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Numerical analysis of a catalytic radiant burner: effect of catalyst on radiant efficiency and operability

Marc D. Rumminger, Richard D. Hamlin, Robert W. Dibble*

Combustion Analysis Laboratory, Department of Mechanical Engineering, University of California, Berkeley, CA 94720-1740, USA

Abstract

In this paper we study a new class of porous direct-fired radiant burners which burn part of the fuel catalytically. The burner consists of a multiple-layer porous medium, with one layer that is partially coated with an oxidizing catalyst. Simulations are performed to investigate the effect of platinum catalyst loading, location of catalyst layer, and its thickness on burner performance for single layer and bilayer porous media. Significant efficiency gains are found, but only when the catalyst was placed on the downstream edge of the porous medium. The porous medium was generally not hot enough to cause significant deterioration of the catalyst. Only a thin layer of catalyst is required for efficiency improvements. Enlarging the catalytic zone into cold temperature regions has almost no effect on burner performance. Heat release due to the catalyst occurs inside the porous medium, thus resulting in a higher radiant efficiency. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic combustion; Radiant heater; Numerical simulation; Platinum; Porous solid

1. Introduction

Many industrial processes, such as paper drying, paint drying and polymer thermoforming, require infrared thermal radiation. Electric heating elements are popular among industrial users because of their versatility. Replacing these electric elements with gas-fired porous radiant burners could reduce energy consumption and decrease processing costs for industrial users.

A porous direct-fired radiant burner stabilizes a premixed natural gas flame partially within a porous medium. The burners emit a substantial fraction of the heat as thermal radiation and emit low levels of pollutants. Most current radiant burners utilize gas-phase combustion exclusively. In this paper we study a class of radiant burners which burn part of the fuel catalytically. The burners consist of a multiple-layer porous medium, with one layer that is partially coated with an oxidizing catalyst. Because of the catalytic material, some of the heat release occurs on the surface of the porous medium.

Catalytic radiant burners convert chemical energy to radiant heat more efficiently than electric elements if electricity generation (>60% loss) and transmission losses (~5% loss) are considered. In areas where coal is an important fuel, the benefits of using natural gas-fired burners include reduced SO_x emissions, NO_x emissions and CO_2 emissions. Additionally, radiant burners can be designed to emit radiation at specific wavelengths by adding certain elements to the porous medium [1].

The addition of an oxidizing catalyst, like platinum or palladium, to a radiant burner might be able to

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*Corresponding author.

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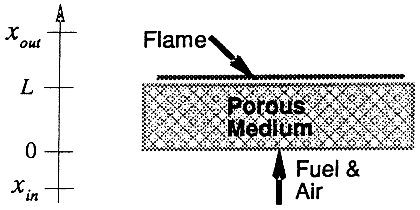
increase the operating range and stability of a radiant burner. Beneficial surface reactions can be encouraged by coating part of the porous solid with a noble metal catalyst, thereby causing the flame to anchor in a position that optimizes performance. Kendall et al. [2] of Alzeta (Santa Clara, CA) reported that partially catalytic radiant burners showed increased radiant efficiency (radiant flux/input chemical energy) and reduced pollutant emission. They applied platinum by spraying a dilute solution of hexachloroplatinic acid (H_2PtCl_6) on the surface of a ceramic fiber burner. Radiant output increased, nitrogen oxide emissions decreased, and carbon monoxide emissions decreased. They observed that the flame moved deeper into the porous medium, thus resulting in additional heat transfer from the flame to the porous medium.

The 1991 experiments of Kendall et al. [2] involved a preliminary investigation. Much research needs to be done on the promising technology of catalytic radiant burners. In this paper we use a numerical model to determine whether selective placement of catalyst can improve performance, as well as lower costs. We describe the addition of surface chemistry to an existing radiant burner model and then use the model to investigate how catalyst loading and location affects burner performance.

