

Numerical Investigation of Methane-Fueled, Catalytic Microreactor Start-Up

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Abstract

An extensive numerical investigation on catalytic microreactor light-off was performed using a coupled 2-D full elliptic code for the gas-phase and a transient 1-D heat conduction code for the catalytic channel wall. A planar channel having 10 mm length and 1 mm height was considered. Detailed gaseous and catalytic chemistry for lean methane/air combustion on platinum was employed, along with full treatment of all heat transfer mechanisms inside the channel (heat conduction in solid, surface radiation heat transfer). The study addressed the effect of wall properties, hetero-/homogeneous chemistry interactions, radiation, and pressure on the transient behavior of catalytic microreactors.

Introduction

In recent years, research efforts have focused on portable, hydrocarbon-fueled power generating devices [1]. Catalytic microreactors, in particular, have received a lot of attention due to their operational benefits at small scales [2]. While all such studies, both numerical and experimental, have provided valuable insight on the steady-state behavior of catalytic microcombustors [3], studies on their transient behavior and in particular on the crucial issue of microreactor start-up remain limited [4].

An extensive numerical investigation was carried out to investigate the ignition and transient behavior of methane-fueled catalytic microreactors. Wall thermal properties, elevated pressure, radiation exchange in the channel and gas-phase chemistry were studied, and their influence on catalytic light-off and elapsed time until the reactor reaches steady state was assessed.

Numerical model

A full-elliptic 2-D laminar CFD code was used to simulate the flow domain in a plane channel of length $L=10$ mm, height $2b=1$ mm and wall thickness $\delta=0.1$ mm (Fig. 1). The quasisteady assumption was employed for the 2-D gaseous flow inside the channel, with the time-dependent energy balance for the 1-D solid wall; this method was used successfully in previous studies to simulate ignition in methane-fueled catalytic partial oxidation (CPO) reactors [5]. A time step of 50 ms was chosen, sufficient for gas-phase equilibration under all cases considered.

Pressures of 1 and 5 bar were studied and the fuel-to-air equivalence ratio ranged between $\varphi=0.4$ and 0.6. Two types of wall materials were examined: cordierite (ceramic) and FeCr alloy (metallic) walls, with thermal conductivities $k_s=2$ and 16 W/mK and heat capacities $\rho_s c_s=3.8$ and 4.4 MJ/m³K respectively. Inlet velocity range was $U_{IN}=0.3-0.5$ m/s and 1.5-2.5 m/s at 5 and 1 bar, respectively. The mixture preheat was set at $T_{IN}=850$ K, while radiation heat transfer exchange between catalytic surface elements and well as each element and the reactor inlet and outlet enclosures was

accounted for by the net radiation method for diffuse-gray areas [6], with all associated emissivities set equal to $\varepsilon=0.6$. Radiation transfer temperatures for the inlet and outlet enclosures were set equal to the respective fresh mixture and exhaust gas temperatures. The external wall surface was treated as adiabatic. An orthogonal staggered mesh of 84x24 and 80x20 (x - and y -coordinates) in the gas and solid wall, respectively, yielded a grid independent solution.

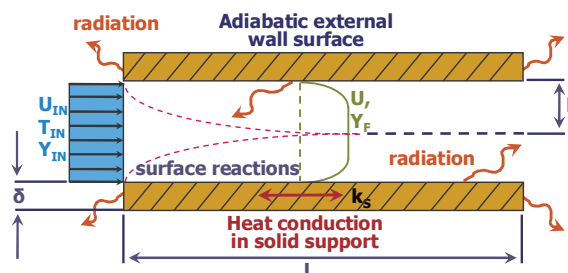


Fig. 1. Schematic of the plane catalytic channel. $L=10$ mm, $2b=1$ mm, $\delta=0.1$ mm.

The elementary heterogeneous scheme of Deutschmann et al. [7] was used to describe the oxidation of CH_4 on Pt. The simulations included the C1/H/O elementary gaseous mechanism of Warnatz et al [8], with proper kinetic parameter corrections for the pressure range 1 bar $\leq p \leq 6$ bar, according to [9].

