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Numerical investigation of the effects of surface recombination and initiation for laminar hydrogen flames at atmospheric pressure

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A numerical investigation into specific surface effects in flame propagation of lean and rich laminar hydrogen flames at different wall boundary conditions and fuel/air ratios has been performed by means of two-dimensional simulations.

The use of hydrogen as fuel in engines and other power devices is promising for a decrease of pollution because the product of the combustion of hydrogen is water. However, the wide application of the fuel is above all retarded with large consumption of energy as well as with high flammability of hydrogen–air mixtures (HAMs). The combustion of the mixtures often transforms to detonation regime over a wide range of hydrogen concentrations. Information on the influence of wall properties on flame propagation in HAMs is of importance to provide safe conditions of transport and 'mobile' storage of hydrogen.

Note that contemporary data on wall effects in hydrogen combustion at 1 atm refer to conditions of a burner.[1,2] Under these conditions, calculations showed that, for atmospheric pressure of HAM and a wall temperature of 600 K, the catalytic wall retards homogeneous combustion of hydrogen more than the recombination wall.

The aim of this work was to study surface effects on the velocities of flame front at atmospheric pressure and wall temperature (300 K) at different wall boundary conditions, reactor diameters, and fuel-to-air ratios. A surface reaction of chain initiation was also taken into account, as well as specific features of the branched-chain mechanism of hydrogen oxidation.

The reduced kinetic mechanism of hydrogen oxidation at atmospheric pressure can be represented as follows:[3]

$H_2 + O_2 \rightarrow 2OH$	(0)	$k_0 = 1.92\times10^{14}e^{-21890/T}$ cm^3 mol s (ref. 4)
$OH + H_2 \rightarrow H_2O + H$	(1)	$k_1 = 4.63\times10^{12}e^{-2100/T}$ cm^3 mol^{-1} s^{-1} (ref. 5)
$H + O_2 \rightarrow OH + O$	(2)	$k_2 = 1.99\times10^{14}e^{-8460/T}$ cm^3 mol^{-1} s^{-1} (ref. 6)
$O + H_2 \rightarrow OH + H$	(3)	$k_3 = 1.88\times10^{14}e^{-6897/T}$ cm^3 mol^{-1} s^{-1} (ref. 7)
$H + O_2 + M \rightarrow HO_2 + M$	(4)	$k_4 = 6.47\times10^{15}(T/298)^{-0.8}$ cm^6 mol^{-2} s^{-1} (ref. 8)
$H + HO_2 \rightarrow 2OH$	(5)	$k_5 = 1.69\times10^{14}e^{-440/T}$ cm^3 mol^{-1} s^{-1} (ref. 6)
$H_2 + HO_2 \rightarrow H_2O_2 + H$	(6)	$k_6 = 3.00\times10^{13}e^{-14400/T}$ cm^3 mol^{-1} s^{-1} (ref. 6)
$OH + O \rightarrow H + O_2$	(7)	$k_7 = 9.29\times10^{12}$ cm^3 mol^{-1} s^{-1} (ref. 9)
$O + HO_2 \rightarrow OH + O_2$	(8)	$k_8 = 3.25\times10^{13}$ cm^3 mol^{-1} s^{-1} (ref. 6)
$OH + HO_2 \rightarrow H_2O + O_2$	(9)	$k_9 = 2.89\times10^{13}e^{250/T}$ cm^3 mol^{-1} s^{-1} (ref. 8)
$2HO_2 \rightarrow H_2O_2 + O_2$	(10)	$k_{10} = 2.00\times10^{12}$ cm^3 mol s (ref. 10)
$H_2O_2 + M \rightarrow 2OH + M$	(11)	$k_{11} = 1.3\times10^{17}$ e$^{-22750/T}$ cm^6 mol^{-2} s^{-1} (ref. 10)
$H + H + M \rightarrow H_2 + M$	(12)	$k_{12} = 2.2\times10^{15}$ cm^6 mol^{-2} s^{-1} (ref. 8)