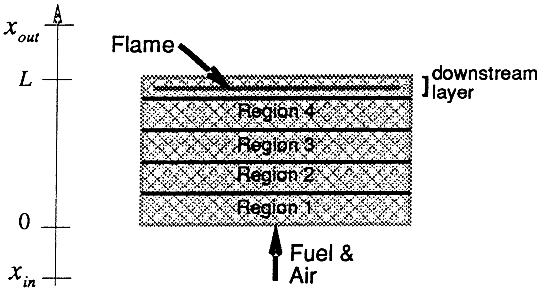
2. Model description

The number of possible variations of porous direct-fired radiant burners is staggering. Burners can be constructed with different pore sizes, fiber diameter, porosity, material, and thickness. Multiple-layer structures can also be formed, thus adding to the number of possibilities. With so many parameters to vary, experimental parametric studies would be costly and time-consuming. A numerical model allows free variation of burner properties for investigation of many different burner designs with minimal effort. Furthermore, a numerical model of a porous radiant burner provides unique insight to burner processes.

A radiant burner simulation package has been developed in our laboratory. It simulates radiant burner operation and includes multi-step gas-phase chemistry, radiant transfer in the porous medium, and heat transfer between the gas and solid. The model is currently being used to analyze non-catalytic radiant burners [3]. This code is an extension of Sandia National Laboratory's one-dimensional premixed flame code. In the model, combustion of premixed fuel and air occurs in an adiabatic, infinite duct that contains a porous medium. Fig. 1 shows the computational domain for the simulation. Fuel and air enter at the bottom ($x=x_{\mathrm{in}}$), flow into the porous medium – which extends from $x=0$ to $x=L$ – and exit at $x=x_{\mathrm{out}}$ after reacting. A portion of the porous medium is coated with a oxidizing catalytic material.



(a) Single Layer



(b) Bilayer

Fig. 1. Computational domain for the radiant burner model. $x=0$ and $x=L$ are the edges of the porous medium. Catalyst was added to various regions within the porous medium.

Chemical kinetics are managed by the Chemkin FORTRAN subroutines [4]. We use a reduced gas-phase mechanism with 19 species (plus N_2 and Ar) for methane combustion [5] that is useful for predicting flame structure and burner performance when we are not interested in NO_x emissions. We use the transport package from Sandia [6] to calculate viscosities, diffusivities and thermal conductivities as a function of temperature, mixture concentration and pressure.

We implement the surface chemistry with the Surface Chemkin subroutines [7], a set of subroutines that manage the elementary heterogeneous chemical kinetics for surfaces. Several approaches for specifying the surface reaction rates have been presented in the catalytic combustion literature, such as global Arrhenius reactions, a power law based on the partial pressures of some gas-phase species (particularly CH_4), the Langmuir–Hinshelwood formulation, and detailed surface reactions with elementary reaction steps.

We use a detailed reaction mechanism for methane on platinum that was developed by Deutschmann et al. [8] and a global reaction mechanism by Song et al. [9]. The rate expression proposed appears to be given with the wrong units in [9]. We use the units for the pre-exponential factor and (mass) concentrations that are given in [10]. The global surface reaction rate ($\dot{r}$, $\mathrm{g\,s^{-1}\,cm^{-2}}$) is

$$\dot{r} = A C_{\mathrm{CH_4}} C_{\mathrm{O_2}}^{0.5} \exp\left(-\frac{E_\mathrm{a}}{RT}\right), \tag{1}$$

where $A=1.3\times10^{11}\ \mathrm{cm^{5/2}\ s^{-1}\ g^{-1/2}}$, $C_{\mathrm{CH_4}}$ and $C_{\mathrm{O_2}}$ are mass concentrations of methane and oxygen in $\mathrm{g/cm^3}$, respectively, and E_a=134.7 kJ/mol. The site density implied by applying the rate formula (Eq. (1)) unaltered to the total actual surface area of the porous medium within the catalytic domain defines the nominal catalytic site density below.

Detailed surface chemistry can qualitatively account for the characteristic behaviors such as hysteresis, ignition, and extinction. As improvements to the detailed mechanism become available, the surface mechanism data file can simply be updated without any recoding of the radiant burner model. At this time, we model detailed reactions on platinum because mechanisms for combustion on palladium and other catalysts are still at early stages of development.

The global surface chemistry model requires far fewer computations and converges much more readily than the detailed model. Since detailed surface chemistry is an especially young and evolving research area [11], the global surface model may provide useful insights into catalytic combustion without excessive computing expenses. One of the disadvantages of a global mechanism is that the complex behavior of the catalyst is not exhibited. Moreover, most global models ignore minor species completely; some make the OH production rate proportional to the main catalytic reaction rate [10].

