Temperature Distributions in a Laminar-Flow Tubular Photoreactor

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The determination of temperature distributions, maximum temperatures, and hot spot locations is of considerable importance in the design, optimization, and operation of photochemical reactors. Frequently, unwanted thermal reactions compete with the desired photochemical reaction(s), resulting in reduced yield and selectivity and increased by-product formation (Calvert and Pitts, 1966, p. 582). The rates of the thermal reactions typically display an Arrhenius temperature dependence, so that good temperature control is essential if side reactions having significant activation energies are to be minimized.

Laminar-flow tubular photoreactors have been the most popular choice for laboratory investigations of kinetics and scale-up and have also been proposed for large-scale use in the production of fuels and other useful products in solar photochemical systems (Biddle et al., 1984; Peterson et al., 1984). They have been the subject of much experimental and theoretical work (Schechter and Wissler, 1960; Dolan et al., 1965; Hill and Felder, 1965; Cassano and Smith, 1966; Walker and Baginski, 1966; Ziolkowski et al., 1967; Harano and Smith, 1968; Hill et al., 1968; Matsuura et al., 1969; Zolner and Williams, 1972). Despite a general recognition of the importance of thermal control in photochemical systems (Calvert and Pitts, 1966, pp. 582, 649; Cassano et al., 1967; Fischer, 1978; Biddle et al., 1984; Peterson et al., 1984), very little is known about temperature distributions and heat transfer in these or any other photochemical reactors.

In this work we compute temperature distributions in a laminar-flow, circular-tube photoreactor of the type previously considered in laboratory and theoretical studies of photochemical reaction kinetics and mixing.

Model and Governing Equations

We consider a hydrodynamically developed, steady laminar Poiseuille flow of a Newtonian fluid containing a photosensitizer A at concentration c_A in a long, optically transparent tube of radius R. The fluid enters an illuminated section of length L (region 2 in Figure 1) where the photosensitizer absorbs radially incident light (as described in the references cited below). The molar extinction coefficient of the photosensitizer—which absorbs radiation but is not destroyed by photochemical or thermal processes—is taken to be ϵ. For simplicity, we assume that ϵ is a constant for all wavelengths absorbed, or equivalently, that only one wavelength is absorbed. We also assume that the reactant(s) and product(s) of the photosensitized reaction do not absorb at the wavelength of interest. Finally, we will assume that the absorbing fluid has constant thermophysical properties (including density), so that the steady governing energy equation is

$$\rho c_p U_o (1 - r^2/R^2) \frac{\partial T_i}{\partial z} = k \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T_i}{\partial r} \right) + \frac{\partial^2 T_i}{\partial z^2} \right] + \delta_{i2} Q(r) \quad (1)$$

where T_i is the temperature in region i. Here, $Q(r) = a\mu C_A I(r)$ is the rate at which absorbed energy is converted to heat, where

$$I(r) = \frac{2 I_o R}{r} e^{-\mu C_A R} \cosh \mu C_A r \quad (2)$$

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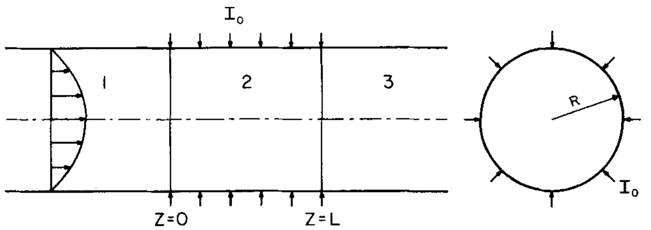

Figure 1. Geometry of laminar-flow tubular photochemical reactor.

is the light intensity as a function of position within the reactor, a is the average amount of energy that is ultimately degraded to heat per photon absorbed, $\mu = \epsilon \ln 10$, and I_o is the light intensity (power/area) entering the illuminated region. The Kronecker delta in Eq. 1 accounts for the fact that all of the heating occurs in the central irradiated region 2. The thermochemical interpretation of the quantity a in terms of radiative and nonradiative energy transfer processes and exothermic reactions has been discussed elsewhere (Pearlstein, 1985).