Results and Discussion

The transient operation of catalytic microreactors is governed by two characteristic times. The ignition time t_{IGN} and the steady-state time t_{ST} are set as the times required for the exhaust gases to reach temperatures equal to respectively 50% and 99% of their maximum values at steady state. During microreactor start-up, it is desired to minimize both these characteristic times.

Elevated pressure is investigated to assess its impact on reactor start-up. Different solid thermal conductivities are studied to determine wall materials minimizing the characteristic reactor times. Radiation

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heat transfer is implemented and its effect quantified to study its impact on the reactor thermal management during ignition and equilibration. Finally, gas-phase chemistry is implemented to study possible implications on the transient behavior of catalytic microreactors.

Pressure effect

Elevated operating pressures have been shown to substantially extend the stable combustion regime of methane-fueled catalytic microreactors under steady state conditions [3]. The reason is that catalytic reactivity of CH_4 on Pt follows a positive $p^{+0.47}$ dependence on pressure and thus a positive pressure effect is expected on the start-up of such microreactors.

In Fig. 2, computed exhaust gas temperatures versus time are plotted for two cases at $p=1$ and 5 bar, with inlet velocities adjusted to maintain the same mass throughput. From the definition of t_{IGN} , it is evident that an increase of the inlet pressure substantially decreases the time required for reactor light-off. In this case, a 5-fold increase of the inlet pressure yields an ignition time of $t_{IGN}=7.8$ s, as opposed to $t_{IGN}=14.1$ s for the atmospheric pressure.

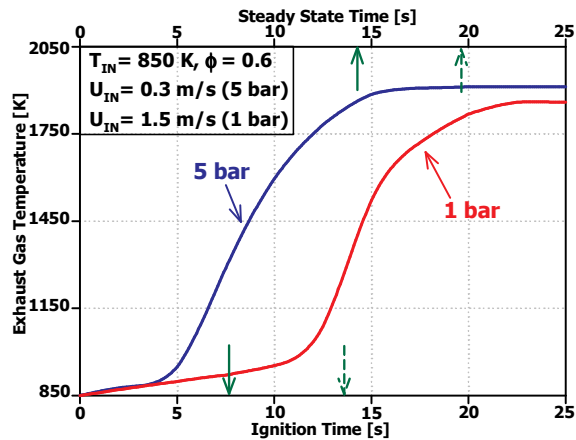


Fig. 2. Exhaust gas temperature versus time for two cases with same mass throughput at $p=1$ and 5 bar. Equivalence ratio $\phi=0.6$, inlet temperature $T_{IN}=850$ K, cordierite wall ($k_s=2$ W/mK). Vertical arrows define t_{IGN} (bottom axis) and t_{ST} (top axis) for $p=5$ bar (solid) and $p=1$ bar (dashed) respectively.

The increase of catalytic reactivity at elevated pressures allows significant fuel consumption at wall temperatures much lower than those at atmospheric pressure. This can have a significant impact with materials of high thermal capacity, which take longer to heat up to the critical temperatures required for catalyst light-off. By the slope of the two curves in Fig. 2, it can be observed that both pressures require almost the same time to reach steady state (~ 6.1 s) following ignition, indicating that after ignition the chemical power input per unit time is more critical in determining how fast the reactor equilibrates.

Inlet velocity effect

The inlet velocity has a direct impact on the time required to ignite the catalyst and afterwards reach steady state, since it is directly proportional to the power input of the reactor and the residence time of the gas in the channel.

The impact of inlet velocity is illustrated in Figure 3. Wall temperature profiles are presented for two cases where the inlet velocity is varied from $U_{IN}=0.3$ to 0.5 m/s, at four time instances. Ignition at the rear is observed, with a heat wave forming near the channel outlet and slowly propagating upstream.