The following coupled ordinary differential equations model the catalytic radiant burner: mass continuity, conservation of gas-phase species, conservation of energy for the gas phase, conservation of energy for the porous solid, radiative heat transfer in the porous solid, conservation of surface and bulk species, and the ideal gas law. The equations and boundary conditions for the non-catalytic burner can be found in [3].

In the global surface model, the surface reaction is incorporated into the gas-phase energy and species conservation equations, and the porous solid energy equation.

For the detailed surface chemistry model, the steady-state equations are: net production rate for each surface specie equals 0, and sum of the site fractions occupied by each surface species equals 1. (In coding, the equation associated with the last surface species is used to enforce the summation condition instead of the production rate condition.) There is a similar formalism for bulk species, but in this case where we have a single bulk species (Pt), it is trivially reduced to the bulk species activity being identically one. The surface reactions and the surface-bulk reactions modify the solid energy equation, whereas the adsorption and desorption modify both the surface and gas energy equation.

We use a quasi-Newton solver [12] to find steady-state solutions.

2.1. *Assumptions*

We assume the flame is one-dimensional and laminar, the gas is optically thin and ideal, combustion occurs at constant pressure, the porous solid is spectrally gray, and the porous solid is a hemispherically isotropic scatterer.

We assume that the catalyst is evenly distributed, that no sintering of the catalyst occurs, that no poisoning of the catalyst occurs, and that the bulk surface of porous medium is inert. This study is an attempt to understand the effect of a catalyst on radiant burner performance, but in an industrial burner, catalyst durability and uniformity will need to be considered too.

2.2. *Mass transfer to the catalyst surface*

Modelers of surface reactions are frequently confronted with the issue of mass transfer to the catalyst. In honeycomb monoliths the limitations can be especially strong because of the straight tube geometry of the channel. The catalyst supports in this paper, in contrast, are made of assemblies of sintered metal fibers or of ceramic foam, which have extremely tortuous flow paths that lead to a large degree of mixing. Since a parcel of gas passing through the porous medium is likely to be well-mixed, we assume that the system is not mass-transfer limited. However, at very high reaction rates or high flow rates, the surface reactions may become significantly mass-transfer limited in spite of the high degree of mixing.

3. Results and discussion

Most simulations began with a non-catalytic solution and subsequently increased catalyst density to a high value or until the quasi-Newton numerical solver failed to converge on a solution. The reason for the convergence difficulty has not been confirmed, but we speculate that the problem stems from the large discontinuity introduced by the catalyst, where the error due to finite differences grows so significantly that a solution that satisfies both the species conservation equations and the energy equations ceases to exist, that is, the error in the residuals due to the species equation and the energy equations cancel each other within the specified convergence tolerance. Consistent with this hypothesis, the species equations could always be solved easily from a given temperature profile while convergence difficulties were only encountered when attempting to also solve the energy equations. The inclusion of a mass transfer model would limit the sharp peak of catalytic activity that occurs at the downstream edge of the catalyst zone, which is likely to improve convergence.

Section 3.1 compares model predictions with experimental results. Section 3.2 discusses single layer burners, in which the flame stabilizes on the downstream edge of the porous medium. Section 3.3 discusses bilayer burners, in which the flame is entirely within the porous medium.

3.1. *Comparison of predictions with experimental measurements*

As mentioned in Section 1, we know only one study of catalytic radiant burners. Kendall et al. [2] added Pt to the surface of an Alzeta Pyrocore® ceramic fiber burner. Kendall's group determined the catalyst loading by noting the amount of Pt that was applied, then dividing by the overall frontal area of the burner (not the detailed surface area) to obtain a loading factor in mg/cm^2. This definition of catalyst loading is not readily amenable to a theoretical definition, however. Thus, the loading that we report is not directly correlated to the loading reported by Kendall et al. [2].

Since there is a scarcity of property measurements on ceramic fiber matrices, we used the following reasonable estimates: Thickness (L) of 4 mm, porosity of 0.93, extinction coefficient of 1000 m^{-1}, convection coefficient based on stacked metal fibers [13], effective thermal conductivity in the solid of 0.05 W/mK, single scattering albedo of 0.7, forward scattering fraction of 0.5. The Pt catalyst coated zone was on the downstream edge of the porous medium and was 2 mm thick.

