The role of homogeneous chemistry during Ignition of propane combustion in Pt-catalyzed microburners

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ABSTRACT

The aim of this work is to numerically investigate the ignition behavior of homogeneous-heterogeneous (HH) combustion of propane in a Pt-catalyzed microburner to delineate the role of homogeneous chemistry during cold-start ignition. A two dimensional model with one-step homogeneous and catalytic mechanisms in a parallel-plate microburner is considered. The ignition characteristics (ignition temperature and ignition time) are explored for catalytic microreactor with and without homogeneous chemistry. We show that the catalytic reaction lights-off first, followed by the homogeneous reaction. Consequently, the homogeneous chemistry does not affect the ignition behavior of the catalytic microburner. The effect of inlet velocity, wall thermal conductivity and gap size on ignition characteristics is explored. The ignition characteristics are not affected by homogeneous chemistry even at larger gap sizes, despite the fact that the homogeneous contribution at steady state increases with increasing gap size of the microburner.

Keywords: Ignition temperature, Ignition time, Transient simulation, Catalytic microreactors, Homogeneous-heterogeneous combustion.

1. INTRODUCTION

Micro-scale combustion in sub-millimeter channels has become interesting topic of research for small-scale power generating systems. Low temperature micro-combustion is desirable to minimize the hot spots and instabilities in the system for hydrocarbon fuelled microreactors. Microburners have been used to produce power via thermo-electrics, thermo-photovoltaics or micro-turbines; for micro-propulsion; and in fuel processing systems [1–6].

The thermal and radical quenching are the two major phenomena which need to be controlled for optimum design of microburners. Thermal quenching happens via

extinction when the heat generated by reaction becomes smaller than the overall heat loss, and via blow-out when residence time is too low (higher flow rates). Radical quenching happens when the adsorption of radicals on the system walls and subsequent recombination leads to depletion of reactant radicals in the bulk phase of the microreactor and hinders the homogeneous reaction. The review of micro- and meso-scale combustion is given elsewhere [7].

The dimension of microburners is less than the quench diameter for flames. However, due to enhanced catalyst-induced heating homogeneous reaction can be sustained at gap sizes well below the quenching distance. Despite the large surface to volume ratio of microreactors the contribution of gas phase reactions cannot always be ignored. Nevertheless the contribution of homogeneous chemistry decreases with the gap size [8, 9] as well as with increasing wall thermal conductivity [10, 11]. Instabilities such as repetitive extinction, oscillating flames and asymmetric flames have been observed in homogeneous (i.e., non-catalytic) microburners. These instabilities can be suppressed by increasing the catalyst reactivity, resulting in more stable combustion [12].

The homogeneous chemistry may have either positive or negative impact on catalytic microburners, depending on the specific application and conditions of the system. The positive impacts of homogeneous chemistry in catalytic microburners include moderation of the super adiabatic surface temperatures during the heterogeneous conversion of fuels [13], extension of extinction and blow-out limits of pure catalytic combustion [14], and feasibility of operating at higher velocities in microchannels [15]. Russo and co-workers [16, 17] have proposed "hybrid micro-combustors", where the catalytic reactor is designed to appropriately promote homogeneous combustion. The negative impacts include loss in selectivity, safety hazard resulting from higher temperatures and reaction runaway or explosive behavior [8]. Higher operating temperatures in presence of homogeneous reactions (as compared to purely catalytic reactions) have been observed numerically [9] as well as experimentally [18, 19].

The interaction of homogeneous and heterogeneous chemistry has been well understood for mesoscale systems [7, 10, 20]. Extensive experimental and numerical investigations have been performed by Mantzaras and coworkers to show the effect of pressure on homogeneous-heterogeneous reacting system for hydrogen/air mixtures [21, 22], propane/air mixtures [23, 24] and syngas catalytic combustion [13]. All these studies showed that the homogeneous combustion cannot be ignored at high pressures and high temperatures. The homogeneous contribution increases as the temperature build-up in the reactor increases; this observation is more significant at higher reactor pressure [13, 21–23] and higher equivalence ratio [25]. The interaction between catalytic and homogeneous chemistries in meso-scale reactors has also been explored for methane/air [20], partial oxidation of ethane [25] and catalytic reforming of logistic fuels [26].

In addition to analysis of steady state behavior and instabilities in combustion, investigation of ignition characteristics for design of microreactors has also been considered to reduce time for ignition and cold-start emissions. The possibility of self ignition of hydrogen/air mixtures, hydrogen assisted propane/air mixture on Pt-catalyzed ceramic micro-channel [18] was achieved under wide composition range. The integrated microburner is designed to self start from room temperature [27] for

methane/air mixtures. The different modes of sustained combustion were explored numerically under unsteady ignition behavior [28]. Ignition in catalytic microreactors for propane/air mixtures were explored for inlet and resistive preheating modes of inlet feed [29, 30]. The ignition temperature decreased with increasing wall thermal conductivity for adiabatic system and the opposite trend was observed for heat loss case [29]. Promoting front-end ignition was shown to provide faster ignition and lower propane emissions [30]. Seshadri and Kaisare [31] showed similar transient behavior for hydrogen-assisted propane ignition in co-feed and sequential feeding modes. Ignition of fuel mixtures in catalytic microburners showed sequential ignition of fuels: the fuel with lower ignition temperature ignited first, followed by ignition of the other fuel [31, 32].

In this work we explore the effect of homogeneous chemistry on ignition behavior of catalytic propane combustion. Specifically, we compare how the presence of homogeneous chemistry affects ignition temperature and the time taken for ignition from cold-start conditions compared to purely catalytic combustion in a Pt-catalyzed microburner. While the interaction between homogeneous and catalytic chemistries is well-studied under *steady state* conditions, the dynamics during cold-start ignition are targeted in this work. We also study the role of various parameters such as inlet velocity, wall thermal conductivity and gap size on ignition of homogeneous-heterogeneous (HH) propane combustion. The simulation methodology is described in the next section, followed by comparison of ignition behavior of catalytic and HH propane combustion. The role of wall thermal conductivity and gap size are discussed thereafter, followed by conclusions drawn from this work.

