

# Heat Transfer Considerations in Design of a Batch Tube Reactor for Biomass Hydrolysis

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## Abstract

Biologic conversion of inexpensive and abundant sources of cellulosic biomass offers a low-cost route to production of fuels and commodity chemicals that can provide unparalleled environmental, economic, and strategic benefits. However, low-cost, high-yield technologies are needed to recover sugars from the hemicellulose fraction of biomass and to prepare the remaining cellulose fraction for subsequent hydrolysis. Uncatalyzed hemicellulose hydrolysis in flow-through systems offers a number of important advantages for removal of hemicellulose sugars, and it is believed that oligomers could play an important role in explaining why the performance of flow-through systems differs from uncatalyzed steam explosion approaches. Thus, an effort is under way to study oligomer formation kinetics, and a small batch reactor is being applied to capture these important intermediates in a closed system that facilitates material balance closure for varying reaction conditions. In this article, heat transfer for batch tubes is analyzed to derive temperature profiles for different tube diameters and assess the impact on xylan conversion. It was found that the tube diameter must be <0.5 in. for xylan hydrolysis to follow the kinetics expected for a uniform temperature system at typical operating conditions.

**Index Entries:** Reactors; heat transfer; hydrolysis; kinetics; pretreatment.

## Introduction

Biomass provides a unique, vast resource for the production of organic fuels and chemicals on a sustainable basis, and biologic conversion routes offer great promise for low-cost production to support large-scale use (1). However, biomass must be pretreated prior to biologic conversion to achieve the high yields essential for economic success (2,3). Currently,

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pretreatment represents the most expensive single step in biomass processing and also greatly influences the cost of biologic steps that collectively comprise the largest total costs (4). Thus, it is important to optimize and improve pretreatment if we are to reduce the cost of products from biomass to be competitive with traditional fossil sources.

The use of dilute acid and uncatalyzed pretreatment technologies is favored by many because of the good enzymatic digestibility realized for pretreated cellulose (5). In addition, dilute-acid catalyzed hydrolysis can achieve high yields of sugars from hemicellulose (5–7). However, there are important inconsistencies in the kinetics of hemicellulose hydrolysis as studied to date (8). Therefore, we are interested in exploring hemicellulose hydrolysis with the goal of improving our knowledge of important mechanisms involved and developing models that will more accurately predict reaction performance. Such information will help optimize current systems, support scale-up, and provide insight for advancing the technology.

In our initial research, we chose to employ a closed-batch system to facilitate material balances and simplify the overall experimental design. However, interpretation of the results is more easily accomplished if we can ensure a constant temperature. This is particularly important because kinetics tend to follow an Arrhenius behavior that makes rates change substantially with changes in temperature. Furthermore, the yields of some thermal biomass reactions, such as cellulose hydrolysis, are very sensitive to the temperature applied (9). Thus, we needed to analyze heat transfer in a batch reactor tube to guide the design and be sure the temperature profile is reasonably uniform.

For these reasons, a model was developed that incorporated heat transfer and traditional reaction kinetics to predict the temperature history for a tube batch reactor system and the possible impact on biomass conversion. Such analysis may also indicate whether variations in experimental results reported previously by others could be explained by variable temperature profiles owing to heat transfer effects. Additionally, the model can be used to determine whether temperature transients could be reduced by submerging the reactor tubes initially in a hotter bath before transferring them to one maintained at the target temperature of the reaction.

## Batch Tube System and Model

The experimental plan is based on mixing biomass with water to achieve target moisture levels and adding weighed amounts of these materials to several cylindrical metal tubes. The tubes are chosen to have a relatively high length-to-diameter ratio to ensure that the temperature depends primarily on tube radius. The tubes are then sealed at each end and submerged in a fluidized sand bath that is held at a set temperature. If transient times need to be reduced, the tubes can first be inserted in a bath held at a temperature above that targeted for the reaction to speed heat up

and then be transferred to a second sand bath that is held at the temperature of interest as soon as the target temperature is attained. One or more of the tubes can then be withdrawn from the bath at selected times and quenched in a water or ice bath to stop the reaction. Measurement of the liquid and solids sugar content and weights can then be used to determine the conversion and yield profiles at each time and temperature.