The radial incidence model, Eq. 2, is admittedly a rather simple approximation to the light intensity distribution in a real photoreactor (Alfano et al., 1986). It has, however, been used in a number of studies of the effects of convective and diffusive mixing on photochemical kinetics in tubular reactors (Schechter and Wissler, 1960; Hill and Felder, 1965; Cassano and Smith, 1966; Harano and Smith, 1968; Hill et al., 1968), where its qualitative validity is now well established (Alfano et al., 1986). We therefore believe that this model of the light intensity distribution is a good starting point for the analysis of heat transfer in photoreactors.

We take the boundary condition at the tube wall to be one of fixed temperature, namely

$$T(R, z) = T_o \quad -\infty < z < \infty \tag{3a}$$

corresponding, for instance, to a thin tube wall and very good forced convection cooling (or heating) of the outer surface of the tube. An example of the approximate realization of this boundary condition is found in the work of Matsuura et al. (1969), in which heated air was passed through an annular quartz jacket surrounding the tubular photoreactor. Far upstream and downstream of the irradiated section, we take

$$\lim_{|z| \to \infty} \frac{\partial T(r, z)}{\partial z} = 0 \tag{3b}$$

The assumption of laminar Poiseuille flow is consistent with the experimental work of Matsuura et al., in which the photolysis of acetone was studied in a circular-tube photoreactor with a Reynolds number (based on tube diameter, average velocity, and an estimate of the He-acetone viscosity according to standard methods [Bird et al., 1960, p. 24]), as well as with the experimental work of Dolan et al. (1965), in which a large part of an extensive study of the photodecomposition of hexachloroplatinic acid in a circular-tube photoreactor was conducted under laminar flow conditions.

In Eq. 1 we have neglected viscous dissipation heating. We have retained the axial conduction term because of its importance in previous experimental work at low Pe (e.g., Matsuura et al., 1969).

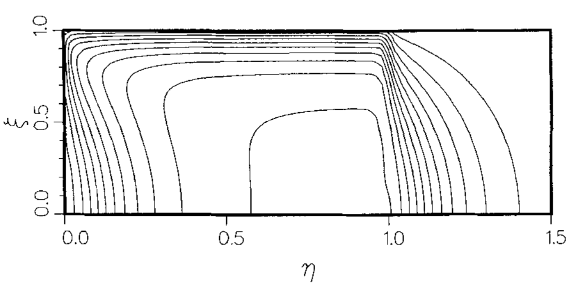

Figure 2. Isotherms in illuminated section ($0 \leq \eta \leq 1$) for $Pe = 10$, $\sigma = 10$, $\gamma = 10.0$.
Maximum temperature, 0.0564; $\Delta\theta = 0.005$

The choice of a photosensitized reaction in this first work on heat transfer in photochemical reactors is guided by two factors. First, photosensitized reactions have been studied in the chemical engineering literature (Shendalman and Hill, 1971; Mendiratta et al., 1975) and are of interest in connection with several photopolymerizations. Second, the assumptions that only the sensitizer absorbs radiation (i.e., that the reactant[s] and product[s] do not absorb) and that the photosensitizer is not consumed ensure that the energy balance can be decoupled from the species balances. The relatively simple model employed here allows for extensive analysis of and insight into the heat transfer process for this reactor. For these reasons, we have chosen the two-dimensional model used here as a starting point in the thermal analysis of photochemical reactors.

Results

The governing equations, Eqs. 1–3, are nondimensionalized according to $r = \xi R$, $z = \eta R Pe$, $\gamma = \mu C_A R$, $Pe = U_o R \rho c_p / k$, and $T = T_o + 2aI_o R\theta/k$. The solution $\theta(\eta, \xi)$ is written in each region as the sum of a fully developed part and an expansion in terms of ξ-dependent eigenfunctions and exponentials in η (Hsu, 1971). The coefficients can be determined analytically by matching the temperatures and heat fluxes at the beginning and end of region 2 (Pearlstein, 1975; Smith et al., 1975). The results are presented as contour plots of $\theta(\eta, \xi)$ for the illuminated region 2 and the adjacent parts of regions 1 and 3. Note that the dimensionless temperature at the wall is $\theta(\eta, 1) = 0$ and that the temperature difference between isotherms, $\Delta\theta$, is given separately for each case.

