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Rarefaction effects on the catalytic oxidation of hydrogen in microchannels

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ABSTRACT

Catalytic oxidation of H_2/air mixtures in the slip regime is numerically simulated in order to assess the slip/jump effects in platinum-coated planar microchannels. A colocated finite-volume method is used to solve the governing equations. A concentration jump model derived from the kinetic theory of gases is employed to account for the concentration discontinuity at the reactive walls. A detailed surface reaction mechanism for hydrogen oxidation on Pt along with a multi-component species diffusion model are used to study the effects of concentration jump coupled with velocity slip and temperature jump on the walls. The slip/jump effects are studied under different operating conditions: wall temperature, channel height, inlet mass flux and surface accommodation coefficient are varied to examine their individual effects. The results suggest that the temperature discontinuity at the wall is the dominant term in the concentration jump boundary condition. The mass transfer characteristics of the reacting flow are least influenced by velocity slip while the temperature jump at the wall alters the mass transfer characteristics the most. The hydrogen oxidation rate on the catalytic wall is strongly affected by the rarefaction effects, especially in the entrance region. The results show that the thermal diffusion effect in calculating the diffusive mass flux of species has a considerable effect on the species distribution inside the channel and cannot be neglected. The effects of slip/jump boundary conditions can change significantly at different inlet fluxes and channel heights.

1. Introduction

In recent years, there has been intensive research on microfluidic systems for compact reactor technologies. Investigations have been conducted to better understand and predict the flow, heat transfer and mass transfer properties of the so-called microreactors. The microreactor technology combines several advantages such as high material compatibility, high surface area to volume ratio, and large potential for heat and mass transfer, with highly sophisticated fabrication processes. Microstructured reactors benefit from high process intensification, a wide reaction range up to explosion limits, reactor safety, faster process development and distributed production which make them suitable for highly endothermic and exothermic chemical reactions. As the push for further miniaturization continues, modeling such systems becomes more and more complicated, since new physical phenomena should be taken into account. One of the complications in dealing with micro-scale devices is that the common continuum assumption can break down as the characteristic length scale of these devices approaches the mean molecular free path. In such a case, the number of inter-molecular collisions decreases and eventually there comes a stage in which the number of collisions between molecules are rare compared to the number of collisions with the surrounding walls, in which case each molecule acts independently to bring forth the gas properties [1]. This makes the gas lose its intimate contact with solid bodies such that the gas slips over the surface, and in the case of heat or mass transfer, a temperature or concentration jump is observed between the surface and the adjacent gas layer. The continuum equations for mass, momentum and energy conservation are usually employed to study the motion of a fluid, in which the properties of the fluid in each point can be defined as an average of microscopic characteristics of the neighboring points. In the slip flow regime, the continuum equations can still be employed but proper velocity slip and, temperature and concentration jump boundary conditions should be specified.

The effects of velocity slip and temperature jump on flow and heat transfer characteristics of non-reacting flows have been extensively studied in microchannels e.g. [2–5]. However, non-equilibrium transport in reacting flows still remains to be studied in-depth. In the case of multi-species transport, another important effect analogous to temperature jump should be taken into account, i.e., the concentration jump. The investigation of the concentration jump was initially performed by Kramers and Kistemaker [6] based on the work of Maxwell on velocity slip and temperature jump. Concentration jump not only affects the rate of reaction and local species concentration, but also velocity slip

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and temperature jump in both reacting and non-reacting systems. Many rate-limiting adsorption/desorption reactions are very sensitive to local temperatures and hence the proper modeling and computation of temperature along with the local species concentration is vital for an accurate prediction of the behavior of such systems. Therefore, all of these non-equilibrium effects should be considered simultaneously in the simulation of microreactors. This is even more pronounced in catalytic reactions since all the reactions take place on the wall. The effect of temperature jump on the performance of reactive systems was investigated and verified experimentally by Shankar and Glumac [7] using low-pressure catalytic combustion systems. The concentration jump phenomenon has been detected in simulations of reacting gas mixtures by Bird [8] and Papadopoulos and Rosner [9].

