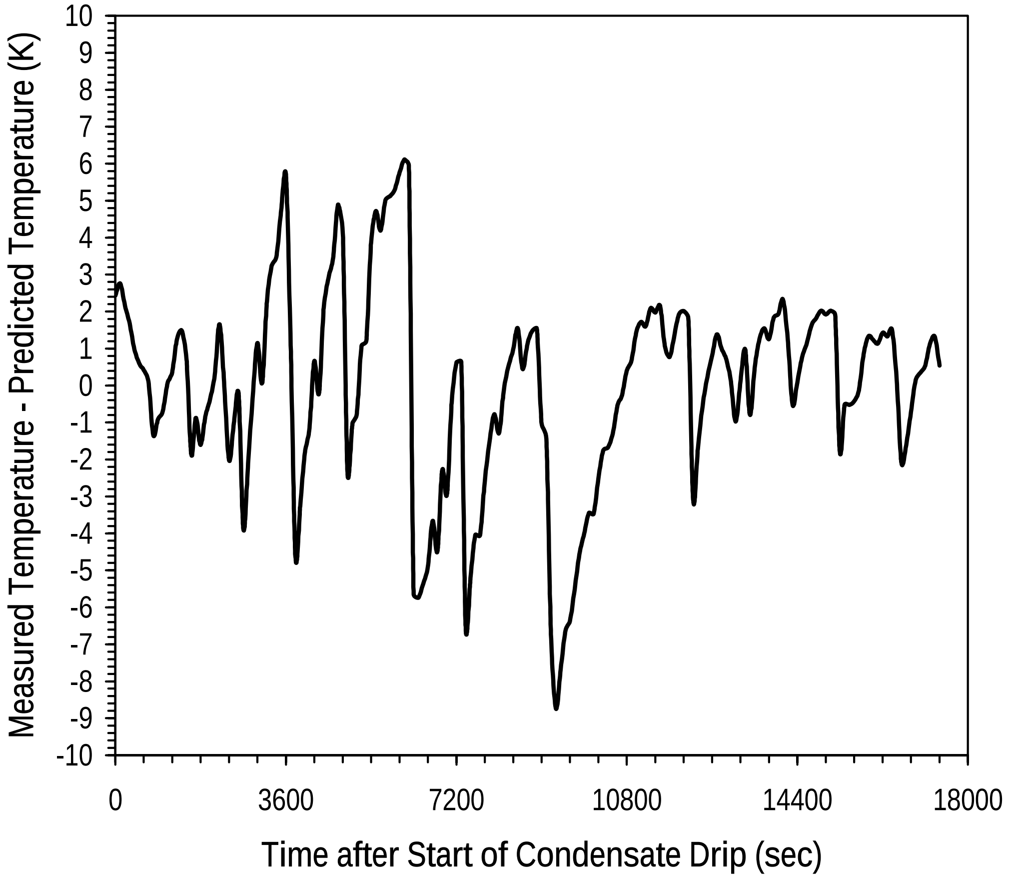
Variation of Difference between Measured and Predicted Temperatures at Top Surface of TBP Layer for Steam Heating Experiment