Fig. 2 shows the predictions of the model compared with the experiments for the firing rate of 317 kW/m^2 (100 000 Btu/h/ft^2). Although the over-prediction seems large, it is not unreasonable when we consider the large uncertainty of the radiant efficiency measurement and the fact that the model has neither heat losses to the burner housing nor gas radiation (whereas the experiment had both). We can clearly see, though, that the model correctly predicts the trends in the experimental data.

3.2. *Single layer burner*

A single layer radiant burner operation was simulated for a variety of catalyst loading conditions and firing rates to determine the effect of the catalyst on the radiant efficiency of the burner and the effect on the flame. The porous medium had the following properties: Thickness (L) of 6 mm, porosity of 0.80, extinction coefficient of 1000 m^{-1}, convection coefficient based on stacked metal fibers [13], effective thermal conductivity in the solid from a correlation by Mantle and Chang [14], single scattering albedo of 0.7, forward scattering fraction of 0.5.

Figs. 3 and 4 shows that the addition of the catalyst causes the flame to flatten out. At very high catalyst loadings, the flame will lift off. Some of the chemical energy that would have heated the gas phase in the flame is confiscated by the catalytic reaction flame and

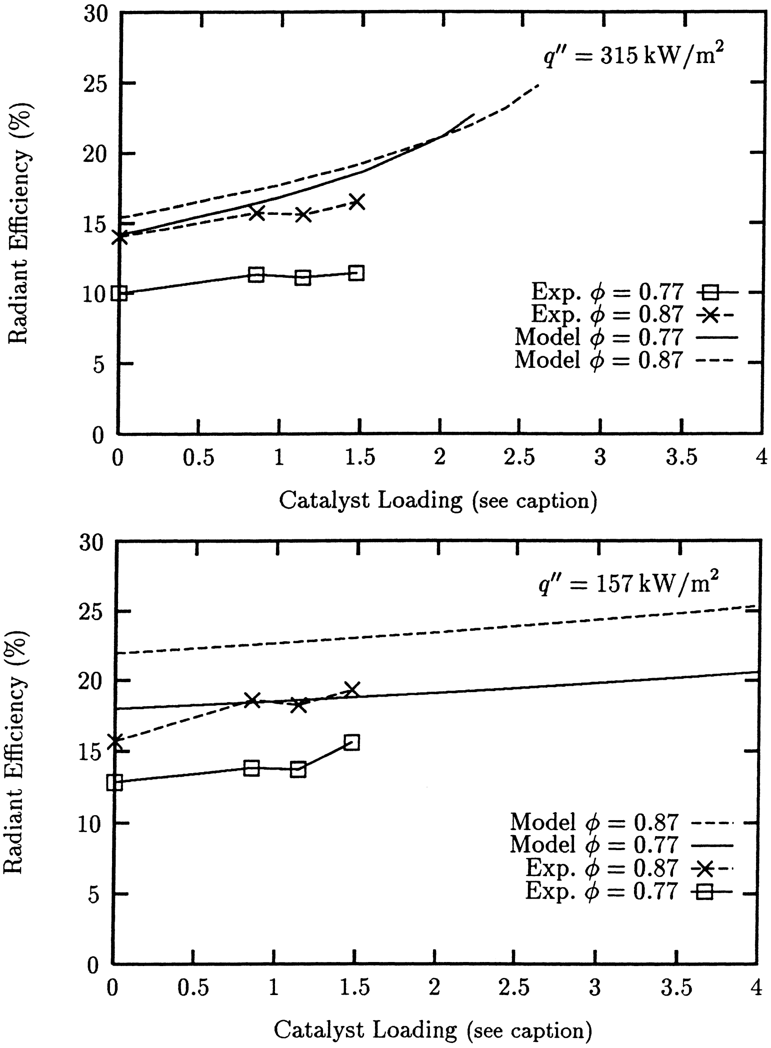


Fig. 2. Alzeta catalytic radiant burner data compared with model results at two firing rates and two equivalence ratios. The lines with points correspond to the measurements and the lines without points are the predictions. The catalyst loading units for the experimental measurement are g/cm^2 (burner projected area), while the model results are given in terms of percentage of nominal loading. (There is not enough information available to facilitate unit conversion without introducing much error.)

radiated away from within the porous medium. (This occurs by raising the gas temperature in the porous medium, and in turn raising the solid temperature by convection, which increases the radiosity of the solid surface.) Thus, the flame has less enthalpy and temperature to drive the gas-phase reactions. The increased forward radiosity occurs very close to the downstream edge of the porous domain, but it is interesting to note that this increase does *not* extend right up to the edge. The downstream edge itself is very nearly at the same temperature (Fig. 3) over a wide range of catalyst loadings for this burner at a given firing rate and equivalence ratio.