2. SIMULATION METHODOLOGY

In this simulation study, we consider the two-dimensional geometry of a planar micro-combustor, consisting of a single flow channel formed between two infinite wide parallel plates as in Figure 1. The length of the reactor is 2 cm, the gap size is 500 μm, and the wall thickness is 50 μm. The initial 1 mm of the reactor wall is non catalytic and the rest of 19 mm wall is catalytic. Due to the symmetric plane between the two plates, we considered only half of the reactor for simulation study.

The reactor mesh is generated using GAMBIT; after the grid independence study, we arrived at a uniform mesh with 1000 nodes in the axial direction, 40 nodes in the transverse direction in the flow domain and 5 nodes in the transverse direction in the solid wall. In case of transient simulations, the time step of 0.1 sec was found to be sufficient to give step size independent results. This was verified by comparing the results obtained with time-steps of 0.2 sec, 0.1 sec and 0.05 sec. Thus for the transient term, we use the first order implicit scheme with time marching of 0.1 sec. The continuity, momentum, energy and species transport equations are solved using FLUENT software for the 2D steady and transient models.

The governing equations solved in FLUENT 6.3 are given in generic transport form as

$$\frac{\partial (\rho \phi)}{\partial t} + \nabla \cdot (\rho \phi \vec{u}) = \nabla \cdot (\Gamma \nabla \phi) + S_{\phi} \qquad (1)$$

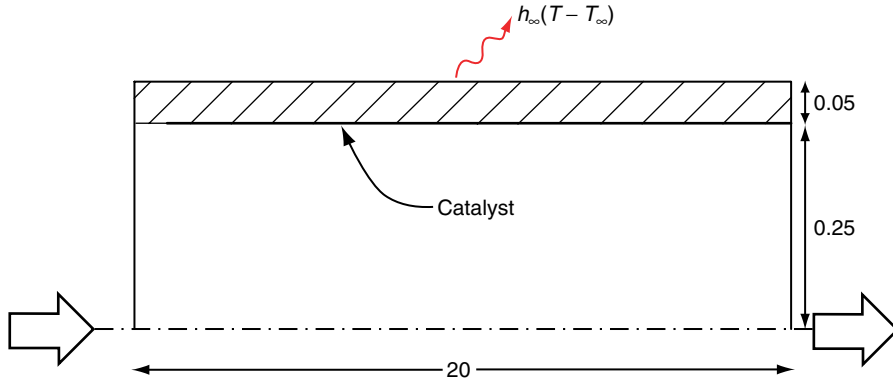$h_\infty(T - T_\infty)$

0.05

Catalyst

0.25

20

Figure 1:   Schematic picture of the microburner. Initial 1 mm channel is non-catalytic. Due to the planar symmetry half of the channel is shown. All dimensions are in mm.

The corresponding variables solved in the various conservation equations are given in Table 1. Note that all the conservation equations are solved simultaneously using the 2D pressure-based SIMPLE solver.

Dirichlet boundary conditions are applied at inlet: propane/air mixture is fed at the desired equivalence ratio, inlet temperature and inlet velocity. At the reactor inner walls, no-slip boundary condition is applied and the species flux at the catalytic boundary is given by the rate of species conversion through catalytic reactions. The rate of catalytic reactions at the interface (as well as the heat of reaction) is supplied through user defined function (UDF). The microburner outer wall loses heat to the ambient via

Table 1: Corresponding terms for the generic transport equation for the conservation equations. The variables *u*, *h* and *Y* represent velocity, enthalpy and mass fraction respectively; coefficients *μ*, *k* and $\mathcal{D}$ represent viscosity, thermal conductivity and diffusivity respectively; *a/v* is the area to volume ratio, v_{ij} are stoichiometric coefficients, and ΔH and *r* are heats and rates of reactions.

Conservation Equations	ϕ	Γ	$S\phi$
Continuity	1	–	–
Momentum	u_i	μ	Δp
Energy, gas phase	h	k_i	$\sum_j \left(-\Delta H_j\right) r_j^{\mathrm{hom}}$
Energy, solid phase	h_s	k_s	$\dfrac{a}{v} \sum_k \Delta H_k r_k^{\mathrm{cat}}$
Species	Y_i	$\mathcal{D}_{i,m}$	$M_i \sum_j v_{ij} r_j^{\mathrm{hom}}$

convection. The pressure outlet boundary condition is applied at the outlet of the reactor, with zero gradients for temperature and species.

The kinetics for homogeneous combustion is implemented from the one-step propane combustion rate proposed by Westbrook and Dryer [34]:

$$r^{hom} = 4.836 \times 10^9 e^{\left(\frac{-1.256 \times 10^8}{RT}\right)} c_{C_3H_8}{}^{0.1} c_{o_2}{}^{1.65} \; kg.mol/\left(m^3 s\right) \tag{2}$$

The limitation of this single step rate equation is that it does not account for the interactions of the free radicals involved in homogeneous chemistry and the catalyst surface. It therefore does not capture the radical quenching mechanism or the formation of radicals at the surface.

One-step reduced order chemistry for catalytic propane combustion on Pt derived by Deshmukh et al. [35] is considered. The catalytic reaction rates are implemented in FLUENT using user-defined function (UDF). The catalytic reaction rate is given by

$$r^{cat} = \frac{\eta k_{C_3H_8}^{ads} C_{s,c_3H_8}}{\left(1+\sqrt{k_{o_2}^{ads} C_{s,o_2}/k_{o_2}^{des}}\right)^2} \; mol/\left(m^2 s\right) \tag{3}$$

where,

$$k_i^{ads} = \frac{s_i}{\Gamma}\sqrt{\frac{RT}{2\pi M_i}} T_r{}^{\beta_i^{ads}} e^{\left(\frac{-E_i^{ads}}{RT}\right)} \tag{4}$$

$$k_i^{des} = A_i T_r{}^{\beta_i^{des}} e^{\left(\frac{-E_i^{des}}{RT}\right)} \tag{5}$$

The rate-limiting step is the dissociative adsorption of the propane, whereas oxygen is the most abundant reaction intermediate. In the above expression, the surface area factor $\eta = 1.7$ and the site density of the active catalyst is 2.9×10^{-9} mol/cm^2. The sticking coefficients for propane and oxygen adsorption are 0.06 and 0.0542, the temperature exponents β_i are 0.154 and 0.766, and the activation energies are 4 kcal/mol and 0 kcal/mol, respectively. The pre-exponential factor for desorption of oxygen is 8.41×10^{12}, the temperature exponent is -0.796 and the activation energy is given by

$$E_{o_2}^{des} = 0.126 T_r{}^4 - 1.849 T_r{}^3 + 9.142 T_r{}^2 - 13.253 T_r + 23.903 \quad \text{where } T_r = \frac{T}{300} \tag{6}$$

These are the same kinetic parameters as were used in our earlier work [33].

