Radiation Heat Transfer in Catalytic Monoliths

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Numerical simulations of heat- and mass-transfer and heterogeneous reactions in catalytic monoliths are reported with the focus on the influence of radiation heat transfer on the thermal behavior of the monolith. Appropriate heterogeneous kinetics and boundary conditions were calculated for two cases including: an automobile catalytic converter in which carbon monoxide is oxidized over a platinum (Pt) catalyst and a catalytic combustor for gas turbine power generation in which methane is oxidized over a palladium oxide (PdO) catalyst. Surface oxidation rates of carbon monoxide are based on measurements of Pt catalyst activity in a catalytic flow reactor, and rates for methane oxidation are based on reaction kinetics for a supported PdO catalyst assigned from differential reactor measurements. These simulations show that in the high aspect ratio passageways (length to diameter) in catalytic monoliths, radiation heat transfer can play a major role in the energy balance on the catalytic surfaces, which determines the transient warm-up behavior and the steady-state location of catalyst light-off. For gray surfaces, however, the predicted steady-state and transient behaviors are not sensitive to the emissivity of the monolith walls.

Introduction

Monolith-supported catalysts play an important role in our technological society. Their most widespread application is in the automobile catalytic converter (Taylor, 1990). Typical construction of automobile catalytic converters includes an alumina washcoat containing a variety of metal oxides for stabilizing washcoat surface area and precious-metal dispersion (Taylor, 1990). Typically, catalytic converters operate at temperatures near 600°C during normal driving and 800°C under high speeds or heavy loads (Narula et al., 1996). A recent article addresses many of the advanced materials needs for catalytic converters, and automobiles in general (Narula et al., 1996).

Catalytic combustor technology differs from catalytic converter technology because of the significantly higher operating temperatures found in catalytic combustion. Catalytic combustors for gas-turbine power generation are nearing commercialization (Hicks et al., 1990) in engines with moderate inlet temperatures ($< 1{,}250$°C). In the long run, they hold promise as an economical combustion technology for ultra-low emissions of NO_x (exhaust levels below 10 ppm). Catalytica and General Electric successfully demonstrated that catalytic combustion can indeed produce power with ultra-low emissions of NO_x, carbon monoxide (CO), and hydrocarbons (Beebe et al., 1995). Catalytic combustion of natural gas promises to be a relatively clean source of power and heat in applications as varied as home heating, drying, incineration, stabilization of gas-turbine combustion, and low-NO_x power generation. The various benefits, uses, and engineering challenges of catalytic combustion are thoroughly reviewed elsewhere (Trimm, 1983; Pfefferle and Pfefferle, 1986; Zwinkels et al., 1993).

For different reasons, thermal management concerns affect current design and development efforts for both catalytic converters and catalytic combustors. In the automotive application, the "cold-start" period of vehicle operations presents a critical design challenge, wherein pollutants pass through the exhaust system unreacted because the emission controls are cold. During cold-start conditions, 60–80% of all hydrocarbons are emitted in federal test procedures (FTP) with light-duty gasoline engines (Kummer, 1980). Several technologies have been proposed to reduce cold-start emissions, with one or more of three typical strategies: (1) electrically heat a catalytic converter; (2) "close couple" a converter by placing it near the exhaust manifold to make use of the sensible energy in the exhaust; and (3) trap or divert the pollutants until the catalytic converter has reached its operating temperature (Kollmann et al., 1994).

In contrast, the ceramic and metallic supports for combustion catalysts are subject to thermally induced stresses and fatigue due to their high operating temperatures, especially

during light-off and emergency shutdowns (Furuya et al., 1994). Catalysts under development for these combustors contain palladium oxide (PdO) dispersed on stabilized alumina (Dalla Betta et al., 1993) and metallic (Dalla Betta and Löffler, 1996) supports. These catalysts are sufficiently active to light-off at 300–400°C. They also maintain high activity up to 900°C (Farrauto et al., 1990), where current combustor designs operate in the steady state. Temperature excursions above 1,000°C exceed the decomposition temperature of PdO, at which point the rate of combustion becomes nearly independent of temperature. Such thermal excursions, as well as advanced applications with gas turbine inlet temperatures from 1,250 to 1,450°C, place severe demands on the catalyst and support materials now under development.

Catalytic converters and catalytic combustors have been the subject of many numerical investigations. It is convenient to characterize these efforts in terms of their description of the gas phase within the catalytic passage, that is, whether the channel is one-dimensional (relying on heat- and mass-transfer coefficient correlations), two-dimensional (assuming axisymmetry, parallel flat plates, or external boundary-layer flow), or three-dimensional (no spatial simplifications). These studies have included: one-dimensional considerations of single passageways (Votruba et al., 1975; Heck et al., 1976; Young and Finlayson, 1976a,b; Sinkule and Hlavácek, 1978; Finlayson and Young, 1979; Marteney and Kesten, 1981; T'ien, 1981a,b; Oh and Cavendish, 1982; Prasad et al., 1983; Ahn et al., 1986; Zygourakis, 1989; Bennet et al., 1992; Tien and T'ien, 1992; Montreuil et al., 1992; Groppi et al., 1993; Oh and Bissett, 1993; Leighton and Chang, 1995), multiple passageways (Flytzani-Stephanopoulos et al., 1986; Chen et al., 1988; Kolaczkowski et al., 1988; Kolaczkowski and Worth, 1995), two-dimensional solutions for single passageways (Heck et al., 1976; Young and Finlayson, 1976a,b; Finlayson and Young, 1979; Bennet et al., 1992; Lee and Aris, 1977; Harrison and Ernst, 1978; Zygourakis and Aris, 1983; Bruno et al., 1983; Ryan et al., 1991; Hayes et al., 1992, 1996; Boehman et al., 1992; Hayes and Kolaczkowsi, 1994; Groppi et al., 1995; Frye and Boehman, 1996; Boehman et al., 1997a,b), external boundary-layer flows (Mori et al., 1977; Schefer, 1980; Brown et al., 1983; Fakheri and Buckius, 1984; Markatou et al., 1991, 1993), and three-dimensional solutions with complex passage geometries (Young and Finlayson, 1976a,b; Sinkule and Hlavácek, 1978; Finlayson and Young, 1979). In catalytic converters, homogeneous reactions are generally neglected, but some studies of catalytic combustors have included global chemistry (T'ien, 1981a,b; Prasad et al., 1983; Ahn et al., 1986; Bennet et al., 1992; Tien and T'ien, 1992; Harrison and Ernst, 1978; Bruno et al., 1983; Hayes et al., 1992; Hayes and Kolaczkowski, 1994; Groppi et al., 1995), and others have included detailed chemical reaction systems (Schefer, 1980; Markatou et al., 1991, 1993). Also, all of these prior studies have included convective heat transfer and chemical heat release from the surface reactions. Most have included conduction heat transfer in the catalytic surface (monolith walls or flat plate), with the exception of Heck et al. (1976), Mori et al. (1977), T'ien (1981a,b), Schefer (1980), Brown et al. (1983), Bruno et al. (1983), Fakheri and Buckius (1984), Markatou et al. (1991, 1993), and Leighton and Chang (1995). Some have included radiation heat transfer, as well (Lee and Aris, 1977; Sinkule and Hlavácek, 1978; Ryan et al., 1991; Bennet et al., 1992; Hayes et al., 1992, 1996; Boehman et al., 1992; Hayes and Kolaczkowski, 1994; Groppi et al., 1995; Kolaczkowski and Worth, 1995; Frye and Boehman, 1996; Boehman et al., 1997a,b). The level of detail in heterogeneous chemistry models has varied from generic global rate laws to global rate laws modified by effectiveness factors that account for pore diffusion in the catalytic layer (Young and Finlayson, 1976a,b; Hayes and Kolaczkowski, 1994), to solution of the governing equations for the surface diffusion of species in the catalytic layer (Zygourakis and Aris, 1983). Guidelines for formulation of models of catalytic converters (Young and Finlayson, 1976a,b; Hayes et al., 1992) and catalytic combustors (Pfefferle, 1995) are available.