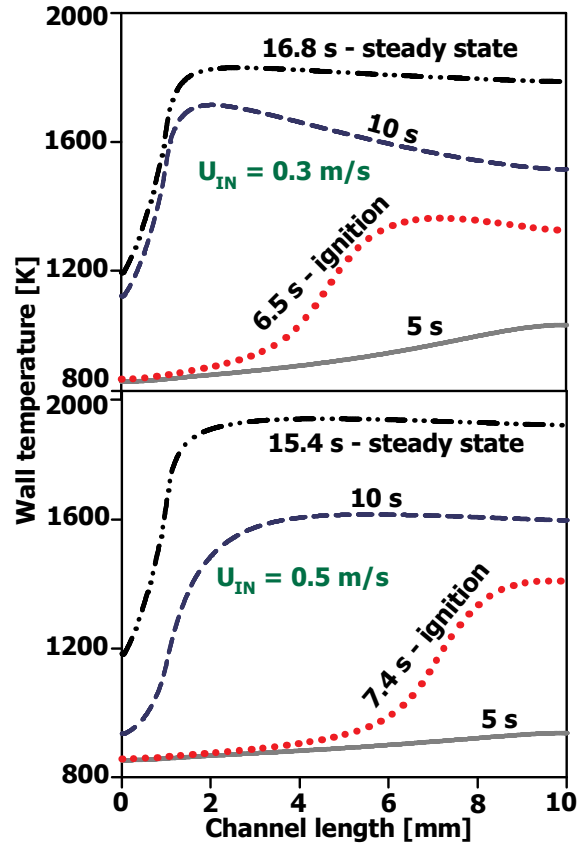


Fig. 3. Wall temperature profiles for two cases at four time instances (from weakly reactive to steady state). Top panel: $U_{IN}=0.3$ m/s, bottom panel: $U_{IN}=0.5$ m/s. Other conditions are: $p_{IN}=5$ bar, $T_{IN}=850$ K, $\phi=0.6$, $k_s=2$ W/mK.

Using the definition of t_{IGN} and t_{ST} as stated before, two opposing trends are observed concerning their dependence on inlet velocity. At low inlet velocity, the reactor benefits from increased residence time of the flow and reduced convective heat losses from the hot catalytic walls back to the gas phase. This allows for faster build-up of heat on the reactor walls and subsequent faster temperature rise, which leads to faster catalyst light-off ($t_{IGN, 0.3m/s} < t_{IGN, 0.5m/s}$). However, once ignited, the low velocity case requires a longer time to reach steady state than the high velocity case ($t_{ST, 0.3m/s} > t_{ST, 0.5m/s}$). The reduced chemical power input of the low

velocity case is not sufficient to compensate for the heat accumulated in the reactor walls and the propagation of the reaction front further upstream is slowed down.

Wall thermal conductivity effect

In order to study the effect of wall thermal conductivity on microreactor start-up, two types of representative reactor wall materials were investigated. The first one has the properties of cordierite ceramic ($k_s=2$ W/mK, $\rho_s c_s=3.8$ MJ/m³K) and the second one the properties of a FeCr metallic alloy ($k_s=16$ W/mK, $\rho_s c_s=4.4$ MJ/m³K). In steady-state operation, the dominant heat transfer mechanism inside catalytic channels is conduction in the channels walls, directly impacting combustor stability through the effective preheat of incoming fresh combustible mixture. During transient start-up, the thermal capacity of the solid has an equally important role, since high heat capacity materials will require larger amounts of thermal power to heat up to steady-state conditions.

Figure 4 illustrates the significant difference between ceramic and metallic materials. Wall temperature profiles are presented for two channels with cordierite and FeCr alloy walls. The latter required almost 50% longer time than that of the former to reach steady state ($t_{ST,FeCr}=30.1$ s, as opposed to $t_{ST,cordierite}=21.3$ s).