The convergence is verified with various monitors at different locations and the residuals are maintained below 10^{-6} in all the cases. The material properties vary with temperature

and appropriate mixing laws are used to calculate mixture averaged properties. The details of material properties and convergence can be found elsewhere [33].

The base case parameters are microburner length of 2 cm, channel gap size of 500 microns, wall thickness of 50 microns, wall thermal conductivity of 20 W/m/K, equivalence ratio of 0.75, heat loss coefficient of 20 W/m^2/K with free steam temperature of 300 K and inlet velocity of 1 m/s. The values of inlet velocity, wall conductivity and gap size are varied from these nominal values. Unless otherwise specified, the parameters are kept at these nominal values.

3. RESULTS AND DISCUSSIONS

The simulations are performed in two stages. Initially, the steady state solver was used to obtain the ignition temperature using natural parameter continuation for catalytic and HH propane combustion. Next, the transient behavior is studied using an unsteady solver in Fluent (with inlet temperature higher than the ignition temperature) to explore the interplay between the catalytic and homogeneous reactions.

3.1. Ignition temperature

The steady state simulations are carried to obtain the ignition temperatures for catalytic and homogeneous/heterogeneous (HH) combustion starting at cold conditions (T_{in} = 300 K). Figure 2a shows the maximum wall temperature in the microburner versus inlet temperature for the propane/air mixture for the base-case parameter values. As we increase the inlet temperature, the steady state solution of the previous point is used as an initial guess for the FLUENT solver. As seen in the figure, the reactor temperature rises steadily as the inlet temperature increases and jumps from the
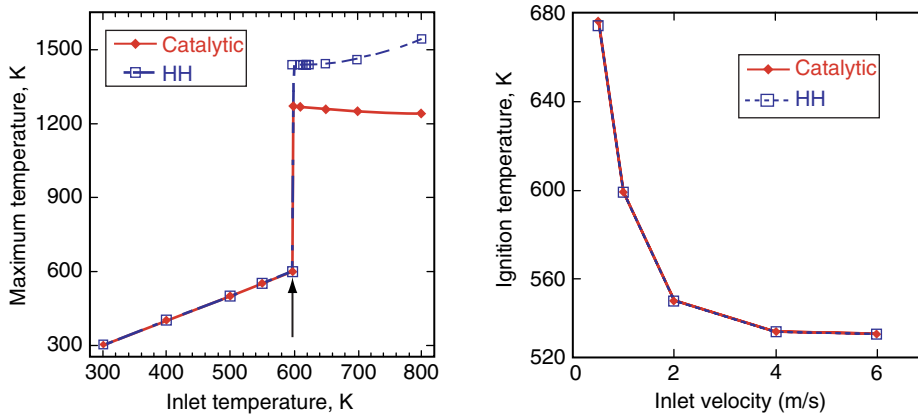

Figure 2:   a) Ignition bifurcation for catalytic and homo/heterogeneous (HH) propane combustion for base-case parameter values. The ignition temperature is 599 K for both catalytic and HH reactions. b) Ignition temperature vs inlet velocity for catalytic and HH reaction systems.

unignited to the ignited branch when the temperature is increased beyond the ignition temperature. The ignition temperature (indicated by vertical arrow in Figure 2a) is the "turning point" in the bifurcation curve, indicated by the highest inlet temperature at which the combustible mixture in the microreactor does not get ignited. The ignition temperature for catalytic and homogeneous-heterogeneous (HH) reactions is same: at 1 m/s inlet velocity, the ignition temperature is 599 K. Beyond the ignition temperature, the maximum reactor temperature for HH propane combustion increases rapidly as the inlet temperature is increased due to the higher gas temperature resulting from homogeneous reaction. Thus, the presence of homogeneous chemistry did not alter the ignition temperature in catalytic microburner, though the maximum steady state temperature increased by about 200 K. The maximum temperature in HH combustion case for propane fuel is predicted at the plane of symmetry, in the bulk gas phase. For the base case parameter values, the maximum wall temperature in HH combustion is only about 15 K higher than the catalytic case.

Similar natural parameter continuation was performed for different operating conditions to obtain the ignition temperature. The ignition temperature is plotted against the various inlet velocities in Figure 2b for catalytic and HH propane combustion. As the velocity increases, the ignition temperature decreases considerably because of higher power input at higher flow rates for the same inlet gas temperature. The ignition temperature first drops rapidly with inlet velocity; at higher velocities (beyond 4 m/s), there is only a modest decrease in the ignition temperature with inlet velocity. These results are consistent with the observations in Refs. [9, 32]. Another important observation is that the ignition temperature is the same for catalytic alone as well as HH propane combustion; the presence of homogeneous reaction did not affect the ignition temperature for catalytic microburners. This can be attributed to the significant difference in the ignition temperatures of catalytic and homogeneous chemistries. Initially, the homogeneous reaction does not ignite due to lower temperature; the temperature builds up in the reactor due to catalytic reaction, leading to subsequent ignition of homogeneous chemistry.

3.2. Transient analysis of ignition

After obtaining the ignition temperature, transient simulations were performed starting from cold-start conditions, with the microburner initially kept at uniform temperature of 300 K. In all the transient simulations, we kept the inlet temperature at 10 K greater than the actual ignition temperature for the respective cases obtained through steady state simulations (from Section 3.1).