As designed, the tubes lend themselves to classic heat transfer modeling. First, it is assumed that the initial temperature is equal to room temperature and uniform over the tube length and radius. Second, it is assumed that heat transfer is only a function of the tube radius because the temperature does not change with angular position and the length-to-diameter ratio for the tubes is high. Third, because fluidized sand baths have high heat transfer coefficients, the outside temperature of the tube wall is taken to be essentially equal to that of the sand bath (10). Fourth, it is assumed that the thermal conductivity of the metal tube wall is much higher than that of the biomass slurry and, as a result, that the temperature of the wall is uniform over its radius.

Based on the experimental approach and its geometric representation, we can develop initial and boundary conditions for the system. First, a new temperature variable,  $v$ , is defined through the relationship

$$v = [(T - T_0)/(T_1 - T_0)]V \quad (1)$$

in which  $T$  is the temperature as a function of the radius,  $T_0$  is the initial tube temperature, and  $T_1$  is the temperature of the bath. Thus, the following initial and boundary conditions result:

$$v = 0 \text{ at time } < 0 \text{ for all } r \quad (2)$$

$$v = V \text{ at } r = R \text{ for } t > 0 \quad (3)$$

in which  $R$  is the inside radius of the tube.

Because the temperature is assumed to be only a function of radius and time, we can apply the unsteady equation of heat conduction in cylindrical coordinates with only dependence on radius to give (11)

$$\frac{\partial v}{\partial t} = k \left( \frac{\partial^2 v}{\partial r^2} + \frac{1}{r} \frac{\partial v}{\partial r} \right) \quad \text{where } k = \frac{K}{\rho C_p} \quad (4)$$

in which  $r$  is the tube radius,  $k$  is the thermal diffusivity,  $K$  is the thermal conductivity,  $\rho$  is the density, and  $C_p$  is the heat capacity. Note that this model only includes conduction, and in reality, heating rates would be higher for low solids concentrations because the effects of convection would be significant.

Based on the initial and boundary conditions, Eq. 4 can be solved for the temperature function  $v$ :

$$v = A J_0(\alpha r) e^{-k\alpha^2 t} \quad (5)$$

in which  $J_0(x)$  is the Bessel function of order zero of the first kind (11). Satisfying the boundary conditions requires that  $\alpha$  be a root of  $J_0(\alpha a) = 0$ , giving

$$v = \sum_{n=1}^{\infty} A_n J_0(\alpha_n r) e^{-k\alpha_n^2 t} \quad (6)$$

After integration of the Bessel function and rearranging, keeping in mind constant initial temperature  $v = 0$  and a surface maintained at  $V$ , we arrive at

$$v = V - \frac{2V}{a} \sum_{n=1}^{\infty} e^{-k\alpha_n^2 t} \frac{J_0(r\alpha_n)}{\alpha_n J_1(a\alpha_n)} \quad (7)$$

### Calculation of Temperature and Conversion Profiles

The temperature profile in the tube was calculated as a function of time and radius. To support later calculation of the effect of temperature variations on conversion, the crosssection of the tube was divided into 10 concentric rings of equal thickness, and the time-dependent temperature history in each ring was determined from Eq. 7 by a Matlab program. The solution was developed for each of the 10 rings in 1–5 time intervals to derive 10 terms over a total time of 1000 s. Thus, 1000 temperature points were calculated in each of the 10 rings. The values of these first five roots can be found in Appendix IV of Carslaw and Jaeger (11), and for this simulation only the first five roots of the Bessel functions were needed because further roots made minor contributions.

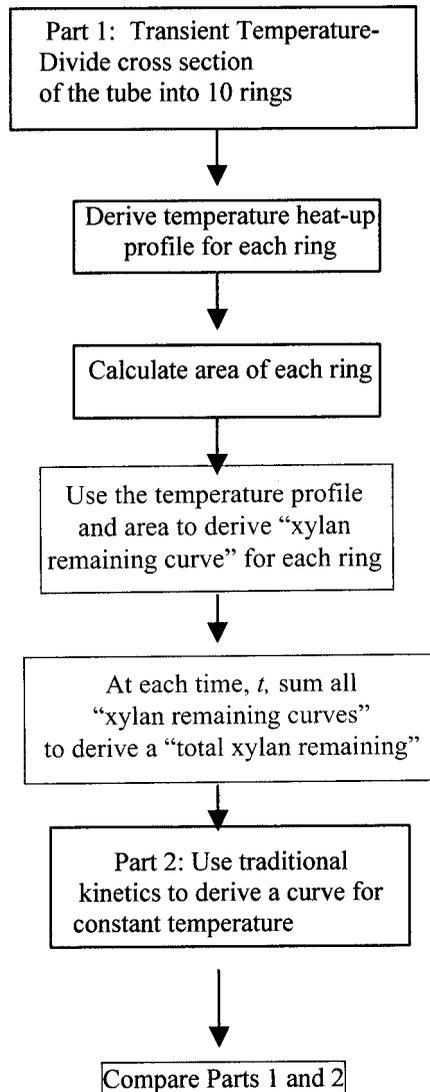
For the purpose of estimating the effect of temperature on the hydrolysis of hemicellulose to sugars, the following kinetic equations were applied to each ring based on published information (12):