Previously, Lee and Aris characterized the influence of gray- and blackbody radiation on catalytic converter behavior (Lee and Aris, 1977). However, their simulations predict an exaggerated effect of radiation on steady-state temperature profiles in the monolith walls. Comparison of their results with the present work and other published work suggests that the discrepancy lies in their formulation of the radiative heat exchange.

Recently, Groppi et al. characterized the influences of developing flows, variable physical properties, conduction, and radiation on monolith catalytic combustor behavior (Groppi et al., 1995). In their simulations, Groppi et al. relied on a correlation for radiation heat transfer that was originally developed by Lee and Aris (1977), which treats radiation as an "effective conductivity." Their simulations showed a weak dependence of monolith behavior on radiation heat transfer, with the primary effect of radiation being on the position of the steady-state light-off profile. This observation lies in sharp contrast to the results of the present work, as well as other published work, wherein radiation heat transfer exerted a significant effect on steady-state and transient catalytic combustion.

This article presents results from two studies of the behavior of catalytic monoliths regarding the sensitivity of catalytic passageways to radiation heat transfer. One set of calculations considers the oxidation of carbon monoxide over a platinum catalyst for conditions relevant to automobile exhaust cleanup, and another set of calculations considers the oxidation of methane over a palladium oxide catalyst for conditions relevant to power-generation systems employing catalytic combustion. The intent of this article is to clarify the impact of radiation heat transfer on the behavior of two important classes of catalytic monolith reactors by examining the influence of surface emissivity and monolith operating temperature. In addition, this article also addresses the formulation of models for radiation heat transfer in catalytic passages. This is an attempt to rationalize conflicting information on radiation in catalytic monoliths that is present in the archival literature.

Numerical

Governing equations

As illustrated in Figure 1, even though the flow channels in ceramic monoliths have rectangular cross sections, they can become circular once the catalytic washcoat has been applied (Narula et al., 1996). A cylindrical coordinate system is a reasonable approximation to this irregular geometry. Within the

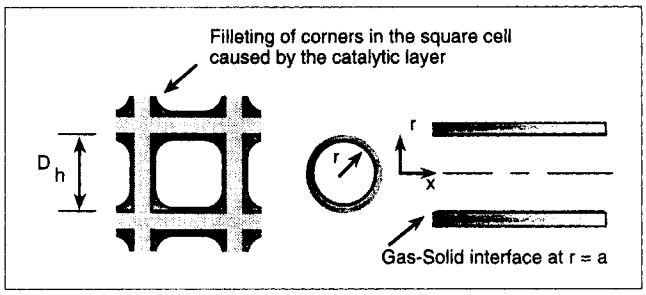

Figure 1. Cylindrical representation of the catalytic passage from a catalytic converter or combustor.

cell, energy and species are exchanged between the gas stream and the catalytically active walls of the monolith. The processes operating in the cells are convection and diffusion of energy and species in the gas stream, heterogeneous reactions on the cell walls, conduction within, and radiation along the walls. In the present work, homogeneous chemistry is neglected for both catalytic converter and catalytic combustor modeling, although homogeneous reactions contribute substantially to the combustion process as shown by Markatou et al. (1991, 1993). For "hybrid" catalytic combustor applications, such as catalytically stabilized lean premixed combustion wherein the monolith performs partial combustion of the fuel, neglecting gas-phase reactions within the monolith is a reasonable approximation. Recent experiments on catalytically stabilized lean premixed combustion demonstrate that catalyst outlet temperatures should remain low ($<1{,}200°C$) to optimize the emissions benefits of catalytic combustion while protecting catalyst integrity (Schlegel et al., 1997). The flow through the cells is laminar and developing over much of the cell length, but the radial velocity component is ignored. These assumptions and approximations are employed in formulating approximate governing equations for the transport and reaction processes.

The applicable governing equations for a transient 2-D model of a catalytic passage are well established. The equations include a set of convection/diffusion equations for energy and species in the gas stream, and an energy balance for the catalytic surface. Surface diffusion of species is built into the reaction-rate law for heterogeneous chemistry. The gas-phase equations are

$$\rho u c_p \frac{\partial T_g}{\partial z} - k_g \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T_g}{\partial r}\right) = 0 \tag{1}$$

$$\rho u \frac{\partial y_i}{\partial z} - \rho D_{im}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial y_i}{\partial r}\right) = 0, \tag{2}$$

where ρ is the density of the gas mixture, k_g its conductivity, and c_p its specific heat; $u(r,z)$ is the local velocity, a function of spatial coordinates, r and z; $T_g(r,z)$ and $T_s(z)$ are the gas phase and surface temperatures, respectively; y_i is the mass fraction of species i; D_{im} is its mixture diffusion coefficient.