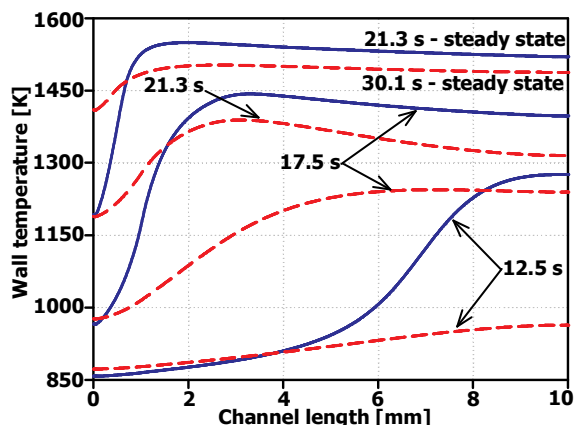


Fig. 4. Wall temperature profiles at 4 time instances for two reactors with cordierite ($k_s=2$ W/mK, solid blue lines) and FeCr alloy ($k_s=16$ W/mK, dashed red lines) walls. Steady state wall temperature profiles are indicated for both cases. Conditions: $p_{IN}=5$ bar, $T_{IN}=850$ K, $U_{IN}=0.3$ m/s, $\phi=0.4$.

This marked difference is attributed to the lower thermal conductivity and lower thermal capacity of the ceramic material. Before ignition, heat conduction in the solid is less pronounced for the ceramic material. Heat cannot be dissipated easily away from the reaction zone close to the channel exit; this leads to the formation of spatially narrow hot zones (see Fig. 4, wall temperature profile at 12.5 s for the ceramic reactor), which in turn promote further fuel consumption and lead to much faster catalyst light-off. This effect is enhanced by the lower thermal capacity of the ceramic material ($\rho_s c_s=$

3.8 MJ/m³K for cordierite, as opposed to 4.4 MJ/m³K for FeCr alloy). A smaller amount of energy needs to be accumulated in the ceramic wall to increase its temperature. In the case of steady inlet velocity (and, thus, steady chemical power input per unit time), reactors made of low thermal capacity materials will equilibrate faster. The above mentioned observations come in stark contrast to findings concerning microreactor steady state stability [3]; while metallic channels are more robust against external heat losses, ceramic ones are better suited during reactor start-up.

Radiation effect

Another phenomenon which is usually neglected in studies on catalytic microreactors is surface radiation heat transfer inside the channel reactor. During the ignition and heat-up time phases, significant temperature gradients can be observed between the front- and back-end of the reactor (e.g. see Figs. 3 and 4).

Transient simulations were performed for $p_{IN}=5$ bar, $T_{IN}=850$ K, $U_{IN}=0.3$ m/s, $\phi=0.4$, $k_s=2$ and 16 W/mK, with radiation transfer either included or neglected so as to study its impact on t_{IGN} and t_{ST} . In the case of low thermal conductivity, radiation played a dual role during start-up, hindering somewhat ignition but promoting fast equilibration to steady state. Specifically, in the case where radiation in the channel was neglected, ignition and steady state were achieved at $t_{IGN}=12.2$ s and $t_{ST}=26.7$ s, respectively, while in the case where radiation was included the corresponding times were $t_{IGN}=12.5$ s and $t_{ST}=24.6$ s. This behavior can be explained with the help of Fig. 5, whereby the energy balance in the solid is presented.

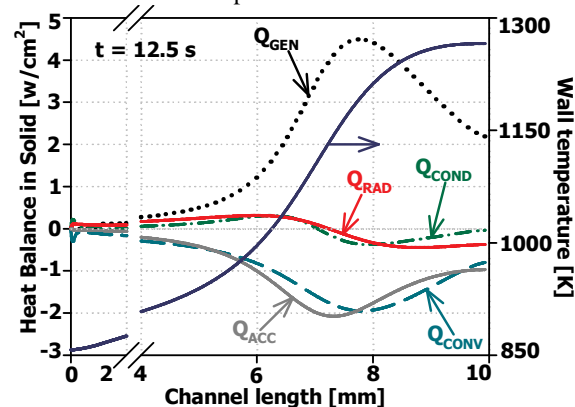


Fig. 5. Streamwise profiles of the energy balance in the solid at a time instance of reactor ignition ($t_{IGN}=12.5$ s); the wall temperature profile at this instance is also plotted. Terms include: generated heat on the wall (Q_{GEN}), heat conducted through the wall (Q_{COND}), heat convected to the gas (Q_{CONV}), net surface radiation (Q_{RAD}) and accumulated heat in the wall (Q_{ACC}). Conditions include: $p_{IN}=5$ bar, $T_{IN}=850$ K, $U_{IN}=0.3$ m/s, $\phi=0.4$, $k_s=2$ W/mK.

