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Contribution of homogeneous reactions to hydrogen oxidation in catalytic microchannels

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ABSTRACT

Combustion of lean H_2/air mixtures in Pt-coated microchannels is investigated numerically in planar geometry. Examining the relative importance of hydrogen oxidation in the bulk gas as compared to surface reactions under different operating conditions is the main focus of the present work. A collocated finite-volume method is used to solve the governing equations. Detailed gas phase and surface reaction mechanisms along with a multi-component species diffusion model are used. In microchannels, due to effective heat and radical losses to the walls, the combustion characteristics are greatly influenced as the channel size is reduced. While catalytic walls help in sustaining gas phase reactions in very small channels by reducing heat losses to the walls owing to exothermic surface reactions, they also inhibit homogeneous reactions by extracting radicals due to typically high absorption rates of such species at the walls. Thus, the radical chain mechanism can be significantly altered by the presence of wall reactions, and the build-up of radical pools in the gas phase can be suppressed as a consequence. In the present work the effects of three key parameters, the channel height, the inlet mass flux and the equivalence ratio of the inlet mixture on the interaction between the gas phase and surface reactions are explored. In each case, the limiting values beyond which the gas-phase reactions become negligible compared to surface reactions are identified for lean hydrogen/air mixtures.

1. Introduction

In recent years, there has been a push for miniaturizing some mechanical and chemical processes in order to meet the increased power demand for micro-devices in almost every field of engineering. Scaling down of conventional power supplies to micro-heat engines, micro fuel cells, micro-turbines and combustors has been proposed as an efficient, safe and reliable energy delivery method for Micro–Electro-Mechanical Systems. Miniaturizing conventional power generators, however, is not simply achieved by reducing the physical size of their macro counterparts.

As the characteristic size decreases, heat and mass transfer at the walls play an important role in defining the combustion characteristics of such systems [1]. The increased heat and radical losses at the walls can suppress homogeneous reactions to a great extent. In order to maintain stable combustion in the gas phase useful strategies such as Swiss-Roll and Heat-Recirculating burners [2,3] have been proposed. Several other studies have been -conducted to sustain homogeneous combustion in sub-millimeter burners. Miesse et al. [4] showed that by chemically treating the vessel walls, gas-phase combustion of methane/oxygen is achievable in sub-millimeter sizes. Also, it was shown that the flame structure is not similar to what is expected in a macro-structured configuration under similar conditions. Spadaccini et al. [5] reported sustainable propane–air reactions in catalytically stabilized sub-millimeter conduits.

Along with experimental studies, several numerical simulations have also been performed in order to study the behavior of different fuels, and the role of heat loss and radical quenching, and wall material on homogeneous combustion [6]. Aghalayam et al. [7] numerically investigated the role of wall quenching of radicals on the extinction behavior of hydrogen/air mixtures in a stagnation-point geometry. It was proposed that in general, the radical quenching on the wall hinders the homogeneous reactions; However, the heat release due to the catalytic surface reactions can reduce this effect. Raimondeau et al. [8] modeled methane flame propagation inside tubular microchannels. The near entrance heat and radical quenching were identified as the main factors controlling flame propagation in these channels which could be controlled by proper insulation and preheating. Maruta et al. [9] numerically studied the extinction limits of self-sustaining methane/air combustion on Platinum in a cylindrical tube. They showed that when heat losses exist, i.e.

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non-adiabatic walls, the extinction limits are due to blow-off at high inlet velocities and heat-loss-extinction at low inlet velocities similar to ordinary gas phase combustion.

Heat transfer characteristics of premixed stoichiometric hydrogen/air combustion inside cylindrical chambers of different dimensions were numerically studied by Hua et al. [10]. They concluded that thermal management of micro-chambers can significantly improve the combustion stability and lead to the design of practical micro-combustors. Leach et al. [11] performed a 1D numerical analysis of the effects of heat losses on the reaction zone thickness in H_2 combustors. They also presented an analytic model for the prediction of reaction zone thickness based on the channel size and thermal properties of the structure. The broadening reaction zone was attributed to the heat exchange between the reacting mixture and the channel walls with thicker reaction zone in channels of higher conductivities. Karagiannidis et al. [12] studied the combustion characteristics of fuel-lean methane/air mixtures in a Pt-coated planar geometry. The presence of catalytic walls is reported to expand the stability limits of gas phase combustion in micro conduits. The positive effect of exothermic surface reactions on the stability of gas phase reaction is highlighted in their work. Li et al. [13] performed a numerical analysis involving combustor size, geometry and boundary conditions to study their effects on the flame temperature of premixed methane/air mixtures. Their findings suggest that a fully-developed inlet velocity profile stabilizes the flame within the chamber. They also showed that the effects of velocity-slip and temperature-jump can be ignored for channel sizes down to 1 mm.

