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

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Introduction

Heat transfer due to condensate dripping through an immiscible organic liquid has been modeled. This study was prompted by safety concerns about a potential runaway reaction between nitric acid and tributyl phosphate (TBP), which forms an immiscible organic layer above aqueous nitric acid solutions. TBP is used as a complexant to separate actinide elements dissolved in nitric acid. The reaction between nitric acid and TBP is highly exothermic and generates potentially explosive product gases. At elevated temperatures, this reaction undergoes a thermal excursion if there is not enough residual aqueous solution dissolved in the TBP to moderate the heat of reaction by its evaporation. Thus, the temperature, the pressure, and the degree of mixing of aqueous components in the TBP layer determine whether or not a given two-layer nitric acid-TBP mixture can be safely stored.

Various mechanisms for heating the TBP layer have been considered. One of these mechanisms is steam condensate dripping onto and percolating through the TBP layer. With steam condensate heating, the nitric acid-TBP reaction, if it occurs, would proceed most rapidly at the top of the TBP layer. The bubbling reaction zone would not necessarily extend down to the TBP-nitric acid interface, so the acid layer might not replenish the water lost by evaporation. To address this concern, an experiment was conducted to study how steam condensate mixes with the TBP layer when steam passes over a TBP-nitric acid mixture.

Description of Experiments

The steam heating experiment was conducted in a constant liquid level mixing vessel connected to a steam generator. To generate the steam, a DC voltage source heated water in a Dewar flask. The source generated 30 watts of power. A mixture of steam and condensate from the Dewar traveled through an insulated tube to a glass mixing vessel containing a two-layer TBP-nitric acid mixture. A flexible tube connected the bottom of this glass vessel to an overflow chamber, which maintained a constant liquid level as condensate entered the vessel. The mixing vessel contained thermowells to measure the temperature of the TBP and nitric acid layers.

Both the mixing vessel and the overflow chamber were set inside a wide mouth beaker that served as a secondary containment vessel and a container for insulation material. Except for a small viewing area, the sides and bottom of the mixing vessel and the overflow chamber were wrapped with glass wool in an effort to minimize heat losses. The top of the mixing vessel was uncovered so that it could be cooled by natural convection to the surrounding air. The mixing vessel had an ID of 0.0572 m and a height of 0.222 m. Glass thermowells were located 0.1080, 0.0984, 0.0889, 0.0794, and 0.0445 m from the bottom of the vessel. During the test the vessel was filled to a level even with the top thermowell, which corresponds to a volume of about 2.75×10^{-4} m^3. Of this total, the TBP layer occupied the top 0.0191 m, corresponding to a volume of approximately 5.0×10^{-5} m^3. This placed the middle thermowell approximately at the TBP-nitric acid interface.

To start the experiments, a nitric acid-saturated TBP layer was prepared by mixing 50 ml of reagent grade TBP with 1.50 x 10^{-4} m^3 of a 50 weight % nitric acid mixture. The TBP and nitric acid layers were allowed to separate and were then added to the mixing vessel. An additional 2.00 x 10^{-4} m^3 of 50 weight % nitric acid was prepared and added to fill the vessel and the overflow chamber until the TBP layer just covered the top thermowell. The Dewar flask was filled with 296 K distilled water and the electrical power source was turned on to generate steam.

After an initial interval during which the water in the Dewar was heated to the boiling temperature, steam generation began. The steam flowed into the mixing vessel as condensate at the boiling point of water (373 K). Virtually all of the steam condensed either in the transfer tube before entering the mixing vessel or on the walls of the mixing vessel. The condensate formed droplets which traveled down the side walls before entering the TBP layer. The condensate flowed through the TBP layer as droplets with an apparent diameter of about 0.003 m. No visible layer of condensate formed on top of the TBP. It was verified through a rough heat balance calculation that the electrical power source was almost 100% efficient in generating either steam or condensate. There was no visible vapor formation in either the TBP or nitric acid layer during the experiment. This was taken as evidence that any TBP decomposition reaction that occurred did not proceed at a significant rate.

The experiment was used to indirectly measure a dispersion coefficient for mixing induced by the droplets. This dispersion coefficient was then used in a model to calculate temperature and composition transients for steam heating of a TBP-nitric acid system at higher temperatures.