Ignition time and steady state times are plotted for catalytic and HH propane combustion at different velocities in Figure 3. Here the ignition time defined as the time required to reach 50% propane conversion at the microburner exit, whereas the steady state time is the time required for the temperature profile in the entire geometry to reach within 1 K of the final steady-state temperature. As the velocity increases, both the ignition and the steady state times decrease due to the lower residence time and higher power input, consistent with the trends reported in literature for methane/air combustion [11]. The ignition time is nearly the same for catalytic propane combustion with and
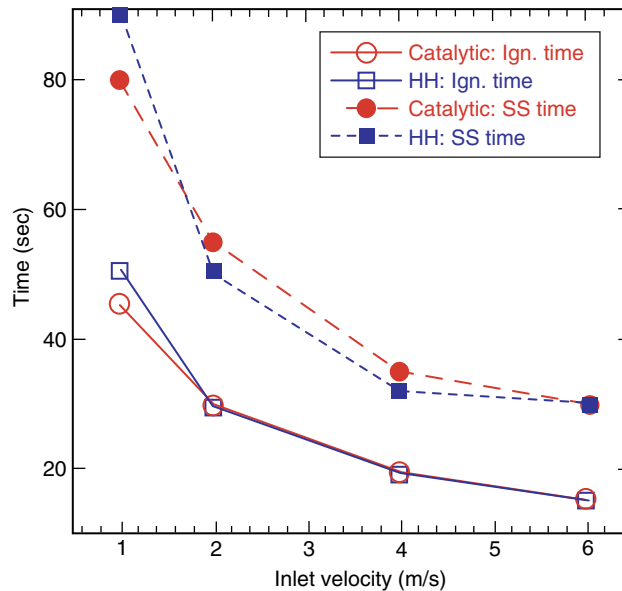
Figure 3:   Ignition and steady state times vs. inlet velocity for catalytic (circles) and HH (squares) propane combustion. Inlet temperature is kept 10 K higher than the respective ignition temperature.

without homogeneous chemistry. The difference between ignition time is less than 1 second for all conditions, except at 1 m/s; even at 1 m/s, the difference between the observed ignition time is small. These results and the ignition temperature results of Figure 2 indicate that homogeneous chemistry does not play a major role during ignition of propane combustion in catalytic microburner.

The total time to reach steady state is slightly lower for HH combustion compared to catalytic combustion for most conditions. This is because the homogeneous flame results in intense heat release in a narrow region upstream of the catalytic zone. The relative difference between steady state times of catalytic and HH combustion are governed by the time scales of catalytic and homogeneous reactions and solid-gas heat transfer. Nonetheless, since the time scale of thermal dynamics of the microburner governs the overall transients, the difference in the ignition time is small (less than 5 seconds for most cases). Interestingly, at the low velocity (1 m/s) and for moderate to high thermal conductivity materials, this trend is reversed. As seen from Figure 3, the time to reach steady state is about 10 seconds higher for HH combustion than catalytic combustion. This may be attributed to the lower maximum temperatures obtained at low flow rates and higher wall conductivities. These results are qualitatively consistent with those of Karagiannidis and Mantzaras [11] for methane ignition.

To further understand the relative contributions of the catalytic and homogeneous chemistries on ignition behavior of HH propane combustion, we plotted the reaction

rates and contribution of homogeneous reaction at various times. Catalytic reaction rate, given as $r^{cat}(a/_V)$, along the active wall and homogeneous reaction rate along the symmetry are shown in Figure 4a and Figure 4b respectively for HH propane combustion at 1 m/s inlet velocity, 0.75 equivalence ratio, 609 K inlet temperature (which is 10 K higher than the ignition temperature) and 20 W/m/K as wall thermal conductivity. Initially, the reactor is cold and rates of homogeneous and catalytic reactions are uniformly 0. As the time progresses the catalytic reaction rate increases as we approach the ignition time (50.5 seconds). Close to the ignition time, the increase in the catalytic reaction rate is very rapid. Due to increase in catalytic reaction, temperature builds-up in the reactor and when the temperature is sufficiently increased, the homogeneous reaction (r^{hom}) starts and increases as the time progresses. While the homogeneous rate increases the catalytic rate is suppressed and the reaction zone narrows down as it reaches the steady state. Similar to the catalytic rate, the homogeneous rate becomes narrow as the time progresses to steady state. At steady state, the flame is anchored at 1.25 mm from the microburner inlet. There is significant contribution from both homogeneous and catalytic chemistries, and the reaction zones overlap for the conditions considered in this paper. Karagiannidis et al. [24] reported the flame to be located significantly downstream when a leaner propane-air mixture was used. The effect of homogeneous chemistry on catalytic reaction is both a function of kinetics, as well as conditions such as catalyst loading, equivalence ratio and operating pressure.

The ratio of the net homogeneous and catalytic rates is plotted in Figure 4c to observe the effect of homogeneous chemistry on catalytic reaction. The shaded region represents the complete contribution of catalytic reaction (i.e., homogeneous contribution is less than 1%). The ignition time is 50.5 seconds; after the temperature builds up in the microburner, the homogeneous reaction begins (just above ignition time) and dominates towards the steady state by suppressing the catalytic reaction. Under these base-case conditions, the contribution of homogeneous chemistry to the net conversion at steady state is 54.5%. However, an important observation is that homogeneous chemistry does not ignite until the conversion reaches almost 98%. Similar results are obtained at other conditions as well: irrespective of the final contribution of the homogeneous chemistry, homogeneous reaction starts only after the ignition time.

Figure 5 shows the homogeneous contribution for HH propane combustion at different velocities. The respective ignition times are denoted by symbols. As discussed earlier, the ignition time decreases with increasing inlet velocity. In all cases, the homogeneous contribution is below 1% until the ignition time. The homogeneous contribution (i.e, homogeneous chemistry accounting for more than 1% of the total propane conversion) begins at 51, 31, 19.5 and 15.5 seconds for velocity of 1, 2, 4 and 6 m/s respectively, which are slightly higher than the ignition times shown by the filled solid circles. The time required to reach steady state also decreases with increasing inlet velocity: the steady state times are 90, 50, 32 and 30 seconds, respectively.