$$X_{r,i} = X_{0,i} e^{-kt} \quad (8)$$

$$\text{where } k = k_{i0} e^{-(E/RT)} \quad (9)$$

in which  $X_{r,i}$  is the xylan remaining at time  $t$  in any ring  $i$ , and  $X_{0,i}$  is the amount of xylan in ring  $i$  initially. The value of  $E$ , the activation energy, and  $k_{i0}$ , a kinetic constant, were taken from Estaglalian et al. (12).

The mass of xylan remaining in each ring at each time was calculated based on reported kinetics but using the temperature predicted by the heat transfer analysis. First, the fraction of total original xylan,  $X_{0,i}$ , in each ring  $i$  was calculated by determining the area of each ring and dividing by the total cross-sectional area of the tube. Second, the fraction of xylan remaining,  $X_{r,i}$ , in each ring was calculated using the time and corresponding temperature from the solution to the conduction Eq. 7 in Eqs. 8 and 9. An average of the temperatures at the inner and outer radius for each ring in Eq. 9 was employed by the Matlab program to determine the kinetic rate constant for each time interval.



The approach outlined was applied to estimate the temperature and xylan-remaining profiles by the algorithm shown above.

## Simulation Results

Figure 1 presents the predicted temperature profiles in each of the 10 radial intervals for reactor diameters of 0.5-in. (radius = 0.64 cm) and 1.0 in. (radius = 1.27 cm) with a 160°C sand bath temperature. Thus, we see that it takes some time for the temperature to approach the wall temperature over the entire tube radius. Furthermore, the model predicts that it will take 3 min to heat the center of the 0.5-in. tube to 140°C vs 14 min for the 1-in. tube.