Calculation of the Dispersion Coefficient for Condensate Droplet Mixing

The dispersion coefficient is calculated from a model fit to the measured steady state temperature profile. The model fit is based on the steady state solution to the one-dimensional heat transfer equations for the TBP and aqueous layers. In terms of the steam saturation temperature, T_{sat}, the surface temperature, T_0, the temperature at the bottom of the test vessel, T_b, and the temperature at the TBP-aqueous interface, T_i, the steady state solutions for the TBP and aqueous layers, respectively, take the form:

$$T = T_0 - St\left(T_{sat} - T_0\right)\frac{v_{sd} z}{\alpha} \tag{1}$$

and:

$$T = \frac{T_i\left(\exp\left(\frac{v_{sd}(z-h)}{\alpha_{aq}}\right) - \exp\left(\frac{v_{sd}\left(h_{aq}-h\right)}{\alpha_{aq}}\right)\right) + T_b\left(1-\exp\left(\frac{v_{sd}(z-h)}{\alpha_{aq}}\right)\right)}{1-\exp\left(\frac{v_{sd}\left(h_{aq}-h\right)}{\alpha_{aq}}\right)} \tag{2}$$

where the interface temperature is given by.

$$T_i = T_b + St\left(T_{sat} - T_0\right)\left(\exp\left(\frac{v_{sd}\left(h_{aq} - h\right)}{\alpha_{aq}}\right) - 1\right) \tag{3}$$

In these equations, v_{sd} is the superficial velocity of the falling condensate droplets, z is the distance from the liquid surface, h and h_{aq} are heights of the TBP and aqueous layers, and α and α_{aq} are the thermal dispersivities of the two liquid layers. The heat transfer parameters in these expressions are grouped in a Stanton number, St, defined as the ratio of heat transfer to the surface by droplet impingement, thermal convection, and radiation, to convection away from the surface:

$$St = \frac{\rho_c c_{p,c} v_{sd} + h_{rad} + \frac{k_{m,v}}{H}}{\rho c_p v_{sd}} \tag{4}$$

where h_{rad} is a radiation heat transfer coefficient, $k_{m,v}$ is the thermal conductivity of the steam, and H is the height of the vapor space above the two-layer mixture.

The dispersion coefficient is the sum of the molecular dispersivity and an axial dispersivity, $\alpha_{t,d}$, that accounts for the condensate droplet flow. Axial dispersion for liquid droplets falling through quiescent liquid layers has not been widely studied. For this reason, a correlation for liquid backmixing in bubble columns is utilized. To be useful in modeling droplet mixing, the bubble column mixing correlation must be defined in terms of the velocity of the liquid phase entrained by the bubbles. One such correlation was proposed by Joshi (1980). The Joshi correlation takes the form

$$\alpha_b = c_b d_b v_{l,c} \tag{5}$$

where α_b is the dispersion coefficient for bubble mixing of the liquid layer, d_b is the bubble column diameter, $v_{l,c}$ is the superficial circulation velocity of the liquid entrained by the bubble flow, and c_b is a constant. Joshi obtained values of c_b ranging between 0.29 and 0.33 for correlations of different sets of data.

The liquid circulation velocity for droplet flow includes both the flow rate of the droplets and the added mass of the continuous phase entrained by the droplets. For laminar (Stokes) flow, the added mass occupies half of the droplet volume (Darwin, 1953). It follows that the liquid circulation velocity for falling droplets is 1.5 times the superficial droplet velocity. With these considerations, the correlation for the axial dispersion coefficient for the droplet flow becomes

$$\alpha_{t,d} = 1.5 c_d d v_{sd} \tag{6}$$

where v_{sd} is the superficial droplet velocity and c_d is a coefficient which should be numerically equal to c_b. The same model is used to calculate dispersion in the aqueous layer. A Stanton number of 3.80, a dispersion coefficient c_d of 0.329, a TBP layer surface temperature of 360.5 K, and bottom temperature of 300.7 K were used to fit the data. The value for c_d agrees with the values for c_b obtained by Joshi for bubble column mixing.

Analytic Solution for Surface Temperature Transient in the Absence of Reaction

A transient solution for the TBP surface temperature is obtained by expressing the dispersion term in the unsteady state heat transfer equation as the difference between heat transfer to the surface, defined in terms of the Stanton number, and thermal dispersion from the surface into the TBP layer, multiplied by a characteristic propagation velocity for the droplet flow through the TBP layer, v_c. Using this characteristic velocity, the general solution becomes:

$$T - T_\infty = C_1\left(\cos(\theta) + i\sin(\theta)\right)\exp\left(\frac{v_c^2 t}{2\alpha}\left(1 - 2St\frac{v_{sd}}{v_c}\right)\right)\left(\cos\left(\frac{v_c^2 t}{2\alpha}\sqrt{4St\frac{v_{sd}}{v_c} - 1}\right) \pm i\sin\left(\frac{v_c^2 t}{2\alpha}\sqrt{4St\frac{v_{sd}}{v_c} - 1}\right)\right) \tag{7}$$

where T_∞ represents the steady state surface temperature as $t \to \infty$.