The energy balance for the catalytic surface is

$$\rho_s c_{p_s} h\frac{\partial T_s}{\partial t} - k_s h\frac{\partial^2 T_s}{\partial z^2} - k_g\frac{\partial T_g}{\partial r}\bigg|_{r=a} = \dot{R}(-\Delta H) - \dot{q}_r, \tag{3}$$

where ρ_s is the density of the substrate, k_s its conductivity, c_{p_s} its specific heat, and h its half-thickness; $\dot{R}$ is the surface reaction rate with the heat of reaction, ΔH; and $\dot{q}_r$ is the net radiation heat flux.

The boundary conditions for these equations describe the fluxes of each species at the catalyst surface (Eq. 4); a thermal continuity condition between the gas temperature at the surface and the surface temperature (Eq. 5); zero flux at the center of the cell (Eq. 6); and adiabatic boundaries for the substrate at either end of the monolith (Eq. 7). Also, it is assumed that radial heat flow is symmetric over a depth h between wall surfaces, so no energy flows radially through the catalytic surface. The following equations summarize these boundary conditions:

$$-\rho D_{im}\frac{\partial y_i}{\partial r}\bigg|_{r=a} = \dot{R}_i \tag{4}$$

$$T_g|_{z,r=a} = T_s|_z \tag{5}$$

$$\frac{\partial y_i}{\partial r}\bigg|_{r=0} = \frac{\partial T_g}{\partial r}\bigg|_{r=0} = 0 \tag{6}$$

$$\frac{\partial T_s}{\partial z}\bigg|_{z=0} = \frac{\partial T_s}{\partial z}\bigg|_{z=L} = 0. \tag{7}$$

The initial conditions are that the catalyst surface has a specified temperature distribution, and that the gas-phase temperature and concentrations are uniform at the inlet but may vary with time:

$$T_s(r,z,0) = T_s^o(r,z) \tag{8}$$

$$T_g(r,0,t) = T_g^o(r,t) \tag{9}$$

$$y_i(r,0,t) = y_i^o(r,t).$$

For the cases presented here, the initial wall temperature is assumed to be isothermal and equal to the inlet gas temperature. In the energy balance at the surface (Eq. 3), the radiation flux $\dot{q}_r$ is the net radiation heat flux at a point on the catalytic surface determined from the net radiation method for a gray surface, following the approach outlined by Siegel and Howell (1981). This method yields a system of equations for the net outgoing radiation heat flux at all points on the surface. The net radiation heat flux $\dot{q}_r$ is determined from the current temperature of the catalytic surface and the net outgoing radiation from all other sections of the catalytic surface. Using the net radiation method, for a gray surface, this yields the following system of equations:

$$\frac{1}{\epsilon_r}\dot{q}_r(x) - \sum_{n=1}^{N}\frac{1-\epsilon_r}{\epsilon_r}\dot{q}_r(x_n)F_{x-x_n} = \sigma T^4(x_n) - \sum_{n=1}^{N}\sigma T^4(x_n)F_{x-x_n}, \tag{10}$$

where F_{x-x_n} denotes a finite-area to finite-area shape factor. The radiation shape factors for cylindrical geometry were obtained from Buschmann and Pittman (1961). For blackbody radiation, Eq. 10 simplifies to a single relation for $\dot{q}_r$, instead

of a system of equations:

$$\dot{q}_r(x) = \sigma T^4(x) - \sum_{n=1}^{N} \sigma T^4(x_n) F_{x-x_n}. \quad (11)$$

Although shown here in dimensional form, the system of equations is solved in dimensionless terms based on mean or mixture averaged properties and dimensionless groups that include the Peclet number and three different Damköhler numbers. The non-dimensionalization is described in detail elsewhere (Boehman, 1993).

Numerical methods

The system of equations governing the behavior of a catalytic passage is inherently stiff, because the interplay among mechanisms involves coupled nonlinear boundary conditions. An implicit numerical scheme is needed to provide some flexibility in the choice of time step in transient solutions and spatial step size in steady-state solutions. Second-order central differencing is used to discretize the second derivatives in Eqs. 1–3. First-order backward differencing, referred to as first-order implicit Euler differencing, is used to discretize the time derivative in Eq. 3. The axial first derivatives in Eqs. 1 and 2 are discretized using second-order backward differencing, referred to as the second-order implicit Euler scheme.

The stiffness of the model dictates small step sizes, but passages within a catalytic converter and catalytic combustors have high aspect ratios ($L/D \approx 25$–150). Thus, a large number of axial nodes are needed to have sufficient numerical stability, unless an implicit technique is used. Second-order implicit Euler discretization of the gas-phase equations permits computational cells with high aspect ratio and maintains numerical stability for computational cell aspect ratios as high as 80 to 1. Such high aspect ratios and large axial grid spacing significantly reduce the computational burden of this model.

Solutions for the transient model, Eqs. 1–3, are based on a "cascading" procedure. Gas-phase energy and species equations are solved simultaneously. Advancing the gas-phase equations along the axial coordinate entails solution of a set of linear equations, subject to a nonlinear boundary condition, Eq. 4. At each axial position in the model, Eq. 4 is satisfied through Newton–Raphson iteration. Then the transient energy balance on the catalytic surface is marched in time to account for any changes in diffusive transport rates or heating of the gas mixture. A new set of boundary values for the gas-phase equations is assigned, and the energy and species equations are solved again.