As is known, the stationary propagation of a reaction wave should be considered with no regard for a chain origination reaction[11]. A two-dimensional planar problem was examined. Characteristic scales of the process were chosen as follows: $t_0 = 1/(k_1^0[H_2]_0)$, $x_0 = (D_3/k_1^0[H_2]_0)^{1/2}$, $U_0 = x_0/t_0 = (D_3k_1^0[H_2]_0)^{1/2}$ (the scales of time, length and velocity, respectively; D_3 is the diffusivity of H_2). We determine the dimensionless variables and parameters $\tau = t/t_0$, $\xi = x_0$, $\eta = y/y_0$, $\varpi = U/U_0$, Y_i = [concentration of the ith component]/$[H_2]_0$, $\delta_i = D_i/D_3$ (D_i is the diffusivity of the ith component). The velocity and coordinates of the propagating flame front were designated in terms of the diffusivity of H_2 (D_3): $\varpi = U/(D_3k_1^0[H_2]_0)^{1/2}$, $\xi = x/(D_3/k_1^0[H_2]_0)^{1/2}$, $\eta = y/(D_3/k_1^0[H_2]_0)^{1/2}$. Here, U, x and y are corresponding dimensional values, k_1^0 is the preexponential factor of reaction (1). Diffusivities (D_i/D_3, $i = 0$–6) δ_0, δ_1, δ_2, $\delta_3 = 1$, δ_4, δ_5, δ_6 in H_2 + air mixture refer to OH, O, H, H_2, O_2, HO_2 and H_2O_2, respectively. The set of reaction-diffusion equations for the above reaction mechanism takes the form (m, $n = 0$–6: refer to reacting particles OH, O, H, H_2, O_2, HO_2, H_2O_2):

$$\begin{aligned}\partial Y_i/\partial\tau &= \delta_i(\partial^2Y_i/\partial\xi^2 + \partial^2Y_i/\partial\eta^2) + \sum_i\sum_{m\neq i,n}K_nY_mY_n - \sum_i\sum_{m=i,n}K_nY_mY_n \\ \partial T/\partial\tau &= \delta_7(\partial^2T/\partial\xi^2 + \partial^2T/\partial\eta^2) + 1/(C_p\rho)\sum_i\sum_{m,n}Q_iK_iY_mY_n\end{aligned} \quad (1)$$

where m, $n = 0$–6, $i = 0$–12, $K_i = k_i/k_1^0$ for bimolecular reactions, $K_i = k_iM/k_1^0$ for termolecular reactions, $M = 760\times10^{19}/T$. The rate of heat release in reaction chain is given by the latter equation of set (1). Here, C_p is the mass-weighted mean specific heat capacity at constant pressure, cal g^{-1} K^{-1};[12] $\delta_7 \approx \delta_3$ is thermal diffusivity of the mixture, T is temperature (K), ρ is the density of the mixture, g cm^{-3}.[12] Specific heats Q_i and diffusivities were taken from refs. 13, 14; f is the mole fraction of an initial component.

The reaction-diffusion equation for O atoms as an example is given below:

$$\partial Y_1/\partial\tau = \delta_1(\partial^2Y_1/\partial\xi^2 + \partial^2Y_1/\partial\eta^2) + K_2Y_2Y_4 - K_3Y_1Y_3 - K_7Y_0Y_1 - K_8Y_1Y_5.$$

The solutions of set (1) fulfill the following boundary conditions for flame propagation from the right to the left (l is the distance between the reactor axis and the reactor wall; symmetry conditions are specified along the axis):

$$\begin{aligned}&Y_i(\xi,\eta) \rightarrow 0\ (i \neq 3, 4),\ T(\xi,\eta) \rightarrow 300\ \text{K},\ \xi \rightarrow \pm\infty; \\ &Y_3(\xi,\eta) \rightarrow f_{H_2},\ Y_4(\xi,\eta) \rightarrow f_{O_2},\ \xi \rightarrow -\infty; \\ &\partial Y_3(\xi,\eta)/\partial\eta \rightarrow 0,\ \partial Y_3(\xi,\eta)/\partial\eta \rightarrow 0,\ \xi \rightarrow +\infty; \\ &Y_i(\xi,l) = 0\ (i \neq 3, 4)\ \text{or}\ [\partial Y_i(\xi,\eta)/\partial\eta]_l = 0; \\ &[\partial Y_i(\xi,\eta)/\partial\eta]_l = 0\ (i = 3, 4);\ T(\xi,l) = 300\ \text{K}.\end{aligned} \quad (2)$$

