TRANSIENT SIMULATION OF THE HYDROGEN-ASSISTED SELF-IGNITION OF FUEL-LEAN PROPALE-AIR MIXTURES IN PLATINUM-COATED MICRO-CHANNELS USING REDUCED-ORDER KINETICS

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ABSTRACT

Transient simulation of the hydrogen-assisted self-ignition of propane-air mixtures in platinum-coated micro-channels was carried out under ambient condition using a two-dimensional model taking into account reduced-order reaction schemes, heat conduction in the solid walls, convection and surface radiation heat transfer. The self-ignition behavior of the hydrogen-propane mixed fuel is compared to the selectively inlet feed preheating mode. The simulations carried out indicate that hydrogen can successfully cause self-ignition of propane-air mixtures in catalytic micro-channels of 0.2 mm gap size, eliminating the startup devices required. The minimum hydrogen content for propane self-ignition is found to be in the range of 0.8 % - 2.8 % (on a molar basis). It increases with wall thermal conductivity increase and decrease of the inlet velocity or propane composition. The higher propane-air ratio results in earlier ignition. The ignition characteristics of hydrogen-assisted propane resemble qualitatively the selected inlet feed preheating mode. The transient response of the mixed hydrogen-propane fuel reveals sequential ignition of propane and hydrogen. Front-end propane ignition is observed in all cases. Low wall thermal conductivities cause earlier ignition of the mixed hydrogen-propane fuel, subsequently resulting in low exit temperatures. The transient-state behavior of this micro-scale system is described, and the startup time and minimization of hydrogen usage are discussed.

Keywords: self-ignition, micro-combustion, catalytic combustion, platinum catalyst, transient combustion modeling, reduced-order kinetics.

INTRODUCTION

In order to meet the demand for portable power sources with high energy density, recent experiments have focused on utilizing hydrocarbon fuels as energy sources to replace conventional batteries [1]. The latter have low volumetric and gravimetric power density, relatively short life cycle and are made of materials that are difficult to recycle. The high specific energy of hydrocarbon fuels (approximately 40 MJ kg⁻¹ versus 0.5 MJ kg⁻¹ for lithium-ion battery) [2] and the ability to recharge a hydrocarbon-fueled power source by merely adding more fuel, are driving attributes of a future fuel-to-electricity technology.

The direct combustion of hydrocarbon fuels in micro-combustors to produce power and/or heat is one of the approaches to extract power. Efforts to utilize hydrocarbons combustion in micro-scale devices have resulted in designs that are scaled down versions of large-scale power generating devices [3]. However, the requirements for moving parts along with the higher temperatures of self-sustaining homogeneous flame in these micro-scale devices challenge devices capabilities such as sealing, insulation, and fabrication, etc. Another alternative approach is to combust hydrocarbon fuels in micro-reactors with minimal moving parts resulting in further reduction of the system size and to produce heat which can be further converted into electrical power using thermoelectric energy conversion modules [4]. The increased surface to volume ratio of such micro-scale devices leads to considerable radical quenching and heat losses resulting in unsustainable homogeneous flame [5]. Catalytic combustion in such micro-scale devices is preferred because the surface reaction occurs at much
lower temperatures and can be sustained at much leaner fuel-air ratios as compared with homogeneous flame [6]. Thus the design constraints of the micro-scale system are facilitated. Furthermore, fuel ignition occurs at much lower temperatures, and certain fuels such as hydrogen and methanol have been found to be self-starting and self-sustained at the micro-scale eliminating the need for startup devices [7, 8].

Hydrogen-air mixtures have been found to be self-igniting over platinum wires and foils under fuel-leaner conditions [7, 9] but fuel-richer mixtures exhibit ignition temperature above room temperature. In addition, catalytic combustion of hydrogen over the noble metal catalysts has low activation energy, resulting in extremely fast reaction. The self-ignition nature of hydrogen-air mixtures in ceramic micro-combustors offers an opportunity to self-ignite hydrocarbon fuels, referred to as hydrogen-assisted ignition [7, 10]. This concept may be a way toward elimination of ignition sources from micro-scale devices, resulting in further reduction of micro-scale system size. In addition, since hydrogen is a main target for fuel cell applications, one can envision storage of small amounts of hydrogen during micro-scale device operation from reforming of hydrocarbons that are subsequently used for startup.