The inlet velocity has a strong effect on the percentage contribution of the homogeneous reaction at steady state conditions (compare the "flat" portions of the
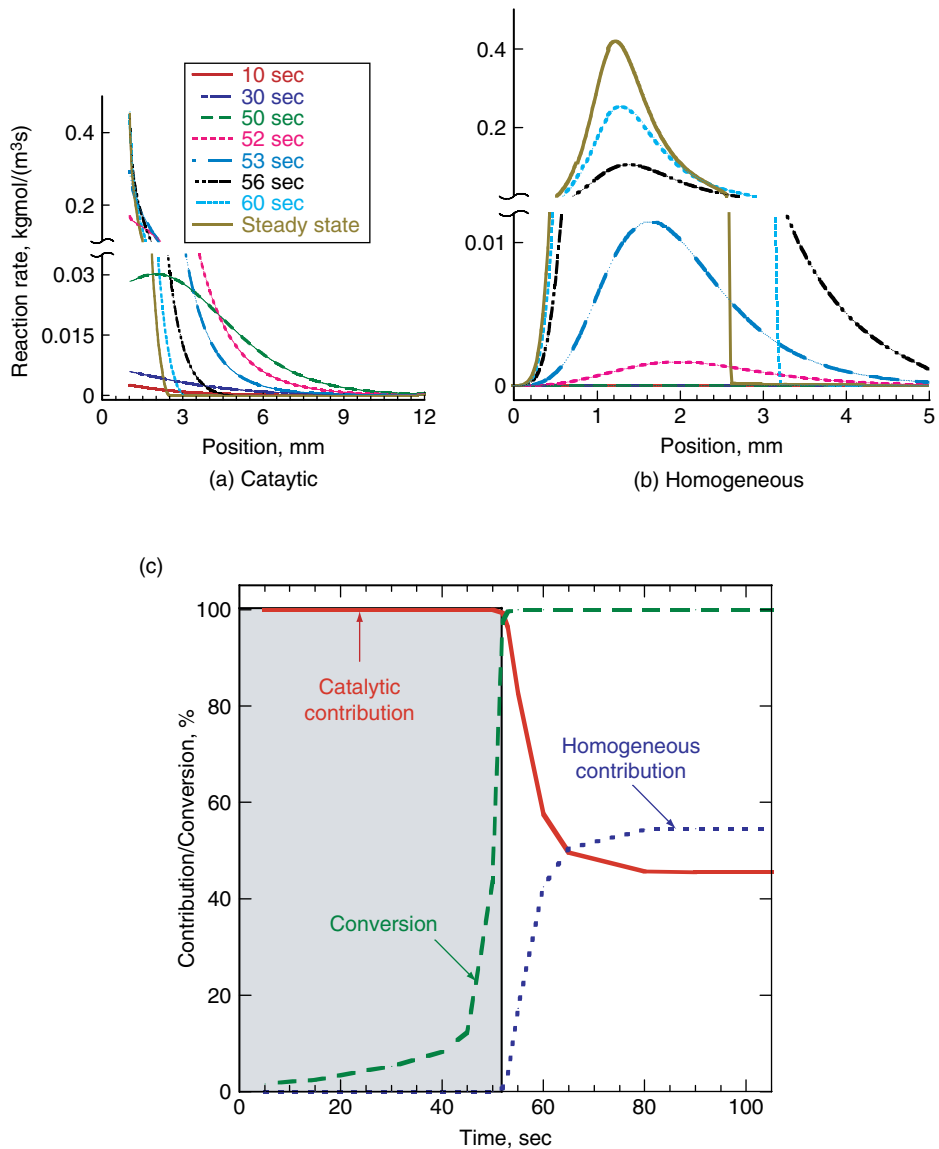
Figure 4:   Rates of (a) catalytic and (b) homogeneous combustion vs. axial position in the microburner at various times; and (c) relative contribution of catalytic and homogeneous reactions at 1 m/s and other base case parameter values. Conversion vs. time from start-up is also plotted in the same plot. The shaded region represents times where catalytic contribution is greater than 99%.
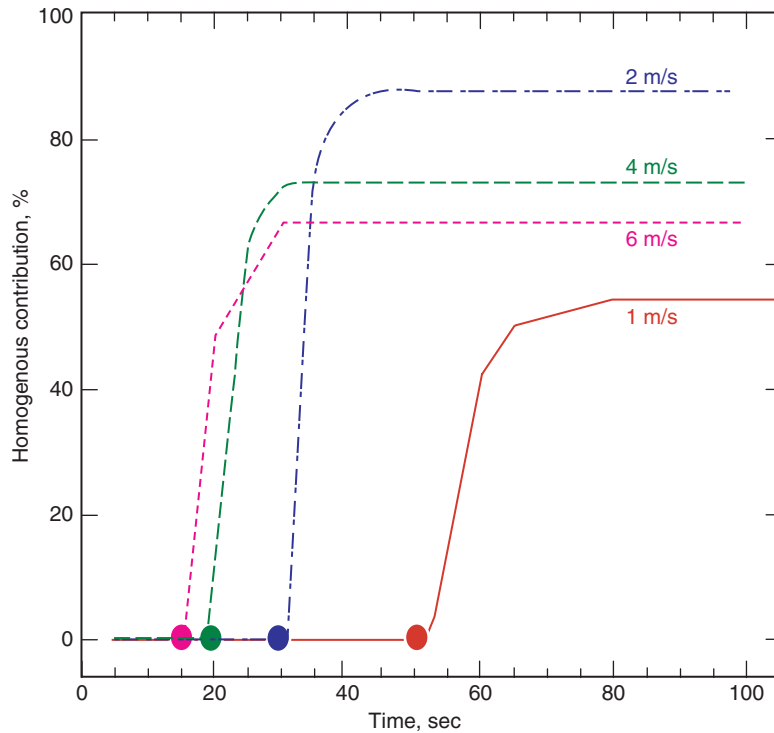
Figure 5:   Contribution of homogeneous reaction at different velocities under transient HH propane combustion. The solid circles represent the ignition times at respective velocities.

curves in Figure 5). At lower velocities, the contribution of the homogeneous reaction is low. Indeed, Stefanidis et al. [9] reported that the homogeneous contribution is minimum close to microburner extinction (which occurs at 0.4 m/s for this microburner). The homogeneous contribution initially increases as the velocity increases, due to increase in the microburner temperatures. The maximum contribution of homogeneous combustion occurs at the inlet velocity of approximately 2 m/s. When the inlet velocity is increased further, the percentage contribution of homogeneous reaction decreases due to lower residence time (consistent with [9]). In all these cases, however, homogeneous combustion does not have any role to play prior to ignition of the reacting mixture in the microburner. In other words, irrespective of the final steady-state contribution, homogeneous chemistry does not play a major role during microburner ignition for lean propane/air system. The homogeneous combustion increases the microburner temperature (see Figure 2) without any significant effect on the ignition behavior. While the increase in the wall temperature is relatively modest at

moderate and high wall conductivities, the rise in wall temperature is significant at lower wall thermal conductivity (k_w = 1 W/m/K). Therefore, based on our results for Pt-catalyzed microburners, it is advisable to operate under conditions where the homogeneous reaction is suppressed.