Fig. 5 shows that radiant efficiency increases monotonically and substantially with catalyst loading for these single layer burners.

The thickness of catalyst required for these effects is small. Moreover, catalytic coatings that penetrate

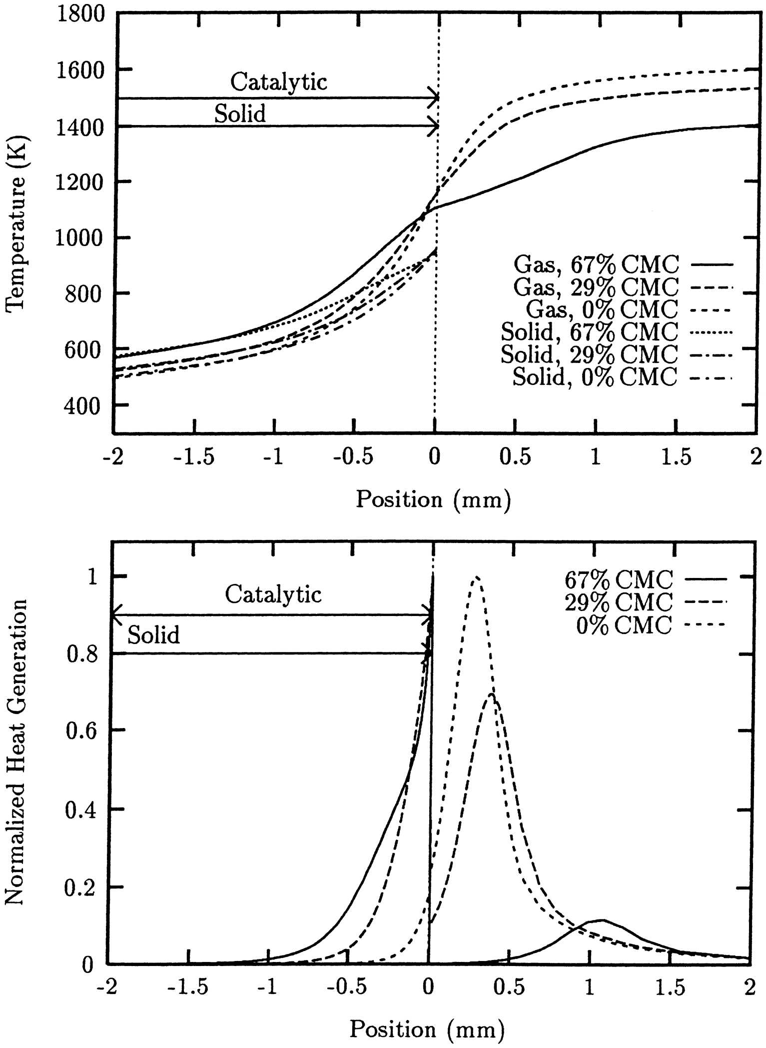


Fig. 3. Temperature and heat release profiles for catalytic radiant burners at three rates of catalytic methane conversion (CMC) (0%, 29% and 67%). Only a portion of the 6 mm thick porous medium is shown. The catalytic layer is 2 mm thick.

deeper into the porous medium result in very little increase in performance for depths greater than the minimum that can practically be applied. Fig. 6 shows that there is no increase in radiant efficiency for catalyst domain thicknesses greater than 1 mm.

Furthermore, placement of the catalyst at a position other than the downstream edge of the burner results in little catalytic activity. Moving the catalyst domain within the porous medium by as much as 1 mm completely reduces the effectiveness of the catalyst (see Fig. 7). It requires orders of magnitude increase in catalyst density within the interior catalytic domain to achieve comparable catalytic conversion to the zero depth catalyst. The reason for this is that the catalytic reaction rate is exponential in temperature, and the temperature falls off very quickly with increasing depth into the porous medium (Fig. 8). Indeed, while a catalyst significantly reduces the activation energy of key combustion reactions, it does not reduce the activation energy to 0.