Most of the literature sources have focused on steady-state behavior including flame stability [11], dynamic instabilities [12], thermal management [13], interaction of homogeneous and heterogeneous chemistry [14], coupling of exothermic and endothermic reactions [15], nonlinear dynamics [16], and strategies to recycle 'excess enthalpy' [17] via reverse-flow operation [18] or heat recirculation [19]. These studies give a good understanding with respect to the steady-state combustion process. However, they do not provide any information on the timescales of these processes. It is important to explore the transient behavior of the micro-combustor during the start-up under ambient condition and changing input conditions.

In case of propane external heating is necessary to ignite the propane-air mixtures and besides the fuel adsorption on platinum is slow [7]. Propane-air mixtures also exhibit auto-thermal behavior, namely, they can be self-sustained. Here, we explore the feasibility of this idea, estimate the necessary hydrogen content needed to self-ignite propane-air mixtures, and investigate the synergism of binary fuels. The main objective of the present work is to delineate the transient behavior of hydrocarbon self-ignition in micro-combustors. The present study undertakes the numerical investigation of hydrogen-assisted self-ignition of propane-air mixtures in catalytic micro-channels under ambient condition. Transient simulations are performed, which include two-dimensional gas-phase description, heat conduction in the solid wall, convection, surface radiation, heat transfer, and reduced-order reaction model.

**NUMERICAL MODELS AND SIMULATION APPROACH**

**Model Geometry and Mesh**

A schematic presentation of the catalytic micro-channel is shown in Fig. 1. The micro-channel is modeled as two parallel infinitely wide plates of gap distance \(d = 0.2\) mm, of length \(l = 20.0\) mm, and solid wall thickness \(\delta = 0.2\) mm. The adopted 0.2 mm geometrical confinement is typical of either catalytic honeycomb reactors for large-scale power generation [20] or of single-channel micro-reactors for portable power generation [8]. Platinum catalyst is coated on the inner channel surfaces. Its
properties are listed in Table 1. FLUENT-KINETICS was used to perform these transient simulations.

### Chemical Kinetics of Catalytic Combustion of Hydrogen

A reduced-order reaction scheme proposed by Bui et al. [21] is used to describe the oxidation of hydrogen over platinum, i.e.

$$r_{\text{cat}, H_2} = \eta A_0 T^\beta e^{-E_{a,H_2} \over RT} C_{H_2}$$

(1)

where the effectiveness factor ($\eta$), the pre-exponential factor ($A_0$), the temperature exponent ($\beta$) and the activation energy ($E_{a,H_2}$) of hydrogen adsorption are of the values of 1.0, 1280 cm·K$^{-0.5}$·s$^{-1}$, 0.5 and 0 kJ·mol$^{-1}$, respectively. Simulations with the application of this scheme have reproduced the measured catalytic ignition temperatures of fuel-lean hydrogen-air mixtures over rhodium and platinum surfaces [22]. A minimum hydrogen-air ratio of homogenous light-off was found equal to ca 0.33 [23, 24]. Therefore, the homogeneous chemistry of hydrogen was neglected and the simulations were restricted to a hydrogen-air ratio lower than 0.2.

### Chemical Kinetics of Catalytic Combustion of Propane

The reduced-order rate kinetics [21] of the oxidation of propane on platinum is described as follows:

$$r_\text{cat, C}_3\text{H}_8 = \frac{k_i \alpha_i \text{C}_{\text{ads, C}_3\text{H}_8}}{1 + \sqrt{\frac{k_i \alpha_i \text{C}_{\text{ads, O}_2}}{k_i \alpha_i \text{C}_{\text{ads, O}_2}}}$$

(2)

where $r_\text{cat, C}_3\text{H}_8$, $C_{\text{ads, C}_3\text{H}_8}$, and $k_i$ are the surface reaction rate of propane, the concentration of adsorbed species $i$ and the ad-/desorption rate constant of species $i$, respectively. The latter is determined in correspondence with:

$$k_{\text{ads}, i} = \frac{s_0}{\Gamma} \sqrt{\frac{RT}{2\pi M_i}} \left( T \over T_{\text{ref}} \right) ^{\beta_i} e^{-E_{a,i} \over RT}$$