4. EFFECT OF WALL THERMAL CONDUCTIVITY

Wall thermal conductivity is a key parameter governing the performance of microburners since it is responsible for heat loss to the surroundings as well as for pre-heating of the incoming gaseous mixture to the ignition conditions. It is not only an important parameter that determines the stability of the system, but is also an important design parameter for minimizing the ignition time in microburners. In this section, we explore the role of thermal conductivity on the ignition behavior of HH propane combustion.

Consistent with the analysis presented in the previous section, the presence of homogeneous combustion does not affect the ignition temperatures of catalytic microburners. The corresponding ignition temperatures are found to be 550 K, 599 K and 692 K at wall thermal conductivity of 1, 20 and 100 W/m/K, respectively, for both catalytic and HH propane combustion. Since the homogeneous chemistry does not play a role on ignition temperature for HH propane combustion, these results are numerically equivalent to the ones reported in earlier work with catalytic combustion only [29, 30].

The ignition times for HH propane combustion are 10.7, 50.5 and 40.3 seconds for 1, 20 and 100 W/m/K respectively. Here we see that the lower thermal conductivity material provides significantly shorter ignition times compared to medium and high wall thermal conductivities. Similar results have been observed for catalytic propane combustion [30] as well as for HH methane combustion system [11]. The corresponding ignition times for catalytic propane combustion alone are 11.5, 45.5 and 46.5 sec. The difference in the ignition time for catalytic and HH combustion is less than 5 seconds, indicating that the homogeneous reaction chemistry does not affect the ignition time significantly.

The contribution of homogeneous reaction rate for HH propane combustion is plotted at various thermal conductivities as shown in Figure 6. At steady state, as the thermal conductivity increases the contribution of homogeneous reaction decreases or catalytic reaction increases [10, 11]. The corresponding homogeneous contribution values are 84.4%, 54.5% and 7% at 1, 20 and 100 W/m/K respectively. The large temperature gradients observed at lower wall thermal conductivities result in higher contribution of the homogeneous reaction at steady state. As the thermal conductivity is increased, the temperature becomes more uniform and the maximum temperature decreases, resulting in a lower contribution of the homogeneous reaction. Irrespective of the wall thermal conductivity, homogeneous chemistry has only a marginal contribution at the ignition time. In view of reactor safety, higher wall thermal conductivity materials are recommended to suppress the homogeneous reactions in catalytic microreactors.

Figure 7 shows the temperature profiles at symmetry (top panel) and contours of homogeneous reaction rates at different times for HH propane combustion at wall thermal conductivities of 1, 20, and 100 W/m/K respectively. Note the different scales in each plot. The temperature plots shows how the temperature profiles build up in the reactor as the time progresses to steady state with the inlet feed mixture preheated to
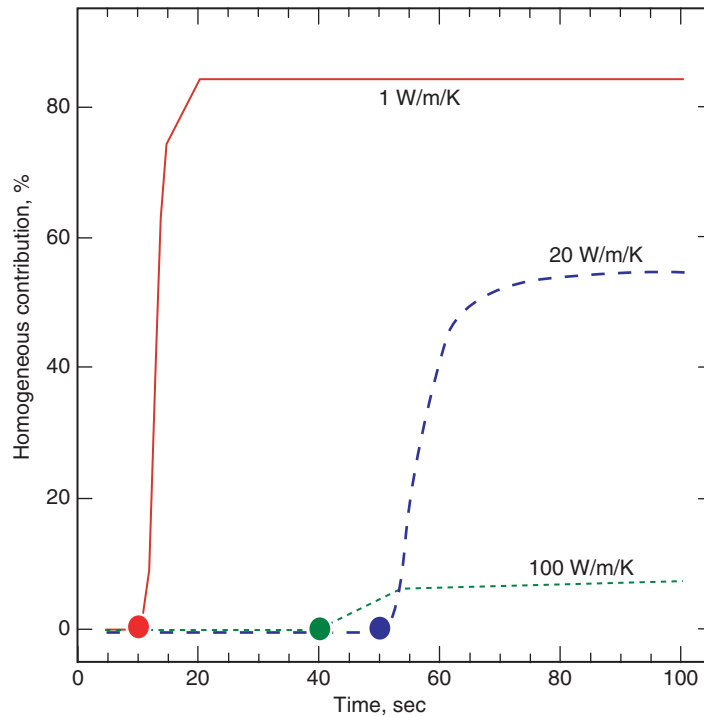
Figure 6:   Homogeneous contribution at different wall thermal conductivities in HH propane combustion. All other parameters are at their base-case values. The solid circles represents the ignition times at the respective wall thermal conductivities.

10 K above the corresponding ignition temperature. The reaction zone is narrow at lower wall thermal conductivity and it spreads as the wall thermal conductivity is increased. At the ignition time, the reaction zone is located at a distance of 4 mm in the 1 W/m/K case, whereas the ignition zone is located upstream at moderate and high wall thermal conductivities. After ignition, the microburner temperature increases rapidly to reach the steady state.