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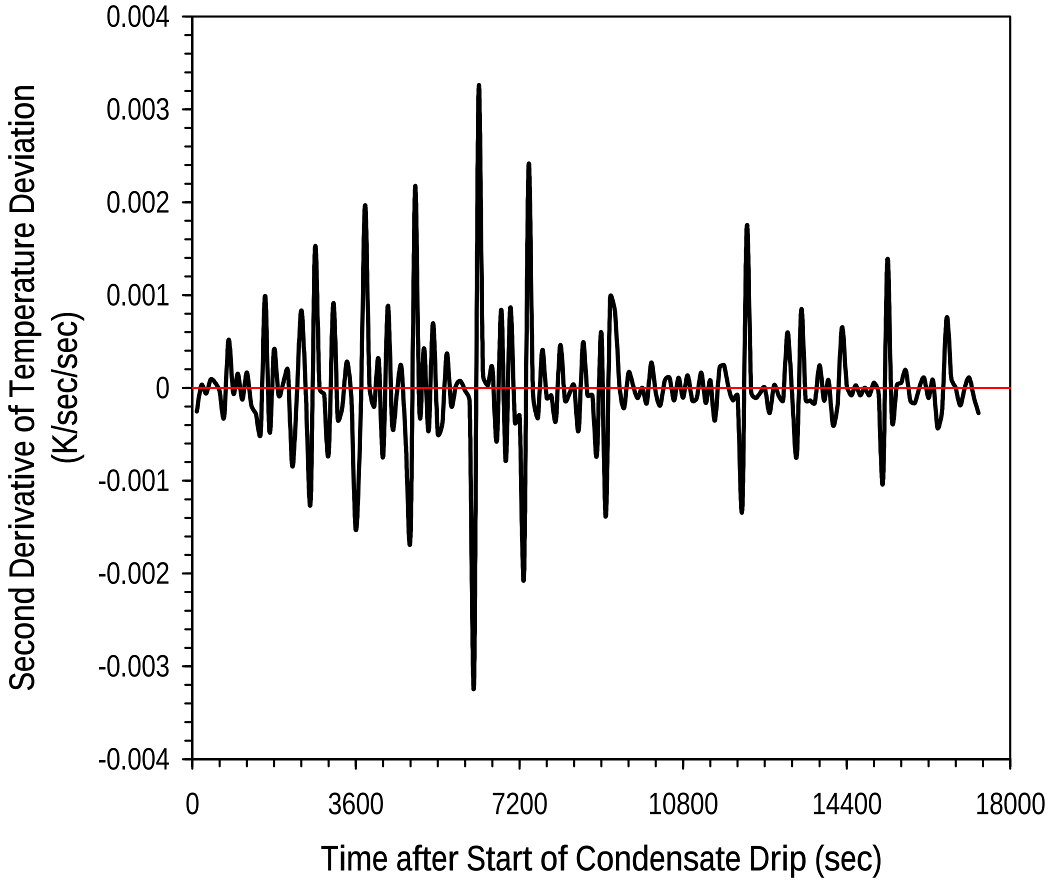
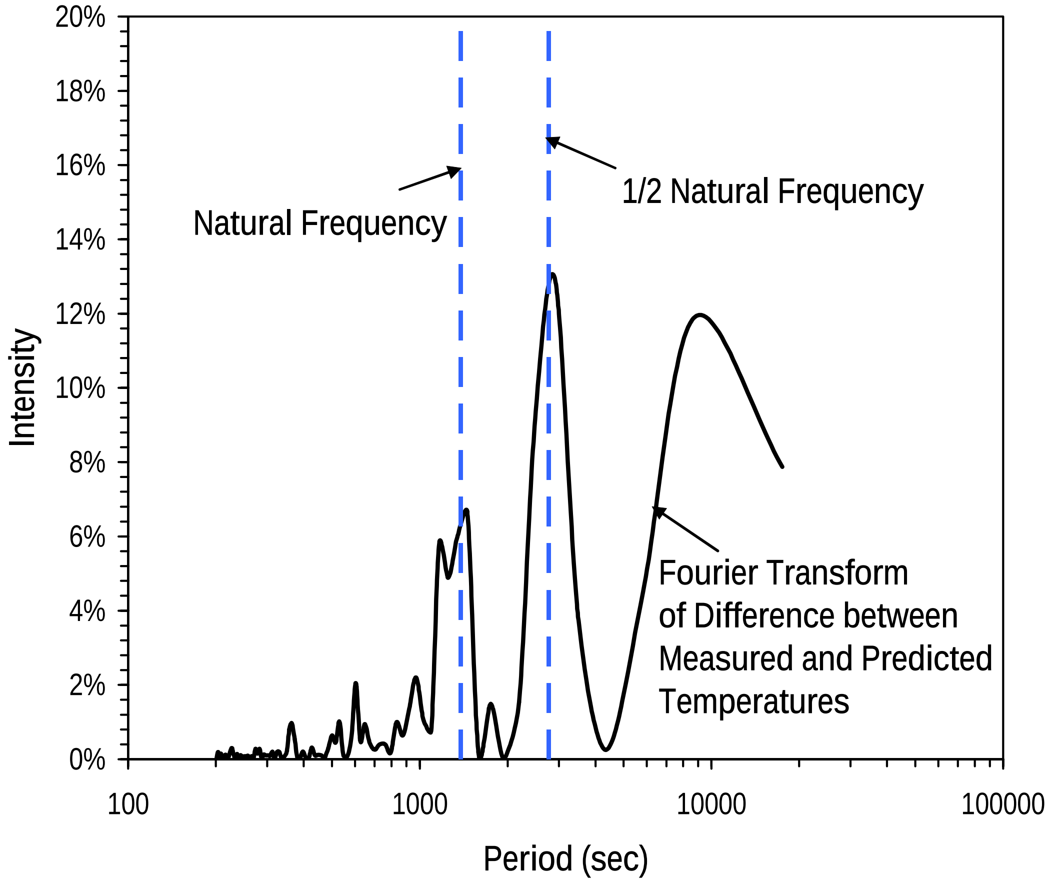
Second Derivative of Variation of Difference between Measured and Predicted Temperatures at Top Surface of TBP Layer