(3)

$$k_{\text{des}, i} = A_i \left( T \over T_{\text{ref}} \right) ^{\beta_i} e^{-E_{d,i} \over RT}$$

(4)

where $s_0$, $\Gamma$, $M_i$ and $T_{\text{ref}}$ are the sticking coefficient, the surface site density of the platinum catalyst, the molecular weight of species $i$, and the temperature of the reference conditions, respectively. The values of these kinetic parameters are given in Table 2. The activation energy of oxygen desorption depends on the coverage of oxygen radical following:

$$\theta_{O_2} = 1 \over 1 + \sqrt{\frac{k_{\text{ads}, O_2}}{k_{\text{des}, O_2}}}$$

(5)

### Boundary Conditions

Uniform velocity distributions and concentration of the incoming mixture were specified at the inlet at 300 K. The initial temperature of the solid wall is spatially uniform and equal to the incoming mixture temperature. The Neumann boundary condition was applied to the

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Table 1. Properties of platinum-coated catalyst.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>catalyst surface site density</td>
<td>$2.7 \times 10^{-9}$</td>
</tr>
<tr>
<td>average pore diameter</td>
<td>$2.08 \times 10^{-8}$</td>
</tr>
<tr>
<td>catalyst porosity $\varepsilon$</td>
<td>0.4</td>
</tr>
<tr>
<td>catalyst tortuosity $\tau$</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Table 2. Kinetic parameters referring to the catalytic combustion of lean propane over platinum.

<table>
<thead>
<tr>
<th>Species</th>
<th>$A_0$ (s$^{-1}$)</th>
<th>$\beta$</th>
<th>$E_a$ (kcal·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$H$_8$ adsorption</td>
<td>0.06</td>
<td>0.154</td>
<td>4</td>
</tr>
<tr>
<td>O$_2$ adsorption</td>
<td>0.0542</td>
<td>0.766</td>
<td>0</td>
</tr>
<tr>
<td>O$_2$ desorption</td>
<td>8.41$\times$10$^{12}$</td>
<td>-0.796</td>
<td></td>
</tr>
</tbody>
</table>

$E_{a,O_2}^* = 52.8 - \frac{3.3 T}{300} - 32.0 \theta_{O_2}$

Surface area factor $\eta = 1.7$, temperature of the reference conditions $T_{\text{ref}} = 300$ K.
A non-slip boundary condition was considered for the inner wall. The heat flux between the fluid and the solid wall was computed using the Fourier’s law, and the continuity of the temperature links between the fluid and solid phases. The discrete ordinates (DO) model was used to consider the effect of the interior surface on the surface radiation [24]. The total heat-loss rate at the exterior surfaces included both the natural convection and the thermal radiation. It was estimated in accordance with:

\[ q = h(T_{w,o} - T_{\infty}) + \varepsilon\delta(T_{w,o}^4 - T_{\infty}^4) \]  

where \( h \) is the exterior convective heat transfer coefficient with a value of 20 W/m²·K [25], \( T_{w,o} \) is the outer wall temperature, \( T_{\infty} \) is the ambient temperature of 300K, \( \varepsilon \) is the solid surface emissivity taken to be 0.8, while \( \delta \) is the Stefan-Boltzmann constant.

**Computation Scheme**

The quasisteady-state assumption (QSS) was applied in treating the surface and gas-phase chemistry to eliminate the high computational cost of the fully transient simulations. Most transient QSS models employed one dimension description for both the bulk-gas and solid phases. QSS requires shorter gas-phase diffusive and convective timescales when compared to than of the heat conduction in the solid phase to provide the equilibration of the gaseous flow temperature to the wall temperature at any time during the transient start-up process [9]. The integration time step \( \Delta t \) was selected to satisfy the QSS approximation referring to the chemical reaction studied whose diffusion and convection times were shorter than the corresponding heat conduction times in the solid phase. QSS approximation is in excellent agreement with the complete DNS simulations [9] when such criteria are satisfied. According to the timescale analysis of Michelon et al. [8], the fixed integration time step \( \Delta t = 50.0 \) ms was selected. This time step was long enough to provide equilibration of the chemical processes and the gas-phase transport and at the same time short enough to resolve the axial solid heat conduction.