This solution has three undetermined parameters, C_1, θ, and v_c. The parameter θ is a phase angle that accounts for the inability for temperature changes to propagate downstream from the condensate phase into the TBP layer. According to the model assumptions, the condensate droplets are in thermal equilibrium with the TBP phase as they fall through this layer. It follows that thermal fluxes must propagate equally through both the droplet and TBP phases. However, a thermal flux from the condensate phase cannot propagate fully through the TBP phase due to the lower thermal capacity of the TBP. In fact, only a fraction of the heat proportional to the relative thermal capacity, i.e., the product of the density and heat capacity, can enter the TBP phase. This apparent contradiction can be resolved by assigning a phase angle to the temperature solution, where the real component, the cosine, equals the ratio of the thermal capacities of the phases. Thus,

$$\cos(\theta) = \frac{\rho c_p}{\rho_c c_{p,c}} \tag{8}$$

The constant C_1 is evaluated from the initial condition. 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. The initial temperature rise equals the difference between the saturation temperature and the initial temperature of the solution, divided by the Stanton number:

$$T_i = T_0 + \frac{T_{sat} - T_0}{St} \tag{9}$$

Finally, a characteristic velocity equal to the geometric mean of the superficial velocities in the TBP and aqueous layers gives the best fit to the measured rate of increase in the temperature.

:

$$v_c = \sqrt{\frac{\rho_c c_{p,c}}{\rho c_p}} v_{sd} \tag{10}$$

With these parameter values, the final solution takes the form:

$$T = T_\infty - \left(T_\infty - T_0 - \frac{T_{sat} - T_0}{St} \right) \exp\left(\frac{\rho_c c_{p,c}}{\rho c_p} \frac{v_{sd}^2 t}{2\alpha} \left(1 - 2St\sqrt{\frac{\rho c_p}{\rho_c c_{p,c}}} \right) \right)$$
$$\left(\cos\left(\frac{\rho_c c_{p,c}}{\rho c_p} \frac{v_{sd}^2 t}{2\alpha} \sqrt{4St\sqrt{\frac{\rho c_p}{\rho_c c_{p,c}}} - 1} \right) + \frac{\rho_c c_{p,c}}{\rho c_p} \sqrt{1 - \left(\frac{\rho c_p}{\rho_c c_{p,c}} \right)^2} \sin\left(\frac{\rho_c c_{p,c}}{\rho c_p} \frac{v_{sd}^2 t}{2\alpha} \sqrt{4St\sqrt{\frac{\rho c_p}{\rho_c c_{p,c}}} - 1} \right) \right) \tag{11}$$

Figure 1 compares the measured surface temperature with the predictions of the transient model. As this figure shows, the model accurately predicts temperatures during both the initial portion of the transient and at later times as steady state approached.

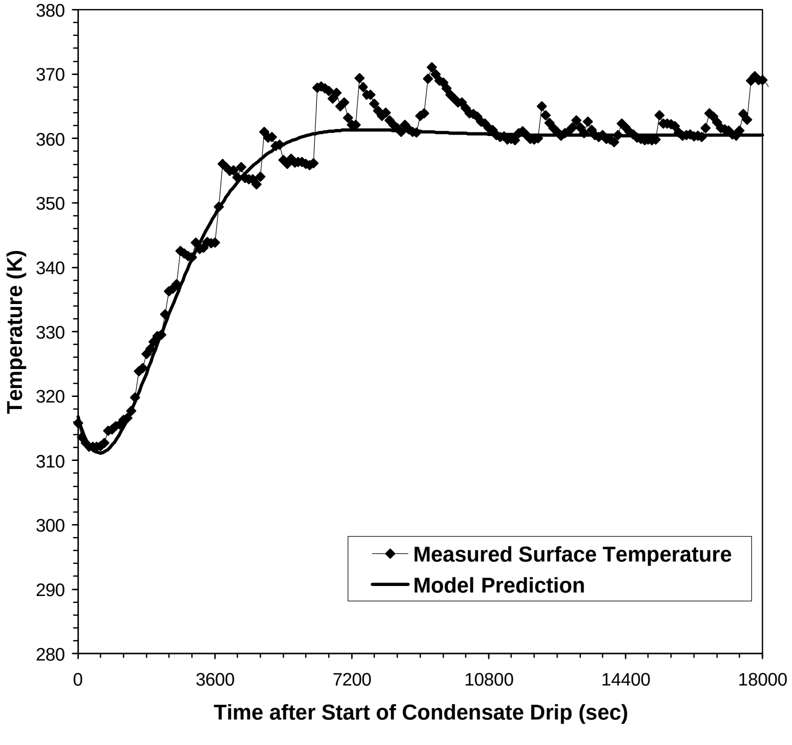

Figure 1. Comparison of Measured and Predicted Temperatures at TBP Layer Surface.

