

IGNITION OF HYDROGEN–AIR MIXTURE IN THE FLOW OVER HOT CATALYTIC SURFACE

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Introduction

Heterogeneous ignition of hydrogen at catalytic surfaces (metal oxides, etc.) is, on the one hand, the potential reason for accidental explosions in industry and atomic power plants and, on the other hand, a promising approach for advanced ignition and flame-holding systems in aerospace applications. One of basic specific features of catalytic ignition and combustion is considerable widening of fuel-lean flammability limit [1]. As an advantage, it can be particularly used for improving pollutant emission indices of aircraft combustors and industrial power plants.

Contrary to homogeneous chemistry of hydrogen oxidation in air, heterogeneous chemistry is still a hot subject of fundamental studies. Heterogeneous chemistry of hydrogen oxidation is more or less well developed only for noble-metal catalysts. For better understanding homogeneous–heterogeneous mechanisms of hydrogen ignition at catalytic surfaces, further studies for simple flow configurations like stagnation and tubular flow conditions are required. Such studies help to identify the set of governing parameters determining the conditions of hydrogen ignition.

The objective of this work is to develop a two-dimensional (2D) computer code for detailed studies of homogeneous–heterogeneous hydrogen ignition in the flow over catalytic surfaces.

Problem Formulation

Figure 1 shows the schematic of the flow of hydrogen–air mixture over a heated constant-temperature catalytic plate of length L and negligibly small thickness. The plate is assumed to be covered with Platinum (Pt) catalyst with constant site density Γ . Cold viscous flow interaction with the hot plate results in the development of laminar thermal and

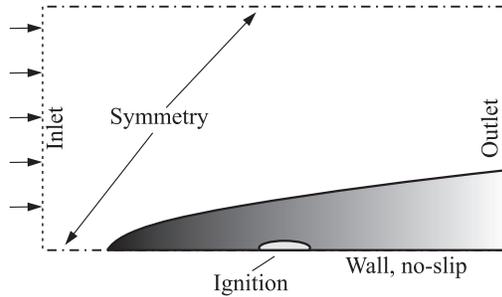


Figure 1 Schematic of the flow

dynamic boundary layers growing downstream from the plate edge. Due to gas heating in the boundary layer and availability of active sites at the catalytic surface, the gas can ignite at the plate at a certain distance from the edge which will be referred to as the ignition distance.

The task to be solved is to determine the ignition distance as a function of plate temperature T_w for the flow of stoichiometric hydrogen–air mixture at normal initial conditions. Of particular interest is the effect of heterogeneous reactions on the ignition distance.

The governing equations for transient, laminar, 2D reactive flow are formulated as follows:

Continuity equation:

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u}{\partial x} + \frac{\partial \rho v}{\partial y} = 0.$$

Momentum conservation equations:

$$\begin{aligned} \frac{\partial \rho u}{\partial t} + \frac{\partial \rho u u}{\partial x} + \frac{\partial \rho u v}{\partial y} &= -\frac{\partial P}{\partial x} + \tau_1; \\ \frac{\partial \rho v}{\partial t} + \frac{\partial \rho v u}{\partial x} + \frac{\partial \rho v v}{\partial y} &= -\frac{\partial P}{\partial y} + \tau_2 \end{aligned}$$

where τ_1 and τ_2 are the stress tensors:

$$\begin{aligned}\tau_1 &= \frac{\partial}{\partial x} \left[2\mu \frac{\partial u}{\partial x} - \frac{2}{3}\mu \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) \right] + \frac{\partial}{\partial y} \left[\mu \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \right]; \\ \tau_2 &= \frac{\partial}{\partial x} \left[\mu \left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) \right] + \frac{\partial}{\partial y} \left[2\mu \frac{\partial v}{\partial y} - \frac{2}{3}\mu \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) \right].\end{aligned}$$

Energy conservation equation:

$$\frac{\partial \rho h}{\partial t} + \frac{\partial \rho h u}{\partial x} + \frac{\partial \rho h v}{\partial y} = \nabla \left(\lambda \nabla T - \rho \sum_{i=1}^{N_e} h_i V_i Y_i \right) + \sum_{i=1}^{N_e} h_i w_i W.$$

Continuity equations for gas-phase species:

$$\frac{\partial \rho Y_i}{\partial t} + \frac{\partial \rho Y_i u}{\partial x} + \frac{\partial \rho Y_i v}{\partial y} = -\nabla(\rho Y_i V_i) - w_i W_i, \quad i = \overline{1, N_e - 1}.$$

Equation for nitrogen mass fraction:

$$Y_{N_2} = 1 - \sum_{i=1}^{N_e-1} Y_i.$$

Equations for surface species:

$$\frac{\partial \theta_m}{\partial t} = \sigma_m \frac{\dot{s}_m}{\Gamma}, \quad m = \overline{1, N_s - 1}; \quad \theta_{N_s} = 1 - \sum_{m=1}^{N_s} \theta_m.$$

Equation for species diffusion velocities:

$$V_i = -\frac{D_i}{X_i} \nabla X_i; \quad D_i = \frac{1 - Y_i}{\sum_{k \neq i}^N X_k / D_{i,k}}.$$

Ideal gas equations of state:

$$P = \frac{\rho R T}{W}; \quad h_i = h_i^0(T_0) + \int_{T_0}^T c_{p,i} dT.$$

In the above equations, x and y are the spatial Cartesian coordinates; u and v are the corresponding velocity components; λ and μ are the molecular thermal conductivity and viscosity; P is the pressure; ρ is the density; T is the temperature; h is the mixture enthalpy; Y_i , w_i , W_i , and h_i are the mass fraction, production rate, molecular mass, and enthalpy of the i th gas-phase species, respectively; N_e is the total number of gas-phase species; $V_{i,x}$, $V_{i,y}$, and D_i are the x and y components of the i th gas-phase species diffusion velocity and the corresponding diffusion coefficient; θ_m , σ_m , and \dot{s}_m are the coverage, number of occupied surface sites, and molar production rate of the m th surface species, respectively; N_s is the total number of surface species; $T_0 = 298$ K is the standard temperature; R is the universal gas constant; and h_i^0 and c_{pi} are the enthalpy of formation and specific heat of the i th gas-phase species, respectively.