Non-uniform meshes with more grids distributed in the reaction region near the wall were used to provide sufficient grid resolution in the computational domain. The grid independence was examined and the final grid density was determined when the centerline profiles of species concentration and temperature did not show an obvious difference. Under these criteria, a non-uniform mesh with 200×60 grid points distribution in the axial and transverse directions was used. The mass, the momentum, the energy, the species conservation equations and the conjugated heat conduction in the solid walls were solved by the computational fluid dynamics (CFD) software, FLUENT-KINETICS. The above conservation equations were implicitly solved with the 2D transient-state double-precision segregated solver using the under-relaxation method. The second-order upwind scheme and the “PISO” algorithm was used to discretize the model and couple the pressure and velocity, respectively. The specific heat, the fluid viscosity, and the thermal conductivity were calculated using the mass fraction weighted average of the species properties. The species specific heat was calculated using the piecewise polynomial fit of temperature. The transient solid energy equation was solved with a second-order accurate, fully implicit scheme and a quadratic backward time discretization [9]. A solution for the coupled solid phase and flow equations was obtained at each time step iteratively: convergence was reached as the solid temperatures at all axial positions did not vary between successive iterations by more than \( 10^{-5} \) K.

Gas-phase and surface reaction rates were evaluated with CHEMKIN [26] and Surface-CHEMKIN [27], respectively. Mixture-average diffusion was adopted and the transport properties were calculated from the CHEMKIN transport database [28].

**RESULTS AND DISCUSSION**

The micro-combustor initially contains only air, starting at ambient temperature of 300 K. The premixed hydrogen-propane-air mixtures are fed starting at time \( t = 0 \) at the desired inlet velocity and equivalence ratio.

**Hydrogen Requirement for Propane Self-Ignition**

Fig. 2 shows the maximum temperature versus the hydrogen mole fraction in the hydrogen-assisted mode at an inlet velocity of 10 m/s. In this case, the propane-air ratio is held constant. As the hydrogen concentration increases starting from zero, the flow rates of propane and air are reduced, as the hydrogen flow rate increases to maintain the total volumetric flow rate fixed. The simulations indicate that hydrogen can successfully
cause self-ignition of propane-air mixtures in catalytic micro-channels with a 0.2 mm gap size eliminating the need for startup devices. Higher hydrogen compositions result in increased maximum temperature. As the hydrogen content increases, the maximum temperature increases slowly until the hydrogen mole fraction reaches a value close to 1.7% - 1.8%. When a particular hydrogen content value is attained, the heat released by hydrogen oxidation is sufficient to ignite propane and a turning point bifurcation is observed. The behavior observed is consistent with the results reported in ref. [7].

The maximum temperature versus the inlet temperature in the inlet feed preheating mode (without hydrogen addition) are also shown in Fig. 2 for comparison. The bifurcation point temperature in the hydrogen-assisted mode is slightly higher than that in the inlet feed preheating mode. In addition, the higher equivalence ratio of propane-air mixtures results in earlier ignition.

Fig. 3 shows the hydrogen content required for propane self-ignition in case of various equivalence ratios at an inlet velocity of 10 m/s. The propane ignition temperature in the inlet feed preheating mode is also shown for comparison. The minimum hydrogen content for propane self-ignition is decreased with the propane-air ratio increase. This behavior is consistent with the experimental observations of Deutschmann et al. [10], who propose that the concentration of hydrogen needed for hydrocarbon ignition decreases as hydrocarbon concentration is increased. This trend in the hydrogen-assisted mode is quite similar to that in inlet preheating mode.

Fig. 4 shows the hydrogen requirement for propane self-ignition in case of various wall thermal conductivities. Both the wall thermal conductivity and the inlet velocity have a significant effect on the hydrogen requirement. The higher inlet velocities result in higher wall temperatures. As a result, the hydrogen content required decreases. Likewise, the hydrogen requirement increases with the increase of the wall thermal conductivity. This is so because the wall hot spots created near the inlet of lower thermal conductivity [8, 13, 19] help the mixtures get ignited in presence of less hydrogen content. The latter required for propane self-ignition varies in the range of 0.8% - 2.8% (on a molar basis).
**Ignition Characteristics and Transient Response**

In this case, the propane-air ratio is kept fixed at 0.7, and the amount of hydrogen is 0.05 % (on a molar basis), in fact in excess of the minimum amount required for propane self-ignition over platinum under the corresponding conditions. Transient responses of the propane conversion, the bulk-gas and the interior-wall temperatures versus various wall thermal conductivities at an inlet velocity of 2 m s⁻¹ are shown in Figs. 5-7, respectively.