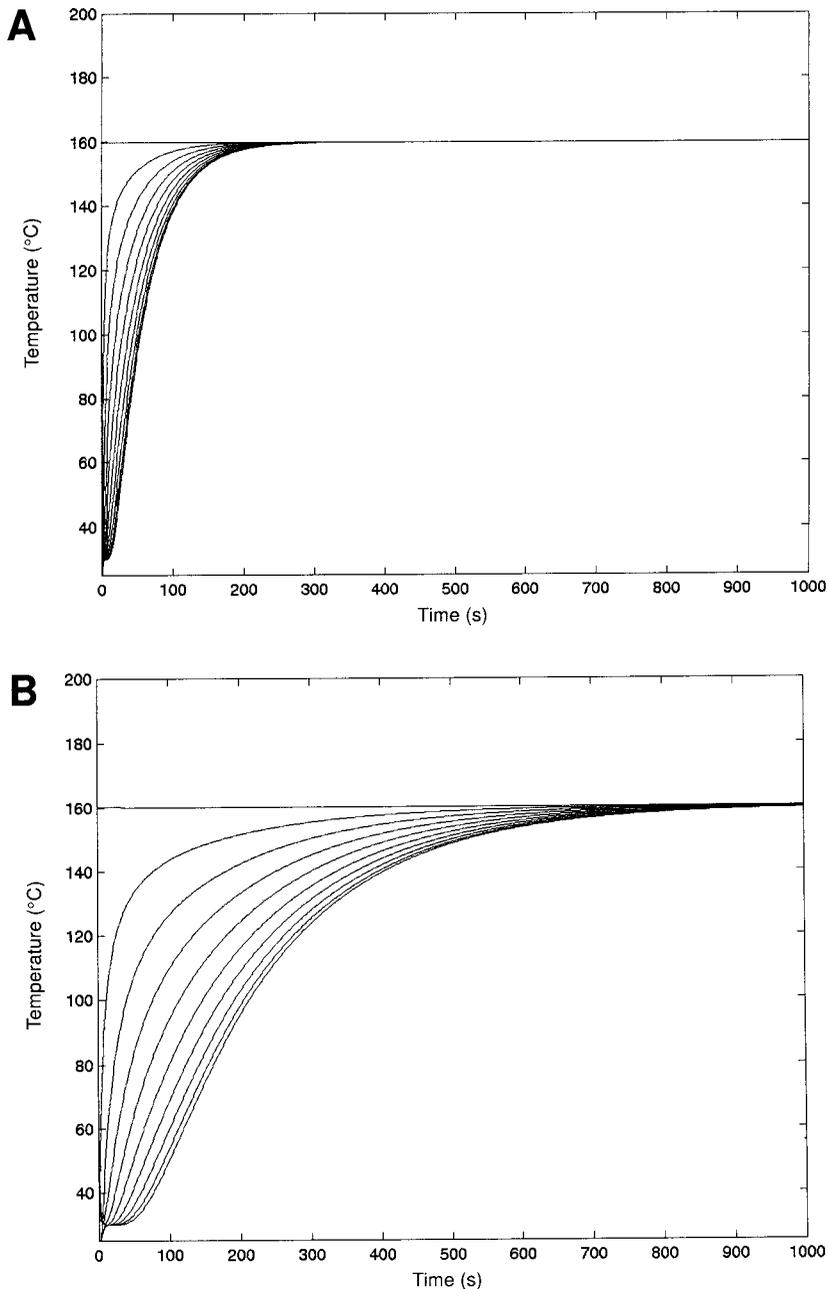


Fig. 1. Profiles showing the temperature vs time in seconds at each 0.1 radius for reactor with a 0.5-in. diameter ( $r = 0.64$  cm) (A) and a 1.0-in. diameter ( $r = 1.27$  cm) (B).

Figure 2 shows the effect of temperature variations in Fig. 1 on xylan conversion for the 10 radial intervals. It is clear that hydrolysis in the inner rings (i.e.  $r = 0.1R$  and  $r = 0.2R$ ), begins significantly later than in the outer rings. However, because cross-sectional area and, therefore, relative xylan quantity is proportional to radius squared, the inner rings have relatively