In order to verify the numerical scheme implemented in the present work, the experimental and numerical results of Appel et al. [14] are utilized. In their work, a range of chemical mechanisms for the surface and gas phase reactions are compared to their experimental results in a 7 mm high channel under different working conditions. As will be discussed in the numerical implementation section, the numerical results of the present work show good agreement with their experimental data.

As discussed in previous studies, key parameters such as the fuel–air equivalence ratio, the mixture temperature, the flow rate, heat losses to the wall and wall thermal conductivity play an important role in defining the interaction between the gas phase and catalytic reactions. The effects of these parameters can also be very different as the channel size is reduced. In the present work, the relative importance of gas phase and surface reactions associated with hydrogen oxidation at different inlet mass fluxes, equivalence ratios and channel heights are assessed for lean H_2/air mixtures in planar microchannels. Detailed gas phase and surface reaction mechanisms are employed in order to fully account for the effects of minor species in determining the homogeneous and heterogeneous reaction pathways.

2. Mathematical model

A schematic view of channel geometry and the coordinate system are shown in Fig. 1. The channel height is H and the main flow is in the x direction.

2.1. Flow field

The governing mass, momentum, energy, and species continuity equations for steady, laminar, reacting gas flow are [15]:

$$\nabla \cdot (\rho \mathbf{V}) = 0 \tag{1}$$

$$\nabla \cdot (\rho \mathbf{V}\mathbf{V}) = -\nabla p + \nabla \cdot \left[\mu(\nabla \mathbf{V} + \nabla \mathbf{V}^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{V})\mathbf{I}\right] \tag{2}$$

$$\nabla \cdot (\rho \mathbf{V} h) = -\nabla \cdot \left(-\lambda \nabla T + \sum_{k=1}^{N_g} h_k \mathbf{J}_k\right) + \Phi \tag{3}$$

$$\nabla \cdot (\rho \mathbf{V} Y_k) = -\nabla \cdot \mathbf{J}_k + w_k \dot{r}_k \tag{4}$$

Here ρ is the mixture density, $\mathbf{V}$ is the mass-averaged velocity vector, p and μ are pressure and viscosity, $\mathbf{I}$ is the identity tensor, λ is the mixture conductivity, h is the mixture enthalpy, Φ is the viscous dissipation term, N_g is the total number of gas phase species, $\mathbf{J}_k$ is the mass diffusion flux, Y_k is the mass fraction, $c_{p,k}$ is the specific heat capacity, $\dot{r}_k$ is the molar production rate due to homogeneous reaction, w_k is the molar mass, and h_k is the enthalpy of the kth species. In the present work, all effects due to thermal radiation as well as the Dufour effect are ignored. The species diffusion mass flux $\mathbf{J}_k$ is determined using the multi-component diffusion equation as [15]:

$$\mathbf{J}_k = \frac{\rho w_k}{\bar{w}^2} \sum_{j=1}^{N_g} w_j D_{kj} \nabla X_j - D_k^T \frac{1}{T} \nabla T \tag{5}$$

In this equation, X_k is the mole fraction of species k, $\bar{w}$ is the mixture molar mass, D_{kj} is the tensor of ordinary diffusion coefficients, and D_k^T are the thermal diffusion coefficients [16].

2.2. Chemical kinetics

The homogeneous production rates in the conservation equations are modeled using a detailed gas phase reaction mechanism due to Maas and Warnatz [17] involving nine gas phase species. Also, a detailed surface reaction mechanism proposed by Deutschmann et al. [18] with five surface species is adopted in the present work in order to model hydrogen oxidation on Platinum.

In the absence of mass accommodation (e.g. etching or deposition) on an impermeable wall, the conservation of mass requires the diffusion mass flux of each gas phase species to be balanced

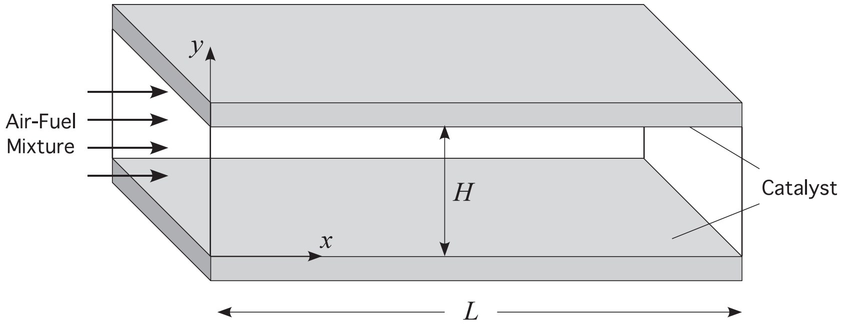

Fig. 1. Schematic view of the channel geometry and coordinate system.