There is very limited work on the concentration jump and its effects on catalytic reactions and the available literature has mainly focused on the temperature jump and velocity slip effects. Raimondeau et al. [10] employed a parabolic numerical scheme to study the flame propagation of methane/air mixtures in tubular microchannels with no wall reactions. The effects of radical quenching and temperature discontinuity on the gas phase reactions were mainly emphasized in their work. Xu and Ju [11,12] derived a concentration slip model and investigated the rarefaction effects on the rate of catalytic reactions in the numerical modeling of hydrogen and methane oxidation. In their work, they considered the combustion of premixed stoichiometric mixtures at very low pressures ranging from 100 Pa to 0.2 atm. The velocity slip and temperature discontinuity at the wall were modeled using the conventional mixture-averaged boundary conditions. Li et al. [13,14] compared the effects of different operating conditions on the flame temperature of methane/air and hydrogen/air mixtures. They also studied the effects of first order velocity slip and temperature jump boundary conditions on the flame temperature. They reported negligible slip/jump effects at low velocities and large channels ($d = 1$ mm) and a considerable temperature discontinuity at the wall close to the flame region due to high radial gradients. More recently, Rahaghi et al. [15] numerically studied the effect of different operating conditions on the performance of micro-combustors down to 600 μm. They also studied the velocity slip effect (first order) on the temperature and species mass fraction profiles and reported its impact to be negligible for these channel heights.

In the present work, the velocity slip, temperature jump and concentration jump effects on the catalytic oxidation of lean H_2/air mixtures in planar microchannels are examined. To this end, the concentration jump, velocity slip and temperature jump boundary conditions derived by Zade et al. [16] are employed. This set of boundary conditions, derived in their most general form, represent various terms in predicting the slip/jump conditions for reacting multicomponent mixtures. Unlike the first-order slip/jump boundary conditions where the mixture-averaged properties are utilized to relate the slip velocity and temperature discontinuity to the field variable gradients, this set of conditions accounts for individual species separately along with possible concentration discontinuity at the wall. Due to very small channel sizes considered in the present study, the homogeneous reactions can be ignored as discussed in detail by Zade et al. [17]. Detailed surface reaction mechanisms are employed in order to fully account for the effects of surface species in determining the heterogeneous reaction pathways.

2. Mathematical model

2.1. Governing equations

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. The governing mass, momentum, energy, and species continuity equations for a steady, laminar, reacting gas flow are:

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

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

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

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

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 thermal conductivity, 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, and w_k is the molar mass of species k. The molar production rate due to homogeneous reaction is excluded from the species continuity equation since homogeneous reaction effects can be neglected [17]. In this formulation, the enthalpy of the kth species h_k and the mixture enthalpy h are defined as:

$$h_k = h_{f,k}^0 + \int_{T_0}^{T} c_{p,k}\,dT; \qquad h = \sum_{k=1}^{N_g} h_k Y_k \tag{5}$$

in which $h_{f,k}^0$ is the standard enthalpy of formation. In the present work, all effects due to thermal radiation and the Dufour effect are ignored. The species diffusion mass flux $\mathbf{J}_k$ is determined using the multi-component diffusion equation as [18,19]:

$$\mathbf{J}_k = \frac{\rho w_k}{\overline{w}^2}\sum_{j=1}^{N_g} w_j D_{kj}\nabla X_j - D_k^T\frac{1}{T}\nabla T \tag{6}$$

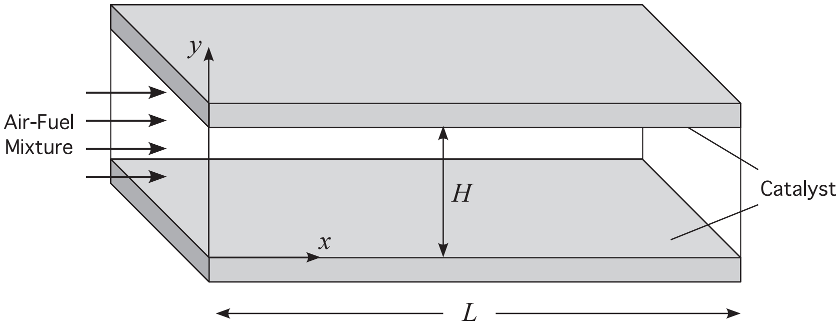

Fig. 1. Planar channel geometry and the coordinate system.