The graybody radiation fluxes are updated at the start of the iterations for each time step. For blackbody radiation, $\dot{q}_r$ is recalculated during each iteration for each time step. For the simulation of graybody radiation, Eq. 10 is solved in two steps. First, the righthand side of Eq. 11 is calculated, which represents the net outgoing blackbody radiation. Next, the second term on the lefthand side of Eq. 10 is calculated based on the current values of $\dot{q}_r$, which represents the amount of incident radiation that is reflected. These two components of Eq. 10 are combined in Eq. 12 to calculate an updated distribution for the net outgoing flux $\dot{q}_r(x)$. This successive substitution process is repeated until Eq. 12 converges to 1×10^{-6}, generally in less than 20 iterations.

$$\dot{q}_r(x) = \epsilon_r \left(\sigma T^4(x_n) - \sum_{n=1}^{N} \sigma T^4(x_n) F_{x-x_n} \right) + \sum_{n=1}^{N} (1-\epsilon_r) \dot{q}_r(x_n) F_{x-x_n}. \quad (12)$$

The numerical method used here is a multistep method and requires an assumption about the initial condition at the start of each sweep. At the first node in the computational domain, the finite difference formula requires a value at an imaginary node upstream of the inlet to the passage. This imaginary node is assigned the same value as the first node, which implies that the inlet conditions extend upstream in the flow prior to the passage entrance.

All simulations presented here were obtained using a mesh size of 21 transverse points across the radius of the passage, and 201 axial points. A mesh refinement study showed that a 21×201 mesh provided satisfactory accuracy. All iterations were considered converged when the residual error was below 1×10^{-6}. Steady-state simulations of catalytic converter behavior and transient simulations of catalytic combustor behavior were performed on an IBM RS6000 workstation and typically required 5 minutes when radiation and conduction were ignored, 46 minutes for blackbody radiation with conduction, and 91 minutes for graybody radiation with conduction. For comparison, some transient and steady-state blackbody radiation cases were performed on a 100-MHz Pentium personal computer, which typically required about 2 to 3 hours.

Thermodynamic and transport properties and the adiabatic flame temperature of the fuel/air mixture are evaluated with the CHEMKIN transport package (Kee et al., 1980). Properties are assumed to be constant, except where noted, and are evaluated at the inlet concentrations and the mean value of the initial inlet gas temperature and the adiabatic flame temperature.

For the catalytic converter simulations the flow field was assumed to be fully developed laminar flow. For the catalytic combustor simulations, the laminar flow field in the monolith cell was allowed to develop and was simulated separately with STANTUBE, a cylindrical coordinates version of the STAN5 boundary-layer model written by Crawford and Kays (1975). STANTUBE produces a solution for the flow field that is treated as a lookup table by the model for the catalytic passage. This procedure for modeling the flow field represents an additional simplification in the description of the monolith cell. Density gradients near the catalytic surface are, in actuality, significant and they do alter the velocity field at the light-off position. Skewing of the velocity profile where there are high near-wall temperature gradients would tend to couple the hydrodynamic, thermal, and chemical fields. However, this is a high-order effect and it was neglected.

Results and Discussion

Catalytic converter simulations

This model has been used for a variety of tasks including the design of a planar catalytic reactor, verification of experimentally determined global catalyst kinetics, and examination of the sensitivity of catalytic passage behavior to inlet flow

Table 1. Inlet Conditions and Physical Parameters for Catalytic-Converter Simulation

Parameter	Range
Flow properties	
Inlet pressure	0.77 bar
Inlet CO concentration	4 mol %
Inlet O_2 concentration	5 mol %
Inlet gas temperature	343°C
Heat of reaction	1.17×10^7 J/kg CO
Mixture adiabatic flame temp.	702°C
Reynolds number, Re_D	160
Prandtl number, Pr	0.704
Substrate properties	
Monolith cell dia., $2r_0$	0.122 cm
Monolith wall thickness, ϵ	0.0305
Monolith length, L	10.17 cm
Wall density, ρ_s	550 kg/m^3
Specific heat of wall, c_{p_s}	1,100 J/kg·K
Wall thermal conduct., k_s	1.4 W/m·K

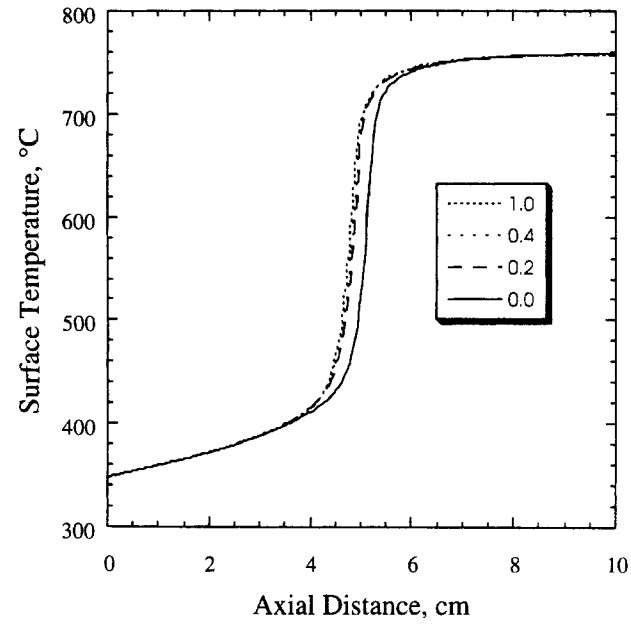

Figure 2. Steady-state axial surface temperature profiles for a monolith catalytic converter for surface emissivities from 0.0 to 1.0 and the conditions in Table 1.

rate and composition (Boehman et al., 1991, 1992). Here the results from parametric studies of radiation heat transfer are presented. The model permits consideration of nonradiating, gray and black surfaces, but it assumes the emissivity to be uniform and invariant with surface temperature. A global rate expression proposed by Young (1974) and Young and Finlayson (1976b; 1979) describes the heterogeneous reactivity for CO oxidation over Pt on alumina:

$$\dot{R}_{CO} = \frac{2.3338\chi_{CO}\chi_{O_2}}{\left(1+1.33e^{6,111/T_s}\chi_{CO}^2\right)} \quad \left(\frac{\text{kg CO}}{\text{m}^2\cdot\text{s}}\right) \qquad (13)$$

Table 1 presents the conditions used in the CO oxidation simulation. These conditions are based loosely on those of Young (1974), referred to as case S4. The effects of gray- and blackbody radiation on light-off position were modeled by comparing the steady-state surface temperature profiles for a range of surface emissivities. As shown in Figure 2, both gray and black surfaces caused the light-off front to move upstream, although only slightly. The effect of radiation can be felt only over short distances of the passage due to the rapid decrease of the radiation shape factors with axial distance. This point is discussed further. For such a high-aspect-ratio passage ($L/D \approx 80$), no radiation exchange occurs between the ends and the central portion of the passage, meaning that under these conditions, radiation heat transfer has a negligible effect on the light-off position.