For $Pe = 10$ and $\gamma = 10$, Figures 2 and 3 show $\theta(\eta, \xi)$ for $\sigma = 10$ and 1, respectively. The effect of σ is clearly apparent in the more fully developed character of $\theta(\eta, \xi)$ at the exit plane in Figure 2 ($\eta = \sigma/Pe = 1$) than in Figure 3 ($\eta = \sigma/Pe = 0.1$). (The

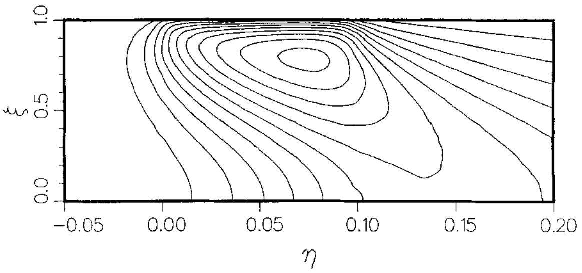

Figure 3. Isotherms in illuminated section ($0 \leq \eta \leq 0.1$) for $Pe = 10$, $\sigma = 1$, $\gamma = 10.0$.
Maximum temperature, 0.0336; $\Delta\theta = 0.003$

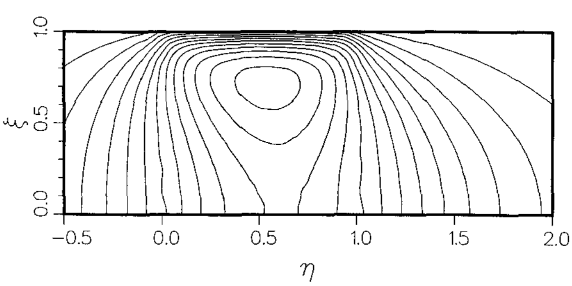

Figure 4. Isotherms in illuminated section ($0 \leq \eta \leq 1$) for $Pe = 1, \sigma = 1, \gamma = 10.0$.
Maximum temperature, 0.0405; $\Delta\theta = 0.003$

apparently larger axial temperature gradient in the $\sigma = 10$ case results from the fact that the aspect ratios of the plots do not correspond to the actual aspect ratios.) In addition, we note that for $\sigma = 10$, the maximum temperature occurs on the centerline ($\xi = 0$), whereas for $\sigma = 1$, the maximum temperature occurs off the centerline. In both cases, the maximum temperature occurs near the exit plane.

To appreciate the importance of axial conduction effects in some of the previous experimental work, we note that $Pe \simeq 2$ in the He-acetone experiments of Matsuura et al. (1969) and show in Figure 4 the temperature distribution for $\sigma = 1$, $Pe = 1$, and $\gamma = 10$. The maximum temperature again occurs off the centerline, close to the η-center of the illuminated region. The approximate axial symmetry of $\theta(\eta, \xi)$ about $\eta = \sigma/(2Pe)$ is due to the pronounced importance of the axial conduction term relative to the advection term. As σ increases, this symmetry will be preserved, even though $\theta(\eta, \xi)$ will be more fully developed in the center of region 2.

In conclusion, we note that a decision as to whether centerline or off-centerline hot spots are more deleterious in a given situation will typically depend on several factors. If thermal decomposition of the reactant(s) or sensitizer is important, then thermal control everywhere is important, owing to the nature of the mass flow rate distribution for a parabolic velocity profile. If, however, thermal decomposition of the desired product(s) is to be avoided, then the maximum temperature near the tube wall will be especially important for high optical densities, in which case the light absorption (and product formation) is concentrated close to the tube wall.

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Notation

a = average energy degraded to heat per photon absorbed
c_p = specific heat
C_A = concentration of photosensitizer A
I_o = incoming light intensity at tube wall $r = R$
$I(r)$ = light intensity distribution
k = thermal conductivity
L = length of illuminated region
Pe = Peclet number, $U_o R \rho c_p / k$
$Q(r)$ = internal heating rate due to light absorption
r = radial coordinate
R = tube radius
T = temperature
T_o = temperature of tube wall
U_o = centerline fluid velocity
z = axial coordinate

Greek letters

γ = optical density, $\mu C_A R$
δ_{ij} = Kronecker delta
ϵ = molar extinction coefficient
η = dimensionless axial coordinate, $z/(RPe)$
$\mu = \epsilon \ln 10$
ξ = dimensionless radial coordinate, r/R
ρ = fluid density
σ = aspect ratio of illuminated region 2, L/R

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