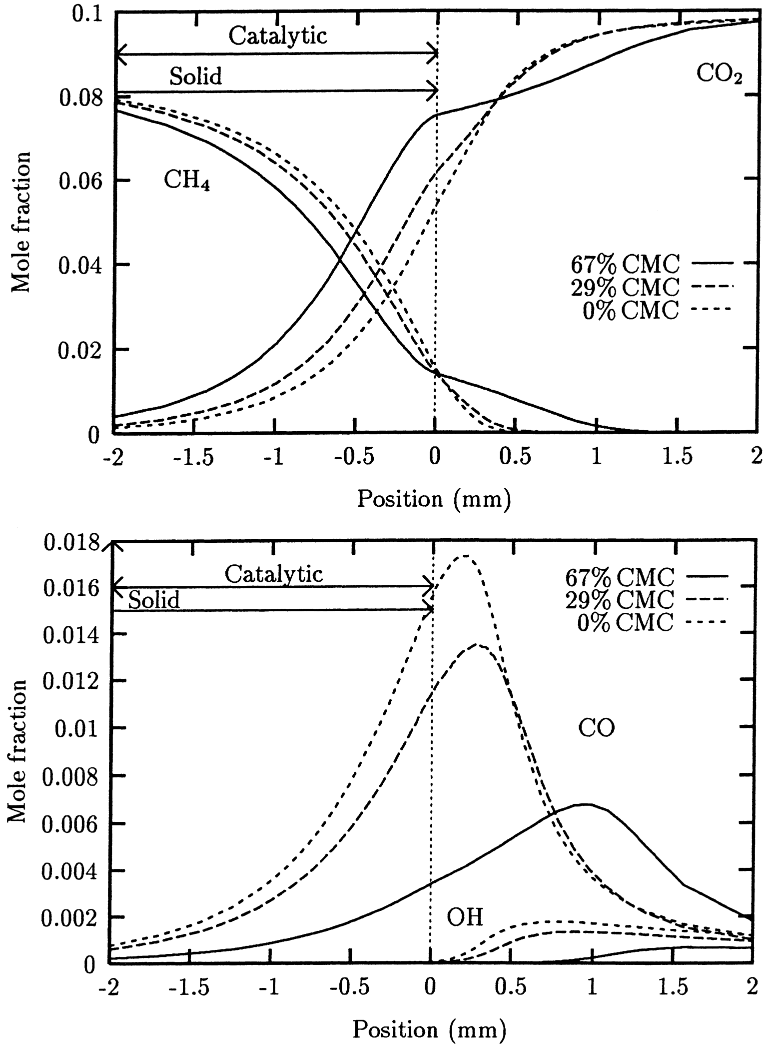


Fig. 4. Species profiles for catalytic radiant burners at three rates of catalytic methane conversion (CMC) (0%, 29% and 67%). Only a portion of the 6 mm thick porous medium is shown. The catalytic layer is 2 mm thick.

Fortunately, locating the catalyst at the downstream edge of the porous medium does not necessarily result in overheating the catalyst to the point where its life is substantially reduced. In fact, of the simulations performed at firing rates of 157 and 315 kW/m^2, the one with highest radiant efficiency had a solid temperature of only 1110 K at the downstream edge (q''=315 kW/m^2, ϕ=0.87, 65% nominal catalyst density, 28.2% radiant efficiency).

3.3. Bilayer burners

The effect of catalyst coating on a radiant burner with a bilayer porous medium is discussed in this section. The porous medium, which is made of ceramic, has a 19 mm thick upstream layer with 25 pores/cm (PPC), and a 3.2 mm thick downstream layer with 4 PPC. (The properties of the porous medium are discussed extensively in [3].) The flame stabilizes