The influence of radiation heat transfer on catalytic converter behavior has been included in simulations by Sinkule and Hlavácek (1978) using a 1-D model, and Lee and Aris (1977), Hayes and coworkers (Bennet et al., 1992; Hayes et al., 1992; Hayes and Kolaczkowski, 1994), Ryan et al. (1991), and Boehman et al. (1992) using 2-D cylindrical models. Both Ryan et al. and Boehman et al. included the influence of radiation on monolith behavior, but did not present comparison of radiative and nonradiative cases. The other studies mentioned did consider the influence of radiation heat transfer through parametric study and their observations are summarized below.

Sinkule and Hlavácek (1978) performed steady-state simulations that considered only black surfaces and a passage with $L/D = 20$. Sinkule and Hlavácek used differential element shape factors for radiation within the passage and to the end cavities, but used auxiliary grid points in their finite difference mesh when evaluating the shape factor to enhance accuracy. They observed that radiation within an *adiabatic* monolith passage (i.e., radiation out the ends of the passage is absorbed by the flowing gases) was only significant near the inlet to the passage. However, they observed a significant decline in surface temperature along the entire monolith with a *nonadiabatic* passage, due to radiation losses to end cavities, which were assumed to be at the inlet gas temperature.

Lee and Aris performed steady-state simulations of CO oxidation considering the effects of the monolith aspect ratio, surface emissivity, and surface conductivity. Their results are directly comparable with the present work. The results of their calculations for CO oxidation over a noble metal catalyst demonstrate that radiation heat transfer moves the light-off position forward, smoothes the steep temperature gradient associated with catalyst light-off, and decreases the post-light-off temperature near the end of the passage, due to radiative end losses. The current model confirms this observation that radiation heat transfer moves the light-off front upstream in the passage. As with Sinkule and Hlavácek, Lee and Aris predict significant radiative loss to the end cavities of the monolith. In contrast to the nonadiabatic case of Sinkule and Hlavácek where radiation was assumed to occur to cavities at the gas inlet temperature, Lee and Aris assumed that radiation occurred to blackbody radiators at the temperatures of the inlet and the exit gases. Since the gas stream warms substantially as it flows through the passage,

the amount of energy that can be lost out the exit by radiation is limited. Yet, Lee and Aris show significant decreases in surface temperature near the exit when comparing nonradiating and black passages, by as much as 30°C (c.f., Lee and Aris, 1977, fig. 11). In addition, although Lee and Aris stated that the ends of their passage are insulated, they show that increasing the conductivity of the catalytic surface by a factor of 10 decreased the peak surface temperature after light-off by 100 K. For a passage with insulated ends, this result violates energy conservation and may indicate that their treatment of radiative exchange within the passage greatly exaggerates the effect of end losses. This point will be discussed further.

Hayes and co-workers developed a finite element method for simulating both catalytic converters and catalytic combustors, which they applied to propane (C_3H_8) and CO oxidation (Bennet et al., 1992; Hayes et al., 1992; Hayes and Kolaczkowski, 1994). They present their method of solution (Hayes et al., 1992), comparison with experimental reactor measurements (Bennet et al., 1992), and explanation of discrepancies between experiment and prediction (Hayes and Kolaczkowski, 1994). In their formulation for radiative heat transfer, Hayes et al. make use of finite area shape factors to describe the exchange between sections of the monolith wall in the finite-element model. They conclude, as Lee and Aris did, that radiation and conduction both act to smooth temperature gradients in the passage, with conduction exerting a far greater influence (Hayes et al., 1992). However, Hayes et al. do not predict substantial decreases in post-light-off surface temperatures due to radiation to the exiting gases, as Lee and Aris did. Also, Hayes et al. show that the influence of radiation heat transfer to the inlet and exit cavities does not penetrate into the monolith passage, despite the relatively low aspect ratio ($L/D = 20$) in their simulation. The predictions of Hayes and coworkers are thus more consistent with the result presented here in Figure 2.

Catalytic-combustor simulations

This model has been used to examine transient warm-up and cooldown behavior of methane-fired catalytic combustors. The model was coupled to a finite-element stress analysis package to investigate the relationship between combustor operating conditions and thermal stress formation (Boehman et al., 1997a,b). Kinetics for the combustion of methane over supported palladium are complicated by the formation and decomposition of palladium oxide, which is far more active than dispersed Pd crystallites for the operating conditions of interest in catalytic combustion. It is well known that the active form of palladium in catalytic combustion is bulk PdO. A kinetic model that incorporates the effects of micro- and macropore diffusion, described fully in Boehman et al. (1997b), represents the heterogeneous reactivity on the supported palladium oxide catalyst. This model was developed from experimental data for 5 wt. % $Pd/\gamma\text{-}Al_2O_3$ supported on lanthanum hexaaluminate in both fixed-bed and annular tubular differential reactors (McCarty, 1995):

$$\dot{R}_{CH_4} = k_{CH_4}(T_s) M_{CH_4} \frac{P}{RT_s} \chi_{CH_4} \quad \left(\frac{\text{kg CH}_4}{\text{m}^2 \cdot \text{s}}\right). \quad (14)$$

Table 2. Inlet Conditions and Physical Parameters for Catalytic Combustor Simulation

Parameter	Range
Flow properties	
Inlet pressure	10 bar
Inlet CH_4 concentration	3 mol %
Inlet O_2 concentration	20 mol %
Inlet gas temperature	400°C, 500°C
Mixture adiabatic flame temp.	1,100°C, 1,190°C
Reynolds number, Re_D	1360
Prandtl number, Pr	0.716, 0.717
Substrate properties	
Monolith cell dia., $2r_0$	0.18 cm
Monolith wall thickness, ϵ	0.009
Monolith length, L	5.0 cm
Wall density, ρ_s	3,200 kg/m^3
Specific heat of wall, c_{p_s}	1,100 J/kg·K
Wall thermal conduct., k_s	6.3 W/m·K

The overall reaction rate coefficient, $k_{CH_4}(T_s)$, is described in this kinetic model as the intrinsic rate modified by two effectiveness factors that account for diffusional limitations in the catalytic layer caused by micro- and macroporosity.