The lower panels of Figure 7 show the reaction rate contours for the homogeneous reaction in the microburner at various times for the three different values of wall thermal conductivity. The maximum reaction rate is two orders of magnitude higher for wall conductivity of 1 W/m/K than the 100 W/m/K case. The reaction zone is narrow at lower thermal conductivity and it spreads as the wall thermal conductivity increases due to increased heat recirculation through the walls. The intense heat release associated with combustion in this region is responsible for the extremely high temperatures observed in the low wall thermal conductivity microburners. The contour plots also show that for the lowest wall conductivity case, the homogeneous reaction lights off at
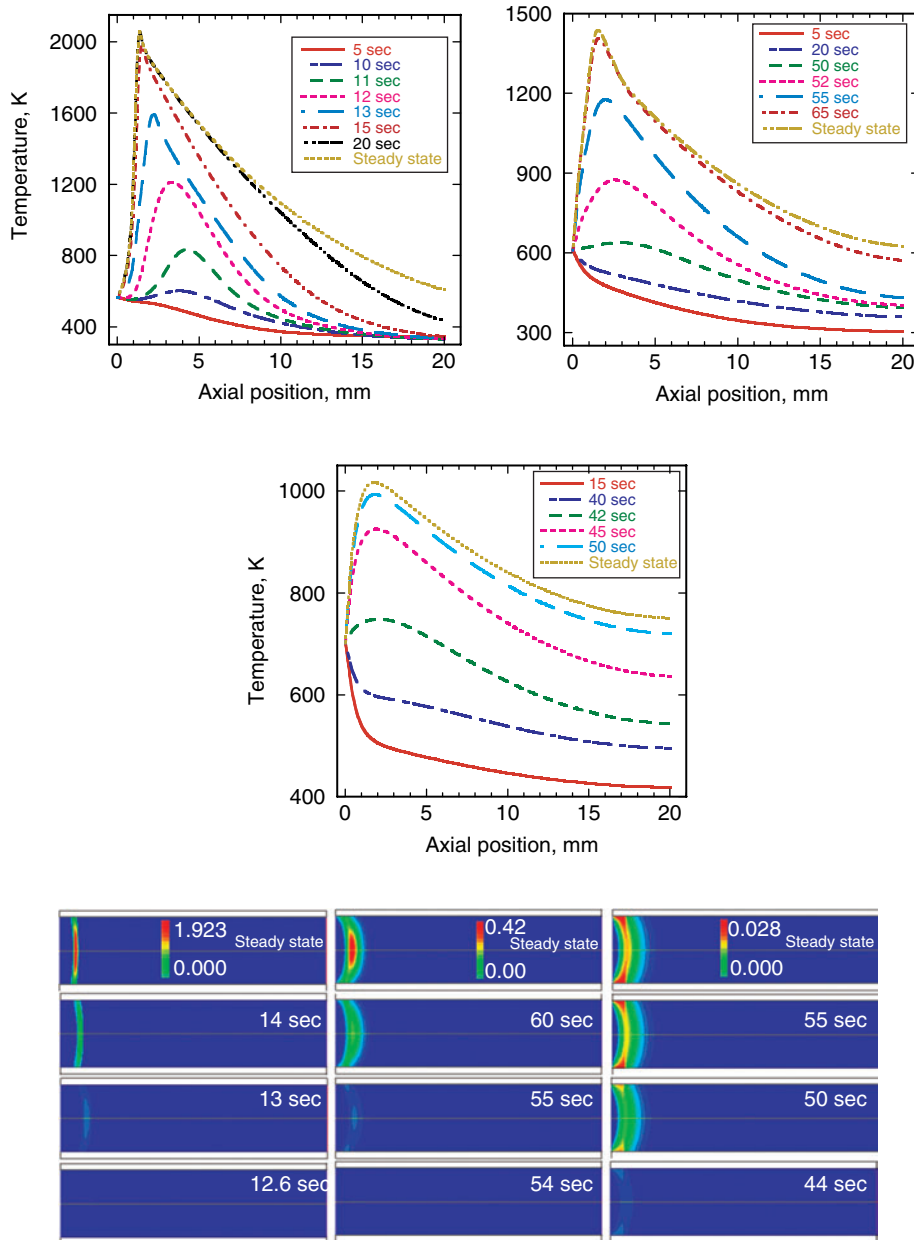
Figure 7: The effect of thermal conductivity on temperature and homogeneous reaction rate at various times for HH propane combustion (1, 20 and 100 W/m/K). Top panel: Gas temperature along the axis of symmetry of the reactor at various times; Bottom Panels: Contours of homogeneous reaction rate (in kg.mol/m^3/s) at different times. Figure is scaled by a factor of 10 in the Y-direction.

approximately 4 mm from the entrance and the reaction zone then moves upstream to its steady state location of about 1.3 mm from the entrance. On the other hand, for moderate and high wall conductivity materials, homogeneous reaction is ignited more upstream; the reaction zone does not move though the rate increases as the microburners warm up.

In summary, the contribution of homogeneous chemistry at *steady state* is high for lower wall thermal conductivity materials, while it decreases as the wall conductivity is increased. Lower wall thermal conductivity materials provides faster ignition but higher temperatures in the system. However, the presence of homogeneous chemistry has only a marginal effect on the ignition behavior of HH propane combustion for different wall materials.

5. EFFECT OF GAP SIZE

It is well known that the flame characteristics are strongly dependent on the gap size of microburners. Specifically, flames are more easily stabilized at higher gap size. Conversely, in case of HH combustion, the contribution of homogeneous chemistry typically decreases at lower gap sizes. In this section, we explore the effect of gap size on the transient behavior of HH propane combustion in the microburner.

Based on our previous work [30], the simulations were repeated for the same inlet flow rate (velocity is doubled since gap size is reduced to half for width of 1 cm in the third dimension) for a lower gap width of 250 microns. In other words, the simulations using steady state (for ignition temperature) and transient solvers are performed for an inlet velocity of 2 m/s. The ignition temperature for 250 microns gap size was found to be 600 K, which is just 1 K higher than that obtained for the nominal sized microburner. Apart from ignition temperature, the ignition time is also found to be almost the same: the ignition time increased slightly to 52.3 sec (for the 250 micron gap size) for HH combustion. The time required to reach the steady state remains the same for HH propane combustion for both gap sizes. We repeated the transient simulations catalytic combustion alone, where the same ignition behavior was observed with the 250 micron gap size. The ignition time did not change significantly, whereas the time to reach the steady state increased to 90 seconds for the 250 microns gap size (from 80 seconds at 500 microns gap size). These results are consistent with Seshadri and Kaisare [32] for mixed fuel ignition in catalytic microburners, where they showed gap size does not affect ignition behavior significantly for the same inlet flow rate used.

The Figure 8 shows the contribution of homogeneous reaction rate under transient conditions with two different channel gap sizes for HH propane combustion. At steady state, as the channel gap size increases the homogeneous contribution decreases (from 54.5% to 37%) and the catalytic reaction dominates. The elapsed time from ignition to steady state for 250 and 500 micron gap sizes are 37.7 and 39.5 sec, respectively. In order to suppress the homogeneous contribution it is advisable operate at lower gap sizes. As observed previously, homogeneous contribution at ignition time (marked by circles in the figure) is negligible.