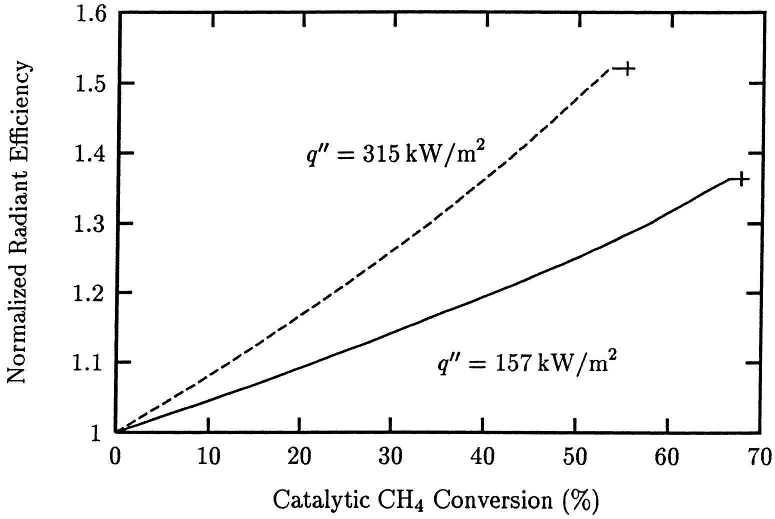


Fig. 5. Single layer normalized radiant efficiency versus catalytic CH_4 conversion. Note: the + points are the highest catalytic loading with successful convergence for each condition.

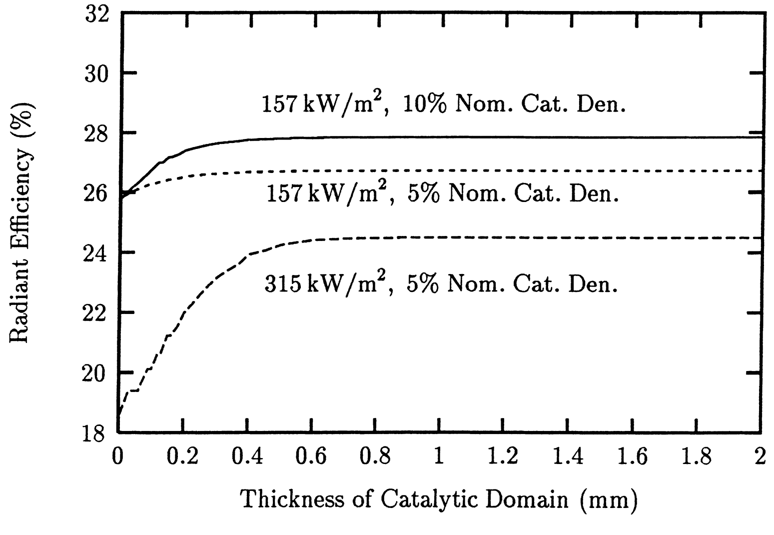


Fig. 6. Single layer radiative efficiency (%) as the depth of a 2 mm thick catalyst layer is varied for two firing rates. The Pt loading is 10% of nominal and the equivalence ratio is ϕ=0.87.

entirely within the porous medium. Catalyst was applied to the upstream layer in four different regions (denoted as R1, R2, R3, R4 – see Fig. 1). Fig. 9 shows the radiant efficiency results for ϕ=0.87 at two firing rates (q''=157 and 315 kW/m^2). Catalyst application to the first three quadrants has little effect on radiant efficiency, as shown by the nearly horizontal lines for those conditions. When catalyst is applied to the fourth region, though, a strong increase in efficiency is seen. The efficiency increase for the bilayer burner is somewhat smaller than for the single layer burner. The radiant efficiency of a non-catalytic bilayer burner

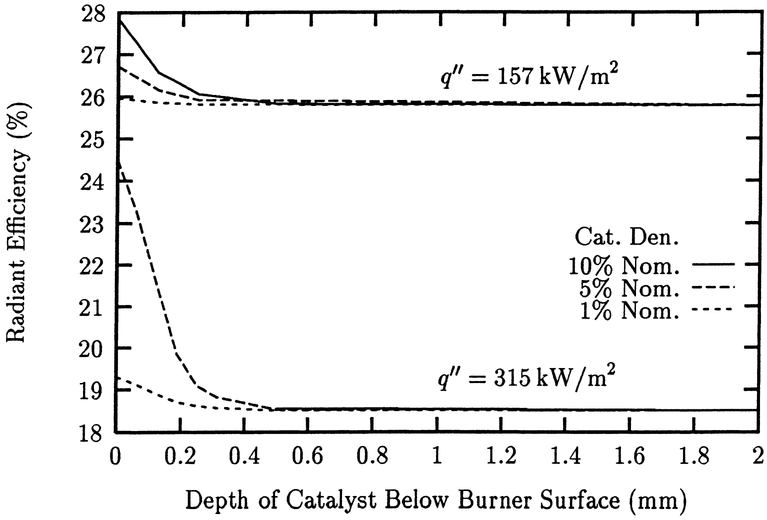


Fig. 7. Single layer radiant efficiency as the depth of a 2 mm thick catalyst layer is varied for two firing rates. The Pt loading is 10% of nominal and the equivalence ratio is ϕ=0.87. Catalyst depth is the distance between the downstream edge of the catalytic domain and the downstream edge of the porous media domain.