Table 2 lists the operating domain and physical properties for the catalytic combustor simulations. The inlet oxygen concentration was set to 20% for all calculations. Two warm-up cases were considered where the inlet gas and initial wall temperatures were equal and set at values of 400°C and 500°C, respectively. Parametric study of the influence of radiation on transient combustor behavior was accomplished by comparing results for no radiation, graybody radiation, and blackbody radiation, with emissivity set to values of 0.0, 0.2, 0.4, and 1.0. As shown in Figure 3, the influence of radiation heat transfer on transient combustor warm-up from an initial tem-

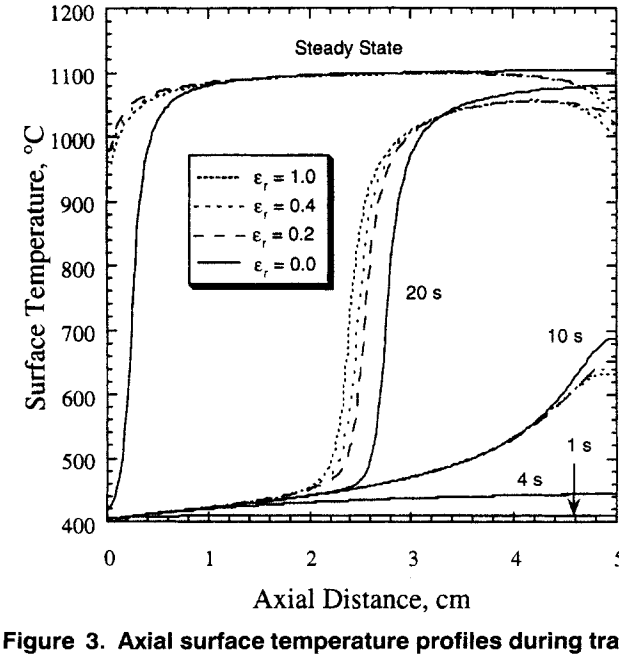

Figure 3. Axial surface temperature profiles during transient catalytic combustor warm-up from 400°C for surface emissivities from 0.0 to 1.0 and the conditions in Table 2.

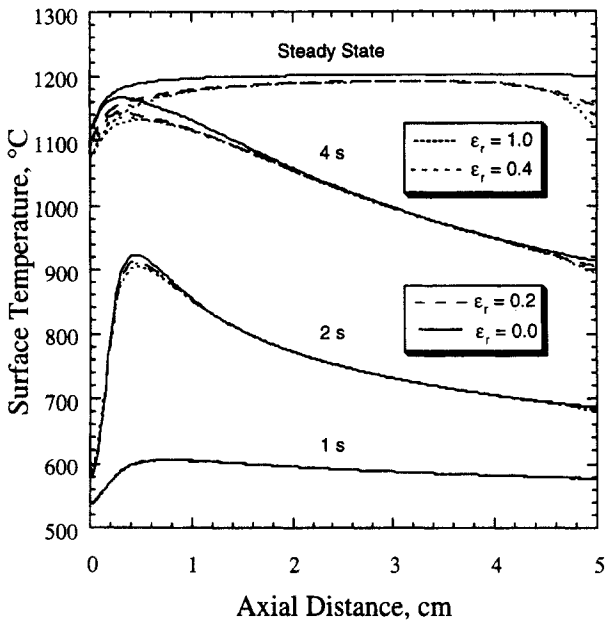

Figure 4. Axial surface temperature profiles during transient catalytic combustor warm-up from 500°C for surface emissivities from 0.0 to 1.0 and the conditions in Table 2.

perature of 400°C was substantial, affecting both the steady-state and transient combustor behavior. Comparing the blackbody and nonradiating cases we see that the steady-state temperature profiles are dramatically different. For the black surface, radiation upstream in the passage enables light-off to propagate to the inlet of the passage. For the nonradiating case, the light-off front does not reach the inlet because the large convective cooling that occurs in the entry region halts the advance of the light-off front. Another observation is that the steady-state temperature profiles for the gray surfaces do not differ significantly from the black case, even for an emissivity of 0.2. The relative insensitivity to variation of the emissivity occurs because radiation out of the ends of the passage, which are considered black disks in all cases, is the dominant effect from radiation heat transfer for this case.

For the inlet temperature of 500°C, the effect of radiation is less pronounced on the warm-up process as shown in Figure 4. As in Figure 3, the effect in Figure 4 is most pronounced at the ends of the passage. But there are two distinct differences from Figure 3. For a 500°C inlet gas, light-off begins near the inlet instead of beginning near the exit and propagating forward, and the absence of upstream radiation does not prevent light-off from reaching the inlet. In contrast to the 400°C case, upstream radiation serves to suppress the surface temperature near the inlet, when one compares the radiating and nonradiating surfaces. Also, close examination of Figure 4 reveals that for all the radiating surfaces, the surface temperature is suppressed, although only by 10°C. Throughout the passage, radiation is more prevalent due to the higher surface temperature reached for a 500°C inlet gas. This increases the transfer of energy from within the passage to the cooler ends of the combustor, which decreases the peak surface temperature slightly below the adiabatic flame temperature of the reactants.

The transient evolution of the radiative heat flux is depicted in Figure 5. Shown in this figure is the net outgoing flux, $\dot{q}_r$, calculated in Eq. 12 for a black monolith passage. The heat flux distribution varies significantly during the warm-up process due to the substantial temperature gradients that arise during the light-off process. Around light-off, the net radiation varies from a positive energy flow into the surface upstream of the advancing thermal front, to a negative energy flow. Light-off is accompanied by temperature differences of 600°C in less than a centimeter distance on the monolith wall. In steady state, even larger heat fluxes arise (negative to indicate net outflows of energy) as the surface warms and radiates out the ends of the passage.