During the middle portion of the transient, the measured temperatures fluctuated between the predicted values and the saturation temperature. These fluctuations probably reflect imperfect mixing at the surface. If so, then the frequency of these fluctuations should match the natural frequency governed by the heat transfer conditions at the surface. The characteristic (or natural) frequency for temperature fluctuations occurs at the maximum possible propagation velocity. The maximum propagation velocity can be determined by differentiating the harmonic component of the temperature solution with respect to the propagation velocity v_c. The resulting natural frequency, β_{max}, is:

$$\beta_{max} = \frac{3\sqrt{3} St^2 v_{sd}^2}{2\alpha} \tag{12}$$

The frequency of the fluctuations in the measured surface temperatures was determined by spectral analysis of the second time derivative of the temperature transient. Taking time derivatives has the effect of a high pass frequency filter, since it amplifies high frequency fluctuations and dampens low frequency trends. To filter out high frequency signals, a 9-point Savitsky-Galoy filter (Press et al., 1992) was applied to the data in two successive passes. Figure 2 portrays the Fourier transform for the second derivatives of the surface temperature fluctuations in the time domain. As this figure shows, the peak fluctuation period from the Fourier analysis of the filtered data corresponds closely to the period for the calculated natural frequency.

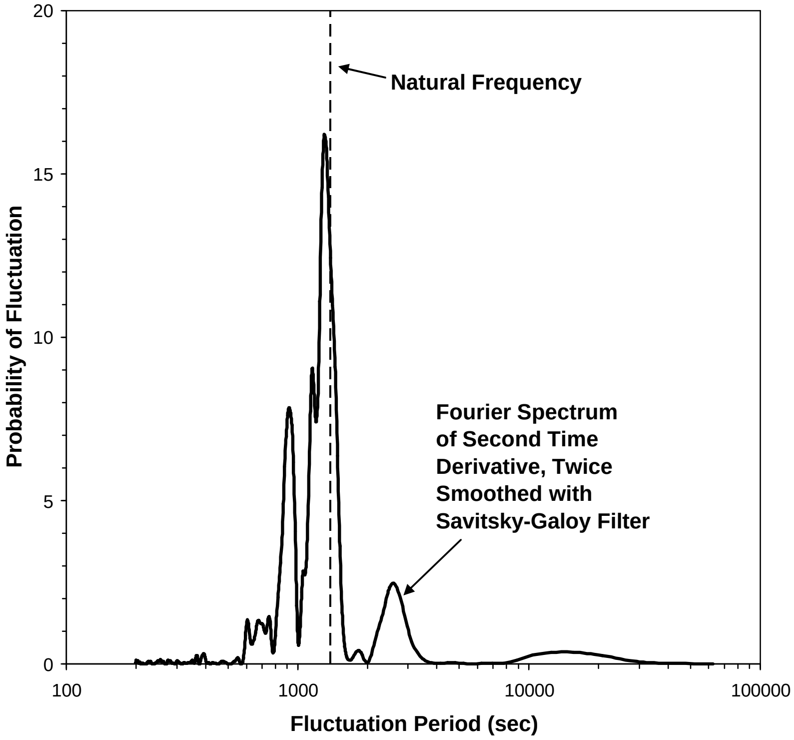

Figure 2. Comparison of Natural Frequency with Fourier Spectrum for Second Derivative of Difference between Measured and Predicted Temperatures at Top Surface.

Conclusions

Experiments were conducted to study how steam condensate mixes with the TBP layer when steam passes over a TBP-nitric acid mixture. The experiments showed that the condensate does not form a separate layer on top of the TBP but instead percolates as droplets through the TBP layer. The temperature at the top surface of the TBP layer undergoes a step change increase when the initial condensate droplets reach the surface. Temperatures at the surface and within the TBP and aqueous layers subsequently approach a steady state distribution governed by laminar convection and radiation heat transfer from the vapor space above the two-layer mixture. The rate of temperature increase and the steady state temperature gradient are determined by a characteristic propagation velocity and a streamwise dispersion coefficient for heat transfer. The propagation velocity is the geometric mean of the thermal convection velocities for the organic and aqueous phases, and the dispersion coefficient equals 0.494 times the product of the superficial droplet velocity in the TBP layer and the diameter of the test vessel. The value of the dispersion coefficient agrees with the Joshi correlation for liquid phase backmixing in bubble columns. Transient perturbations occur in the TBP layer temperatures. A Fourier analysis shows that the dominant frequency of these perturbations approximately equals the natural frequency given by the transient heat transfer solution.

References

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