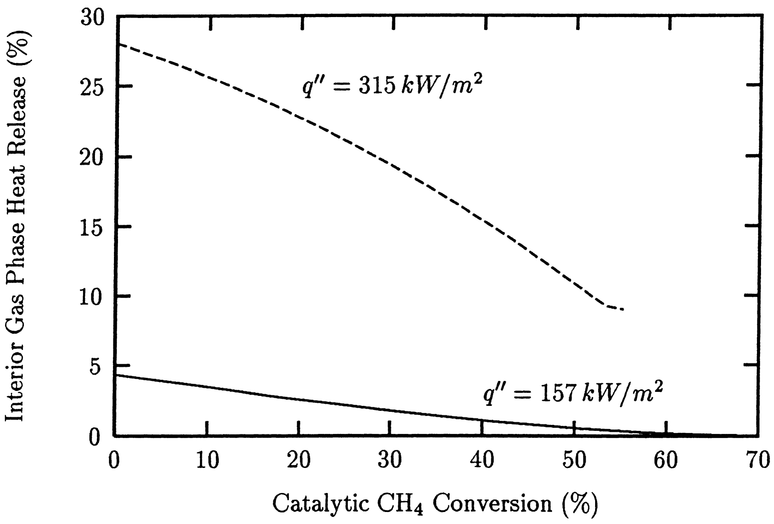


Fig. 8. Interior gas-phase heat release versus catalytic CH_4 conversion efficiency. This is the portion of the total heat release for the single layer burner (firing rate) that occurs non-catalytically (i.e. due to the gas-phase reactions only) within the porous medium domain.

is significantly higher than that of a single layer burner, however.

4. Conclusions

1. Radiant efficiency gains were found when the catalyst was placed on the downstream edge of the porous medium. Placement of the catalyst in a low-temperature zone results in negligible radiant efficiency improvement. The highest temperature of the porous medium was lower than the level at which the catalyst is damaged.
2. Only a thin layer of catalyst is required for efficiency improvements. Expansion of the catalytic

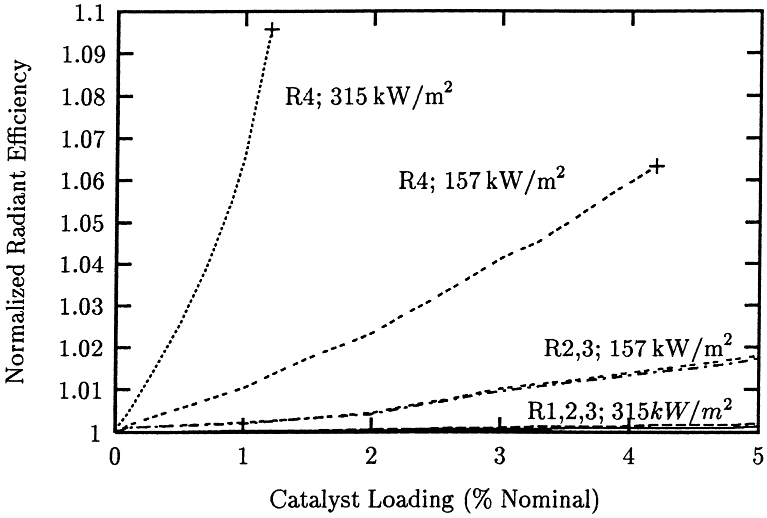


Fig. 9. Bilayer radiant efficiency with catalyst. Equivalence ratio, ϕ=0.87. The radiant efficiency of the non-catalytic burner is 33.5% at q''=157 kW/m^2, and 28% at q''=315 kW/m^2.

zone into cold temperature regions has almost no effect on burner performance.

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