The influence of radiation heat transfer on catalytic combustor behavior has been included in simulations by Fakheri and Buckius (1984), Hayes and coworkers (Bennet et al., 1992; Hayes et al., 1992, 1996; Hayes and Kolaczkowski, 1994), Kolaczkowski and Worth (1995), Groppi et al. (1995), and Boehman and coworkers (Frye and Boehman, 1996; Boehman et al., 1997a,b). Fakheri and Buckius observed that for simulation of a catalytically reacting boundary-layer flow, radiative cooling from the flat catalytic surface significantly altered transient behavior. Radiation served to suppress the reaction, lengthening the time required to ignite the reaction (i.e., transition to light-off).

Boehman et al. (1997a,b) have numerically modeled dynamic stress formation in methane-fired ceramic monoliths and Frye and Boehman (1996) have numerically modeled the effect of fuel composition on transient catalytic combustion. This work merely assumed blackbody radiation within the monolith passage, and did not assess the influence of surface emissivity through parametric study. The present work seeks to present a more detailed representation of the influence of

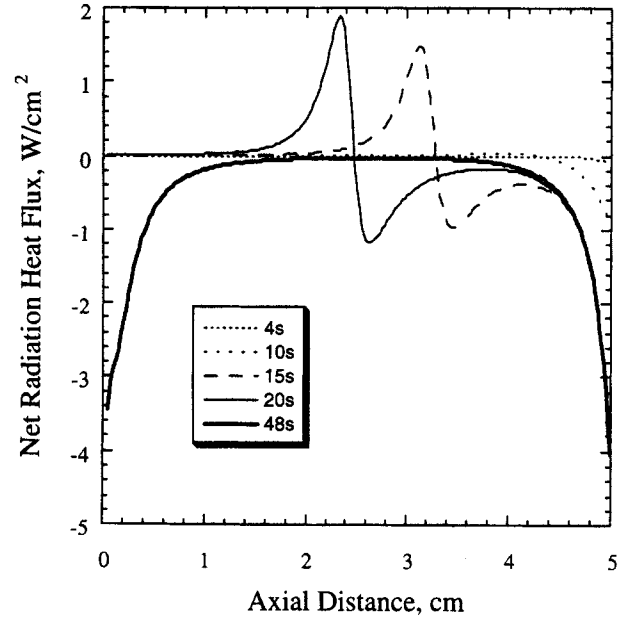

Figure 5. Net radiative heat flux at various times for a black surface and the conditions in Table 2 during transient catalytic-combustor warm-up from 400°C.

radiation heat transfer on catalytic combustor behavior by considering gray surfaces.

In the present context, the most relevant study by Hayes and coworkers is found in Hayes et al. (1996), which considered catalytic combustion of CH_4. In this work, Hayes et al. compared transient experiments and numerical simulations for monolith combustors ranging in aspect ratio (L/D) from 27 to 164. They demonstrated good agreement between prediction and experiment for steady-state and transient surface temperatures, even though they have neglected gas-phase reactions (albeit for very low concentrations of CH_4). Agreement between the predictions and experiments was obtained by setting the emissivity to 0.5 and the downstream cavity temperature to 75°C less than the exit gas temperature. Hayes et al. observe in both experiment and simulation that radiation heat transfer cools the ends of the reactor, and that for surface temperatures at or below 570°C, radiation losses were not significant.

Kolaczkowski and Worth (1995) simulated the interactions between channels within a catalytic combustor where each cell has an aspect ratio (L/D) of roughly 55. They observed that temperatures near both the inlet and exit of the monolith channels decreased when radiation was considered. Their calculations clearly show that radiation does not penetrate into the central region of the channels. They considered the surfaces on the monolith combustor to be gray, but did not report the value of emissivity used in the calculations.

Groppi et al. (1995) simulated the catalytic combustion of CH_4 and considered a variety of parametric sensitivities, including hydrodynamic development, surface conductivity, radiation heat transfer, and homogeneous reactions. They concluded that for ceramic monolith combustors (as considered in the present work), conduction and radiation have a minimal effect on steady-state surface temperature distributions. Their conclusions with regard to radiation are in sharp disagreement with conclusions reached by Hayes and coworkers and in the present work. In their calculations, Groppi et al. did not directly solve the radiation heat-transfer equations, but instead relied on an "effective conductivity" approximation originally developed by Lee and Aris (1977). Also, Groppi et al. ignored radiative losses out of the ends of the monolith. While the use of approximations such as this "effective conduction due to radiation" may have been justified in the 1970s, computing power available today has reduced the need for such numerical strategies. Also, there are some apparent flaws (discussed in the previous section) in the work of Lee and Aris (1977), which may have affected their formulation of this effective conductivity.

The discrepancies between the conclusions of Groppi et al. (1995) and other work discussed here arise from their neglect of radiative cooling from the ends of the monolith passage. The discrepancies in the work of Lee and Aris (1977) may be attributable to their use of differential shape factors instead of finite-area shape factors in formulating the radiative exchange within the monolith passage.

Shape factors

As the discussion here has indicated, simulation of the behavior of catalytic monoliths requires the use of finite-area to finite-area radiation shape factors. Formulation of the radiative exchange within the cylindrical monolith passage requires three shape factors: between a ring section of the cylinder and its base; between two ring sections of the cylinder; and from a ring section of the cylinder to itself. The expressions below were obtained from Buschmann and Pittman (1961), and also are presented by Hayes et al. (1992).

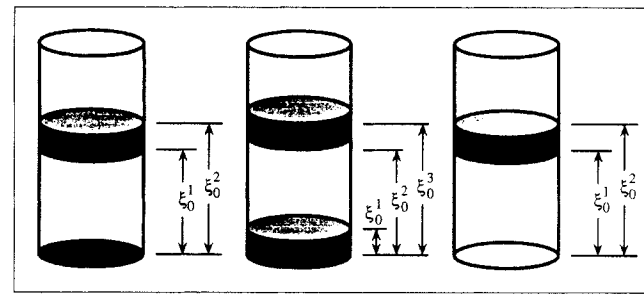

Figure 6. Finite-area shape factors required for simulations using high-aspect computational cells.