Comparison of Natural Frequency for Temperature Fluctuations with Fourier Spectrum for Deviation between Measured and Predicted Surface Temperatures



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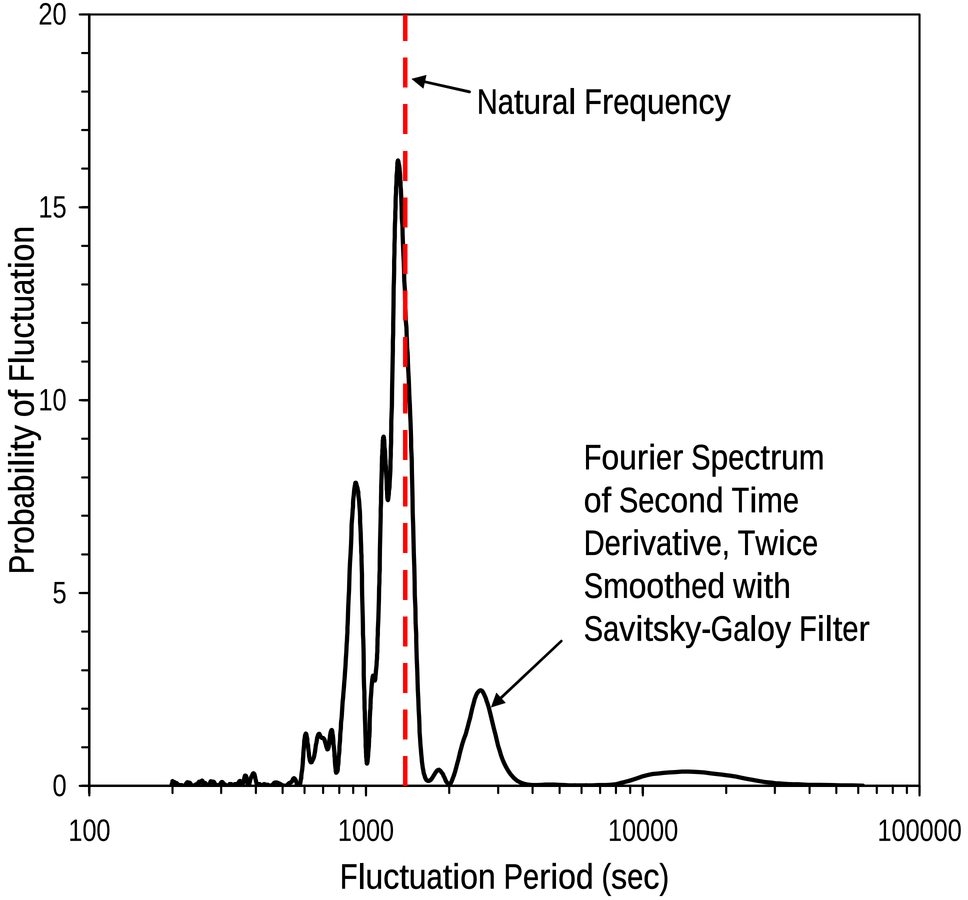
Comparison of Natural Frequency for Temperature Fluctuations with Fourier Spectrum for Second Derivative of Difference between Measured and Predicted Temperatures at Top Surface



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Conclusions

- The dispersion coefficient is the key parameter determining the steady state temperature profile.
  - Dispersion coefficient is modeled using the Joshi et al. correlation for bubble flow, with added mass correction.
- There is a step change to an initial transient temperature at the start of condensate flow.
  - Magnitude of the step change is determined by the ability of the TBP layer to conduct heat and the rates of thermal radiation and convection from the surface.
- The propagation velocity is the key parameter for the transient solution.
  - Propagation velocity equals the geometric mean of the superficial convection velocities for the TBP and condensate phases.
- Temperature fluctuations occur at the natural frequency predicted by the transient solution.
  - Magnitude of the fluctuations is limited by the saturation temperature of the condensate.

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