The reaction rates are plotted for catalytic and homogeneous reactions for HH propane combustion at 250 micron gap size in Figure 9. Here we can observe the lower rates of reaction for homogeneous chemistry under transient as well as at steady state conditions as compared to the catalytic reaction rates. The reaction zone narrows down
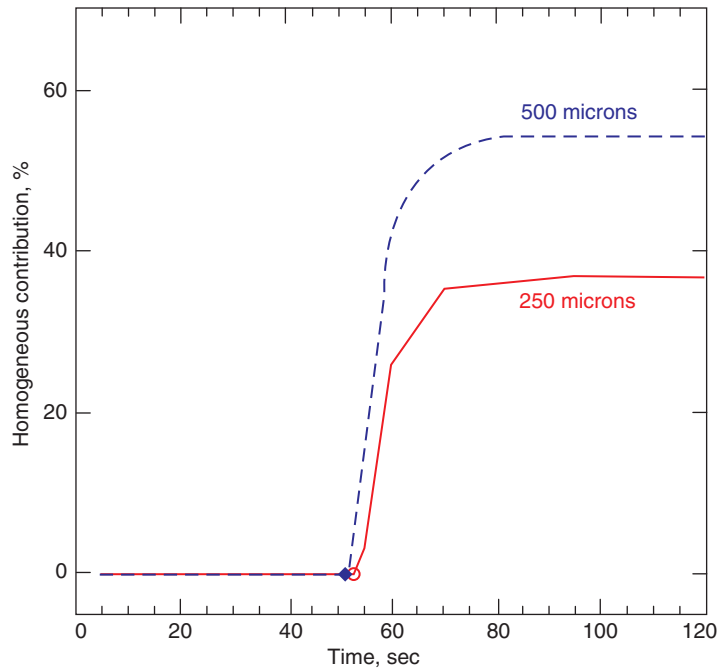
Figure 8:   Percentage contribution of the homogeneous chemistry vs. time in HH propane combustion for two different gap sizes, for constant inlet flow rate (inlet velocity of 2 m/s for 250 microns and 1 m/s for 500 microns gap size). The ignition and steady state times are almost the same for both gap sizes.
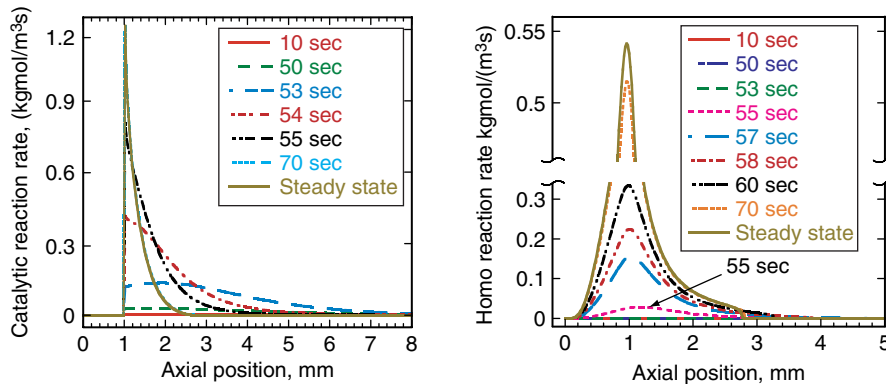

Figure 9:   Reaction rates for catalytic and homogeneous for 250 microns channel gap of HH reacting system at 2 m/s inlet velocity (which corresponds to same flow rate for 500 microns gap size). All other parameters are at their nominal values.

as the time progresses to steady state for both catalytic and homogeneous reactions. The maximum reaction rate for catalytic reaction is greater than twice the homogeneous reaction rates. The homogeneous reaction begins only after 53 seconds (recall that the ignition time is 52.3 seconds) and increases slowly towards steady state. The flame is located at a distance of ~1 mm from the inlet of the reactor for HH combustion.

6. CONCLUSIONS

The ignition behavior of catalytic microburner with and without homogeneous chemistry is explored under transient conditions, to investigate the role of homogeneous chemistry during microburner start-up. We found that the homogeneous chemistry does not affect ignition behavior significantly for propane combustion in Pt catalyzed microburner. The ignition temperature was the same for catalytic propane combustion with and without homogeneous chemistry. Transient simulations revealed that due to significant difference in the ignition temperature of catalytic and homogeneous chemistries, light-off takes sequentially. First, catalytic combustion is initiated with negligible homogeneous reaction (typically less than 1%); as the time progresses towards steady state the homogeneous reactions starts contributing, thereby suppressing the catalytic reaction.

The effect of wall thermal conductivity on ignition time scale is investigated. Again, the same ignition temperature is found for both catalytic and HH propane combustion even at different wall conductivities. Consistent with previous results, ignition and steady state times are shorter for lower wall thermal conductivity materials as expected due to the hot spot formation. Though the ignition and steady state times are lower for less conducting wall materials, the more conducting wall materials have an advantage of lower maximum temperature and lower thermal gradients. The contribution of homogeneous chemistry is negligible during the ignition phase for the entire range of wall thermal conductivity, even though significant differences were observed at steady state. Specifically, contribution of homogeneous chemistry at steady state decreased as the wall thermal conductivity was increased.

We also investigated the effect of channel gap size, where we found that the ignition behavior is same for both gap sizes at a given inlet flow rate for HH propane combustion. Same observations were obtained when the homogeneous chemistry is neglected (i.e., only catalytic combustion). The gap size had a strong influence on the steady state behavior: the contribution of homogeneous chemistry reduces as the gap size decreases. Consequently, higher steady state temperatures in HH microburners are disadvantage compared to purely catalytic microburners. It will be interesting to extend this work to study the effect of catalyst loading, inlet pressure and external heat losses on the ignition behavior of HH combustion for the future, since these factors also affect the relative contributions of homogeneous and catalytic chemistries.

The results presented in this work indicate that it is advisable to operate a microburner under conditions that suppress homogeneous chemistry to reduce the maximum temperature in the microburner. Alternatively, we suggest that suppression or promotion of homogeneous chemistry be determined purely by steady state stability considerations and not through the transient ignition characteristics.

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