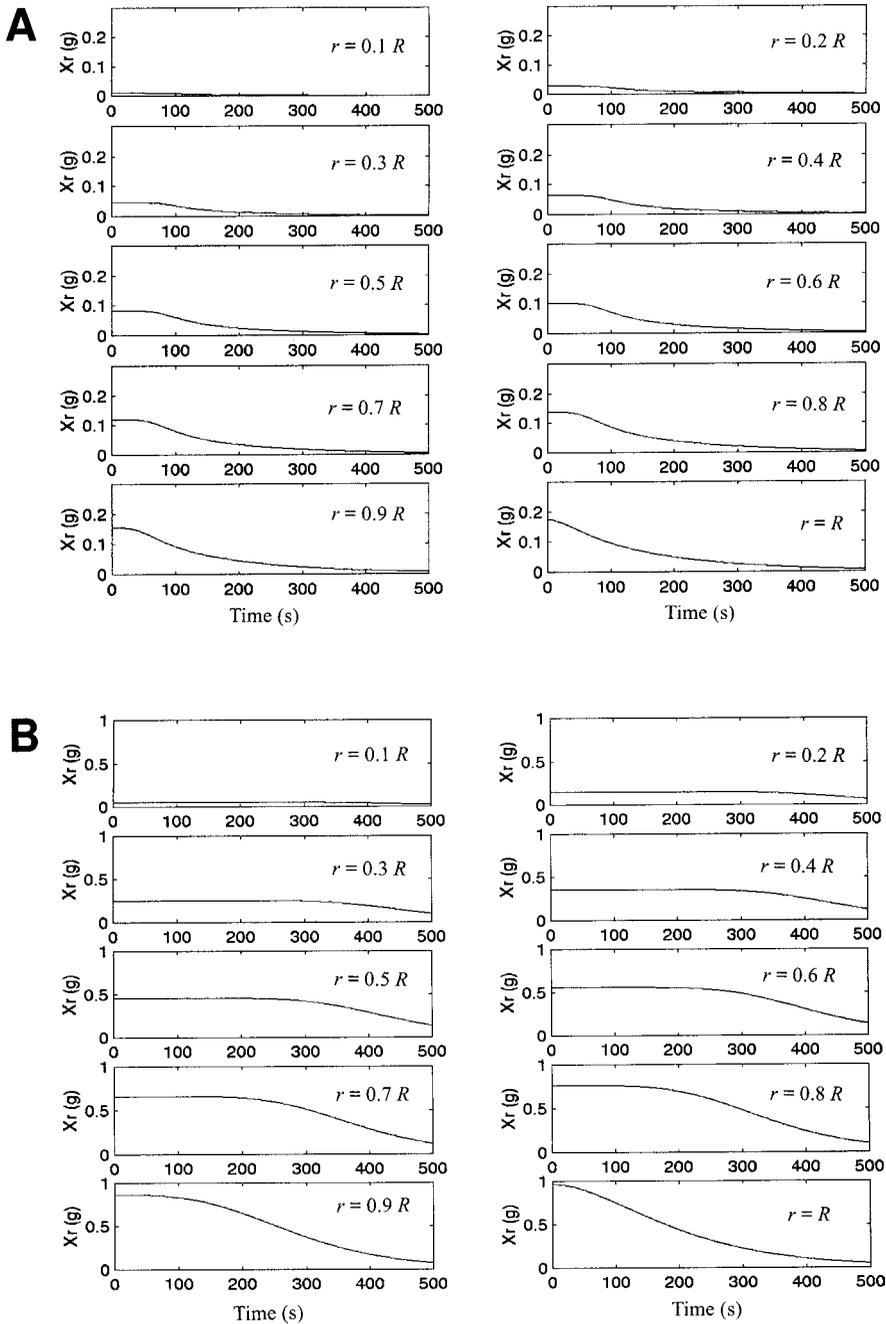


Fig. 2. Mass of xylan remaining ( $X_r$ ) in grams in each concentric ring vs time in seconds for a reactor with a 0.5-in. diameter ( $r = 0.64$  cm) (A) and a 1.0-in. diameter ( $r = 1.27$  cm) (B).

little influence on the total amount hydrolyzed. Thus, for many purposes, heating only 80–90% of the outside radius may be sufficient to achieve target yields because the outer rings have a much greater effect.