When solving set (1), the initial fronts of starting components Y_3 [H_2] and Y_4 [O_2] at the time origin over coordinate were defined according to the composition of HAM. The shapes of the fronts were approximated with $1/2 - 1/\pi[\text{arctg}(b_i\xi)]$ ($i = 3, 4$), the initial fronts of H atoms and T were specified as $Y_i = a_i\exp[-b_i(\xi + \eta)^2]$, where a_i and b_i ($i = 2, 7$) were scale coefficients.[15] These initial shapes correspond essentially to initiation of flame propagation with an external source, as in a number of experiments.[16,17] The

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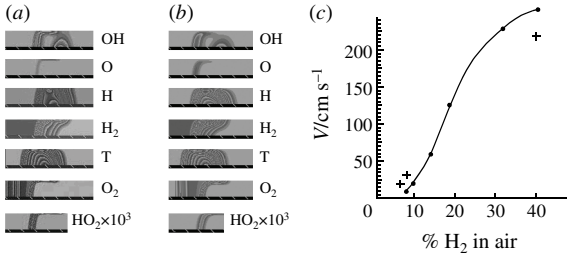

Figure 1 Calculated profiles of chemical components and temperature in a stationary flame front of hydrogen (40%)–air mixture for types 1 and 2 of boundary conditions (d = 1 cm). The top of each frame is the wall of the reactor; the bottom is the axis of the reactor. The flame front moves from the right to the left. P = 1 atm, wall temperature is 300 K. (*a*) Fluxes of H, O atoms and OH, HO_2 radicals at the wall are equal to zero. (*b*) Concentrations of H, O atoms and OH, HO_2 radicals at the wall are equal to zero. (*c*) Laminar burning velocity of HAMs at room temperature and atmospheric pressure (circles[19,20]), calculated in this work for type 1 of boundary conditions (crosses).

chosen shapes of Y_i had no influence on the steady state velocity of flame propagation. The two-step implicit scheme provided the second order of approximation of system (1) over both spatial and time variables.[18]

The calculated profiles of chemical components and temperature in a stationary flame front of 40% H_2 in HAM for boundary conditions of the types 1 and 2 are shown in Figure 1. In Figure 1 the bloom of grey colour indicates spatial distributions of concentrations of Y_i, the grey borders correspond to fixed concentrations, and a darker grey colour corresponds to greater values of concentrations. As is seen in Figure 1, the profile of OH radicals exhibits two maxima, the result is somewhat similar to one obtained numerically[19] for rich HAMs, and it probably has the similar explanation. The top of each frame is the wall of the reactor; the bottom is the axis of the reactor. The use of two types of boundary conditions allowed qualitative establishing the role of surface termination of active centres for different diameters of reactors, as well as for different compositions of HAMs. A relation of the velocity for completely inert surface ($[\partial Y_i(\xi, \eta)/\partial\eta]_l = 0$, $i \neq 3, 4$, type 2 of boundary conditions) to the velocity for terminating surface [$Y_i(\xi, l) = 0$, $i \neq 3, 4$, type 1 of boundary conditions] was the measure of a wall effect $V_{(\text{flux} = 0)}/V_{(\text{conc} = 0)}$. The calculations showed [Figure 1(*c*)] that the mechanism accepted is valid due to the fact that calculated flame velocities for terminating surface are in good qualitative agreement with published data.[18,19]