As evidenced in Fig. 5, during ignition there are large wall temperature gradients inside the catalytic

channel. This leads to increased radiation transfer with a magnitude comparable to that of heat conduction in the solid. Radiation in this instance dissipates heat away from the hot zone at the reactor rear, reducing the wall temperature and thus increasing t_{IGN} . After ignition, radiation helps the faster redistribution of heat inside the channel and thus t_{ST} is reduced (faster equilibration of the reactor). However, at high values of k_s , wall temperatures are more uniform and heat conduction in the wall is the dominant heat transfer mechanism, with radiation having a less pronounced effect.

Gas-phase chemistry effect

Another important parameter often neglected in catalytic microreactor simulations is gas-phase reactions inside the channel. Transient simulations were performed where detailed gas-phase chemistry was included to study its possible effect on ignition and steady state times.

Gas-phase chemistry can affect ignition and steady state times by contributing to the heat balance inside the catalytic channel. This can be achieved directly via heat released from gas-phase reactions or indirectly via incomplete oxidation in the gas phase (leading primarily to CO, which can then adsorb on the catalytic wall and further oxidize thus releasing heat). For $p_{IN}=5$ bar, $T_{IN}=850$ K, $U_{IN}=0.3$ m/s, $\phi=0.4$ and $k_s=2$ W/mK, gas-phase reactions were found to promote slightly reactor ignition and equilibration to steady state. Specifically, with the inclusion of gas-phase chemistry, t_{IGN} dropped to 12.1 s while t_{ST} was reduced to 22 s, compared to 12.1 s and 24.8 s, respectively, when only catalytic reactions were included.

To fully understand the impact of gas-phase chemistry on the wall energy balance, catalytic and gas-phase conversion rates are plotted in Figure 6, along with wall temperature profiles at four distinct time instances for a computed case with (a) and without (b) gas-phase reactions. Back-end ignition is observed in both cases, with a heat wave propagating towards the front of the reactor for both cases.

At the time of reactor ignition, heat generated by the gaseous phase is minimal, as evidenced by the low fuel conversion in the gas phase at $t=12.1$ s. Up to that time, temperatures inside the channel are too low to initiate gas-phase reactions. After ignition, the gas-phase contribution in the fuel conversion is increased substantially; however, flames that are formed in the catalytic channel are weak (due to the large amount of fuel already consumed on the catalytic surface), and are sustainable only by the exothermicity of the catalytic reactions. For this reason, the heat wave propagating towards the reactor front-end (formed by catalytic reactions) always precedes the weak flame. The contribution of gas-phase exothermicity is thus secondary; due to its narrow spatial extent compared to the heat released from catalytic reactions, the heat wave is intensified and travels faster upstream.