Hydrogen ignites in approximately 1.0-2.0 s and directly reaches its steady-state profile, as shown in Fig. 5. Note that the hydrogen conversion profiles change very slightly in most cases. The ignition time $t_{ign}$ is defined as the time taken for catalytic conversion of propane to reach 50.0 % at the exit. As shown in Fig. 6, the higher wall thermal conductivity results in increase of the ignition time from 98 s for insulating materials (0.5 W m⁻¹K⁻¹) to 202 s for materials with moderate wall thermal conductivities (20 W m⁻¹K⁻¹), and 448 s for materials with higher wall thermal conductivities (200 W m⁻¹K⁻¹). This trend is determined by the heat localization within the
walls with lower thermal conductivities, resulting in hot spot formation and faster ignition. In addition, front-end ignition is observed in all cases. The bulk-gas and the interior wall temperatures reach their steady-state values quickly once propane is ignited. The ignition characteristics in hydrogen-assisted mode resemble qualitatively those of the inlet feed preheating mode [7].

Another observation is worth considering. It refers to the low conductivity walls temperatures in steady state which decrease initially, then increase, and subsequently decrease again. This is illustrated in Fig. 7. This trend is outlined because the hydrogen combustion region is located significantly upstream as compared with that of propane. The interior wall temperatures drop slightly in the range between them as a result of heat losses to the surroundings.

Fig. 8 shows the temperatures and the propane conversions at the exit as a function of the cumulative time for various wall thermal conductivities. The triangles represent the ignition time $t_{\text{ign}}$, while the circles denote the ignition time $t_{\text{ign}}$.

decrease again. This is illustrated in Fig. 7. This trend is outlined because the hydrogen combustion region is located significantly upstream as compared with that of propane. The interior wall temperatures drop slightly in the range between them as a result of heat losses to the surroundings.

Fig. 8 shows the temperatures and the propane conversions at the exit as a function of the cumulative time for various wall thermal conductivities. The triangles represent the ignition time at which propane is ignited. It corresponds to 50.0 % conversion. The circles represent the steady-state time required for the propane combustion to reach a steady-state. Complete conversion of propane is achieved in all cases. Lower wall thermal conductivities cause earlier ignition of the mixed hydrogen-propane fuel, subsequently resulting in lower exit temperatures.

In general, the premixed fuel-lean hydrogen-propane-
air mixtures over platinum can result in self-ignition with no external preheater. The platinum catalyst allows instantaneous ignition of hydrogen, and subsequent propane ignition when its ignition temperature is reached. A minimum hydrogen concentration in the range of 0.8% - 2.8% (on a molar basis) is needed. It decreases in case of lower wall thermal conductivities, higher inlet velocities, and higher propane-air ratios.

CONCLUSIONS

Transient simulation of the hydrogen-assisted self-ignition of propane-air mixtures is carried out in platinum-coated micro-channels under ambient condition, using a two-dimensional model taking into consideration reduced-order reaction schemes, heat conduction in the solid wall, convection and surface radiation heat transfer. It is shown that hydrogen can successfully cause self-ignition of propane-air mixtures in catalytic micro-channels with a 0.2 mm gap size eliminating the need for startup devices. The minimum hydrogen content for propane self-ignition is found to be in the range of 0.8% - 2.8% (on a molar basis). It increases with wall thermal conductivity increase, and inlet velocity or propane composition decrease. Higher propane-air ratio results in earlier ignition. The catalytic ignition characteristics of hydrogen-assisted propane resemble qualitatively the selectively inlet feed preheating mode. Hydrogen gets ignited first and the resulting wall temperature increase brings about the subsequent propane ignition. Front-end propane ignition is observed in all cases. Low wall thermal conductivities cause earlier ignition of the mixed hydrogen-propane fuel, subsequently resulting in low exit temperatures.

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