Using the dimensions shown in Figure 6, the shape factor for a ring to the base is

$$F_{\text{ring-base}} = \frac{1}{2\xi_1^2}\left[\sqrt{\left(\frac{\xi_0^2}{2}\right)^4 + \left(\xi_0^2\right)^2} - \sqrt{\left(\frac{\xi_0^1}{2}\right)^4 + \left(\xi_0^1\right)^2} + \left(\frac{\xi_0^1}{2}\right)^2 - \left(\frac{\xi_0^2}{2}\right)^2\right]. \quad (15)$$

Using the dimensions in Figure 6, the shape factor for a ring to a ring is

$$F_{\text{ring-ring}} = \frac{1}{4\xi_2^3}\left[\xi_0^1\xi_2^3 + \xi_1^3\sqrt{\left(\frac{\xi_1^3}{2}\right)^2 + 4} - \xi_1^2\sqrt{\left(\frac{\xi_1^2}{2}\right)^2 + 4} - \xi_0^3\sqrt{\left(\frac{\xi_0^3}{2}\right)^2 + 4} + \xi_0^2\sqrt{\left(\frac{\xi_0^2}{2}\right)^2 + 4}\right] \quad (16)$$

where $\xi_1^2 = \xi_0^2 - \xi_0^1$, $\xi_1^3 = \xi_0^3 - \xi_0^1$, and so on.

Using the dimensions in Figure 6, the shape factor for a ring to itself is

$$F_{\text{ring-itself}} = 1 + \frac{\xi_1^2}{4} - \sqrt{1 + \left(\frac{\xi_1^2}{4}\right)^2}. \quad (17)$$

Simulation of heterogeneous reactions in passages with high aspect ratios (L/D), such as those in catalytic monoliths, requires the use of computational cells that have high aspect ratios. In the present study, the aspect ratio of each cell in the computational domain is 16.4 and 5.6, for the catalytic-converter and catalytic-combustor simulations, respectively. Also, this means that the lengths of each cell in the computational domain are 0.05 cm and 0.025 cm, respectively. While

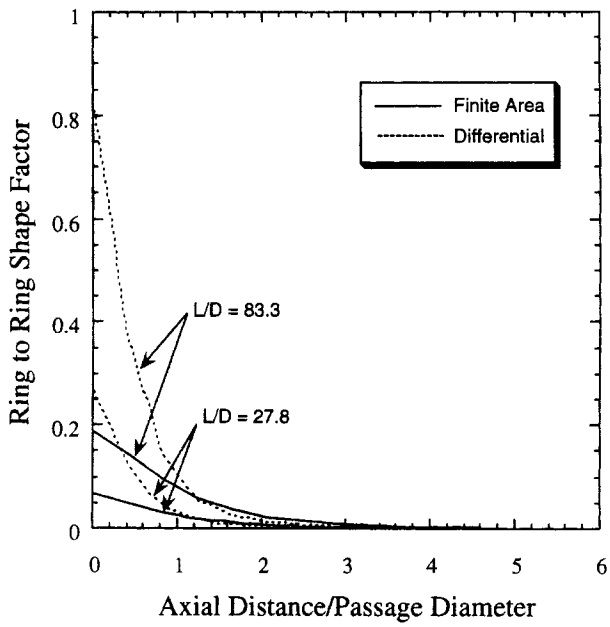

Figure 7. Comparison of finite area and differential shape factors using the aspect ratios (83.3 and 27.8) and mesh size (201 axial nodes) for the catalytic converter and catalytic combustor simulations, respectively.

The differential shape factor has been multiplied by the computational element area to convert the differential shape factor to the same basis as the finite area shape factor.

the implicit marching scheme used in the current model is stable for these axial step sizes, these meshes are sufficiently coarse that the computational cells no longer represent differential elements when calculating radiative heat fluxes. The radiative exchange between each computational cell cannot be accurately described by differential shape factors. Finite-area shape factors must be used.

This observation is supported by Figure 7, which compares ring-to-ring shape factors using finite-area and differential element expressions. The simulations presented here made use of 201 axial mesh points. The aspect ratios (L/D) of the monolith passages were roughly 80 for the catalytic converter simulations and 28 for the catalytic combustor simulations. The discrepancy between the finite area and differential shape factors is substantial for simulation of radiation heat transfer for monoliths with these aspect ratios and meshes that are so coarse. This, in part, explains the disagreement between the results presented by Lee and Aris (1977) and those of other simulations discussed here.

Conclusions

Results from the present work and from the literature indicate that in the steady state, radiation heat transfer exerts a minor influence on catalytic converters under typical operating conditions. The primary effects of radiative exchange in catalytic converter passageways are to smooth the temperature gradient that arises from catalyst light-off and to advance the light-off front forward in the passage. Some previous studies have predicted exaggerated effects of radiation from catalytic converter passages. These discrepancies in previous work may be due to the use of differential element shape factors to describe the radiative exchange. In the high aspect ratio passages typical of monolith reactors, practical computations require the use of high aspect ratio computational cells (finite difference methods) or limited numbers of finite elements (finite elements). The use of relatively large computational cells negates the concept of the differential element, and requires the use of shape factors for exchange between finite areas.

In both steady-state and transient simulations of catalytic combustors, radiation heat transfer can exert a significant influence on catalyst surface temperatures. The most significant effects arise at the ends of the monolith passage, but within the monolith passage the rate of progress of the advancing thermal front during warm-up can be significantly altered by radiative exchange. However, the steady-state and transient behavior of the monolith combustor is largely insensitive to the value of emissivity. This implies that the more expensive graybody calculation is unnecessary and that assumption of black surfaces is justified.

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Notation

a = radius of the cylindrical monolith passage, m
D = hydraulic diameter of the cylindrical monolith passage, m
k_i = overall rate constant for heterogeneous reaction of species i, $m^3 \cdot mol/kg \cdot J$
M_i = molecular weight of species i, kg/mol
Nu = Nusselt number
r = radial coordinate, m
R = universal gas constant, $J/mol \cdot K$
t = time, s
z = axial coordinate, m
ϵ_r = emissivity of the catalytic surface
χ_i = mole fraction of species i
σ = Boltzmann constant, 5.729×10^{-8} $W/m^2 \cdot K$
ξ = coordinate for evaluation of shape factors

Superscripts

i = species i or tensor notation index
o = value evaluated at the inlet of the monolith passage

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