The calculated dependence of $V_{(\text{flux} = 0)}/V_{(\text{conc} = 0)}$ on both H_2 concentration in HAMs and reactor diameter is shown in Figure 2(*a*). The influence of wall chain termination at 1 atm increases with decreasing both diameter and H_2 concentration. Figure 2(*b*) shows that the calculated lower concentration limit makes up about 5% H_2; it is in agreement with published data[18,19] and also suggests the validity of the mechanism accepted. It is seen in Figure 2(*b*) that the influence of surface is most pronounced only in the immediate vicinity of the lower concentration limit; its dependence on the content of H_2 is rather sharp. Therefore, even a flame arrester composed of pipes 1 cm in diameter treated with the substance that effectively terminates reaction chains (*e.g.*, a metal oxide[20]) will not be efficient if the content of H_2 in HAM exceeds 6%. The narrower tubes will maintain stronger resistance to gas flow. It means that the use of small active chemical additives (inhibitors) to prevent explosions of HAMs is considerably more promising.[21]

The influence of the rate of surface chain initiation on the velocity of flame propagation was also investigated. It was expected that the surface evolves H atoms; their flux into the reactor volume was assumed to make up $\partial Y_2(\xi, \eta)/\partial\eta)_l = k_0 Y_1 Y_2/k_1^0$. The calculations showed that chain initiation for the

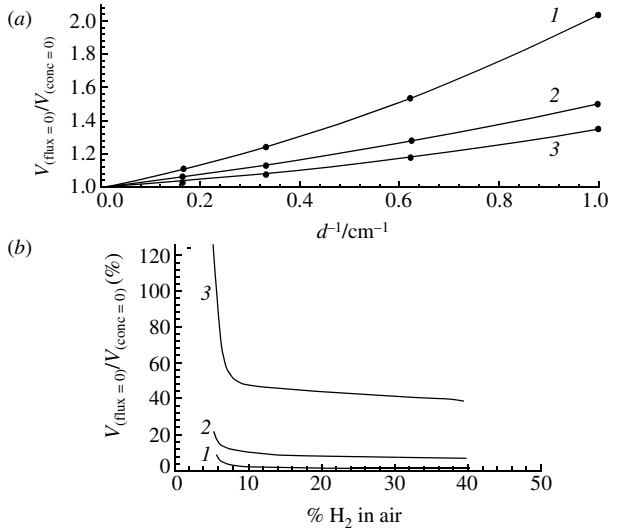

Figure 2 (*a*) Calculated dependence of the relation of the velocity for completely inert surface $V_{(\text{flux} = 0)}$ to the velocity for terminating surface $V_{(\text{conc} = 0)}$ both on H_2 concentration in mixtures and reactor diameter [curves are fitted, (*1*) 6% H_2, (*2*) 8% H_2, (*3*) 40% H_2 in air]; (*b*) Calculated dependence of the percent of the contribution of surface termination on the concentration of H_2 in air from a plot Figure 2(*a*) for three diameters of the reactor (curves are fitted; vertical line designates the lower concentration limit): (*1*) 10 cm, (*2*) 5 cm, (*3*) 1 cm.

mixture of 40% H_2 in HAM takes effect only if the rate constant of surface initiation amounts to the value of homogeneous initiation k_0 taken at 1800 K; in other words, to accelerate flame propagation, the surface should exhibit catalytic properties.

It was speculated[22] that chain branching does not occur in H_2 oxidation at 1 atm. It was of interest to verify whether fast chain initiation could provide stationary flame propagation in the absence of chain branching at given rate constants. For this purpose, it was assumed that the number of free valences does not change in branching step (2); *i.e.*, the reactions of O atoms formed in step (2) were not taken into consideration in further calculations. Under this assumption, only a trivial solution to set (1) was attained. It means that, for the chemical mechanism accepted, the rate of heat release is insufficient to sustain a combustion wave if chain branching does not occur. A wave solution does not exist even at the value of the rate constant of surface initiation k_0, which influences the flame velocity if chain branching is taken into account (see above). Therefore, the calculations performed point to the importance of inclusion of a chain branching step for the description of hydrogen combustion at higher pressures.[3]

By this means it has been shown that the influence of surface chain termination on the flame velocity becomes significant in the vicinity of the lower concentration limit; the surface chain initiation does not affect the flame velocity. Flame propagation does not occur if a chain mechanism without branching even with high rates of chain initiation is used.

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