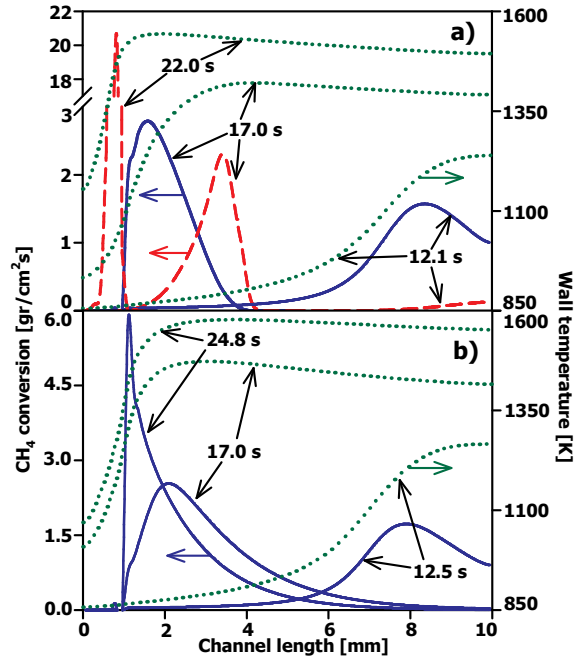


Fig. 6. Computed fuel conversion rates for a case with (a) and without (b) gas phase reactions over the channel streamwise extent at four time instances, including t_{IGN} and t_{ST} . Solid blue lines: catalytic reaction rate, dashed red lines: gas-phase reaction rate. Dotted green lines represent wall temperature profiles.

Although gas-phase chemistry plays a secondary role in reducing ignition and steady state times, it plays an important role in regulating microreactor emissions during start-up. As can be seen in Figure 7, gas-phase reactions alter qualitatively and quantitatively the emissions at the channel outlet.

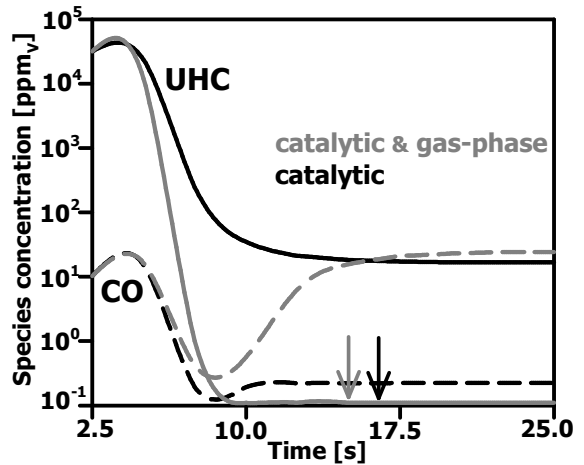


Fig. 7. Unburned hydrocarbon (UHC, solid lines) and carbon monoxide (CO, dashed lines) reactor emissions with respect to time for two cases with (gray lines) and without (black lines) gas-phase reactions. Arrows indicate steady state. Conditions: $p_{IN}=5$ bar, $T_{IN}=850$ K, $U_{IN}=0.3$ m/s, $\phi=0.6$, $k_s=2$ W/mK.

Incomplete gas-phase combustion increases CO emissions from the entire even at steady state; in the case of catalytic reactions only, the desorption energy of CO from Pt is too high for any significant emissions. On the other hand, the weak flames formed in the catalytic channel are responsible for the rapid conversion of fuel even during the ignition and heat-up phase, while if only catalytic reactions are considered a considerable fuel breakthrough is predicted until steady state is reached.

Conclusions

The transient behavior during start-up of methane-fueled catalytic microreactors was investigated using a 2-D CFD quasisteady elliptic code to model a platinum-coated plane channel; detailed catalytic and gas-phase chemistry descriptions and full treatment of all heat transfer mechanisms inside the channel were considered. The effect of pressure, wall thermal properties, radiation transfer, inlet velocity and gas-phase chemistry on the time required for microreactor ignition and equilibration (steady state) was investigated.

Pressure played a profound role in significantly reducing ignition and steady state times due to increased catalytic reactivity. Ceramic channel walls allow for faster ignition and equilibration because their low conductivity and thermal capacity creates hot spots that promote fuel conversion. Low inlet velocities ignite the reactor faster but reach steady state slower than high inlet velocities. Radiation transfer plays a dual role since it can hinder ignition (heat dissipates away from the reaction zone) but fastens approach to steady state (by redistributing heat inside the channel). Gas-phase reactions improve slightly both ignition and equilibration times, with catalytic reactions playing the dominant role. Inclusion of gas-phase chemistry in modeling can be important in the correct assessment of reactor emissions during the heat-up phase (between ignition and steady state), especially if this phase requires significant time to be completed.

Acknowledgements

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