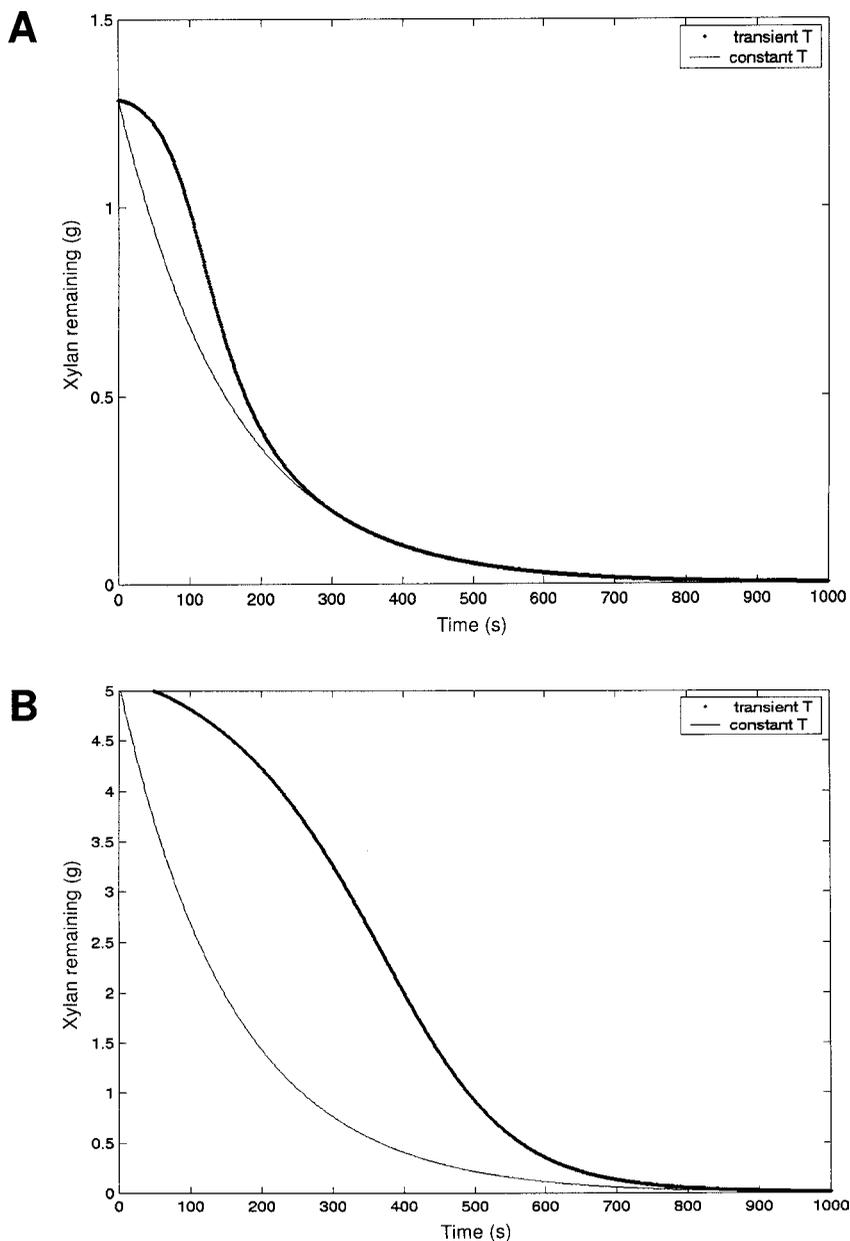


Fig. 3. Xylan remaining in grams vs time in seconds for a reactor with a 0.5-in. diameter ( $r = 0.64$  cm) (A) and a 1.0-in. diameter ( $r = 1.27$  cm) (B).

To allow comparison of the transient profile resulting from the delay in tube heat-up owing to heat transfer effects to a perfect system with virtually instant heat-up, the same kinetic equations were applied but at a constant temperature equal to the target value (e.g.,  $160^{\circ}\text{C}$  in our previous example). Comparison of constant temperature profiles with transient temperature is shown in Fig. 3. Figure 3A shows that early in the reaction, even

with a diameter of 0.5 in., the kinetic profile is somewhat affected by a heating lag. However, after about 50% conversion, the profiles for both cases are nearly identical. Figure 3B clearly indicates that the 1-in. diameter is too large to assume quick heating without effects on the xylan conversion profile.

## Conclusion

The results from this model illustrate the value of analysis in designing experimental systems to ensure that unknown variations in key operational parameters that can affect results are avoided. In particular, a combined heat transfer and kinetic model has been developed to predict the effect of temperature transients owing to heat transfer on reaction kinetics and hemicellulose hydrolysis for a tubular batch reactor. Based on these results, we concluded that a reactor diameter of 0.5 in. or less is needed to ensure that the reaction performance is reasonably described by a constant temperature model. This result is important to keep in mind when reviewing reports of hydrolysis experiments reported in the literature. For larger tube diameters of 1.0 in. or more, the kinetics could be affected by heat transfer limitations unless measures are taken to specifically improve heating. One such option would be to employ two sand baths in series with the tubes submersed first in one heated to a higher temperature than targeted and then transferred into a second reactor held at the desired reaction temperature once the latter temperature is reached. Another option is to charge the reactor with preheated liquid to rapidly bring the system to the desired temperature. Furthermore, data obtained in even larger nontube batch reactors, usually with a volume of 1 to 2 L, could be even more significantly affected unless vigorous mixing is applied to ensure rapid heat transfer. However, even then, careful analysis is important to ensure that the temperature profile follows expectations.

This analysis also shows that the results are heavily weighted by the larger quantity of material contained in the outer portion of the tubes whereas the inner rings contain only a small fraction of the total biomass. This small amount does not significantly affect the overall reaction profile, and the performance will more closely match that for the outer wall temperature than might be expected based on a measurement of the temperature in the middle of a tube. Thus, measuring the temperature at a point other than at the center of a tube, as typical of most studies, may be a better indication of the effect of kinetic performance.

Note that because the heat transfer coefficient for a fluidized sand bath is very high, the model assumed that the wall of the reactor instantly reached the bath temperature. However, for other systems such as oil baths or steam, heat transfer to the outer wall could be important, and appropriate heat transfer coefficients would need to be applied for such a system.

## Acknowledgment

This work was made possible through the generous support of the Thayer School of Engineering at Dartmouth College.

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