For calculating transport coefficients for the multicomponent mixture, the following relationships were used [2]:

Mixture viscosity:

$$\mu = \sum_{i=1}^{N_e} \frac{\mu_i X_i}{\sum_{j=1}^{N_e} \varphi_{i,j} X_j};$$

$$\mu_i = 26.67 \cdot 10^{-7} \frac{\sqrt{W_i T}}{\sigma_i^2} [\text{Pa} \cdot \text{s}];$$

$$\varphi_{i,j} = \frac{1}{\sqrt{8}} \left(1 + \left(\frac{W_j}{W_i} \right)^{0.25} \left(\frac{\mu_i}{\mu_j} \right)^{0.5} \right)^2 \left(1 + \frac{W_i}{W_j} \right)^{-0.5}$$

where μ_i and X_i are the i th species viscosity and molar concentration, and σ_i is the molecule “radius” in the “rigid sphere” model.

Mixture thermal conductivity:

$$\lambda = \sum_{i=1}^{N_e} \frac{\lambda_i X_i}{\sum_{j=1}^{N_e} \varphi_{i,j} X_j};$$

$$\lambda_i = \mu_i \frac{R}{W_i} \left(\frac{c_{pi}}{R} + 1.25 \right) [\text{W}/(\text{m} \cdot \text{K})].$$

For determining reaction rates entering species continuity and energy equations, the reaction mechanism of gas-phase hydrogen oxidation reported in [3] and the mechanism of heterogeneous reactions at Pt catalyst reported in [4] were used. The gas-phase mechanism contains 21 reversible reactions with 8 species excluding nitrogen. The heterogeneous mechanism is based on 16 reactions between 6 gas-phase and 4 surface species excluding Pt. The gas-phase species adsorption rates are described in terms of sticking coefficient γ_i . The sticking coefficient determines the probability of the event that collision of the i th species with the catalytic surface will result in its adsorption at the surface. To convert the sticking coefficient to the Arrhenius kinetic rate constant, the following relation is used [5]:

$$k_{\text{ads},i} = \frac{\gamma_i}{\Gamma^m} \sqrt{\frac{RT}{2\pi W_i}}$$

where m is the sum of all stoichiometric coefficients of surface reactants.

The set of equations is supplemented with initial and boundary conditions. As for initial conditions for the computational domain shown in Fig. 1, the uniform flow of pure air in x -direction over the plate is adopted with air temperature and pressure equal to T_{in} and p_{in} . At the inlet, a uniform flow of hydrogen–air mixture with velocity vector $(U_{\text{in}}, 0)$ at temperature T_{in} is assumed. At the outlet, von Neumann boundary conditions for all gas-phase variables are used. Standard symmetry boundary conditions for all flow variables are used at the symmetry planes. At the plate surface, no-slip ($u = v = 0$) boundary conditions for both velocity components, and constant wall temperature $T_w = \text{const}$ are adopted. In addition, the following boundary conditions for gas-phase species at the catalytic plate surface are used:

$$(\rho Y_i V_{i,y})_+ + \dot{s}_i W_i = 0$$

where \dot{s}_i is the net molar production rate of the i th gas-phase species via adsorption–desorption heterogeneous reactions, and subscript (+) relates to gas-phase properties at the plate surface.

Solution Algorithm

The governing equations for the gas-phase variables were solved using the Explicit Treated Boundary Flux Corrected Transition (ETB-FCT)

method. Chemical source terms were calculated implicitly using the method of local linearization [6]. A time-splitting approach for calculating gas-phase flow variables, as well as gas-phase and heterogeneous chemical kinetics was applied in the computational algorithm.

Results and Discussion

Figures 2 and 3 demonstrate the performances of gas-phase and combined homogeneous–heterogeneous kinetic mechanisms applied herein.

Shown in Fig. 2 is the comparison of predicted and measured ignition delay times for the stoichiometric hydrogen–air mixture at different

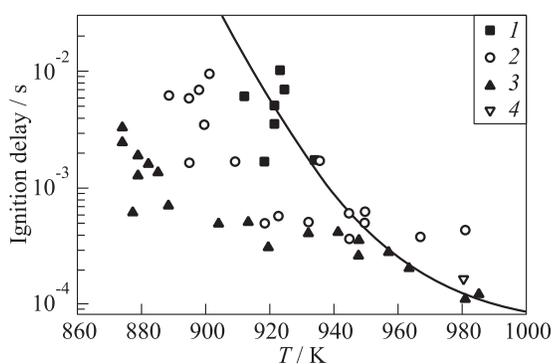


Figure 2 Comparison of predicted (curve) and measured (symbols: 1 — [7]; 2 — [8]; 3 — [9]; and 4 — [10]) ignition delay times for homogeneous stoichiometric hydrogen–air mixture at 1 bar

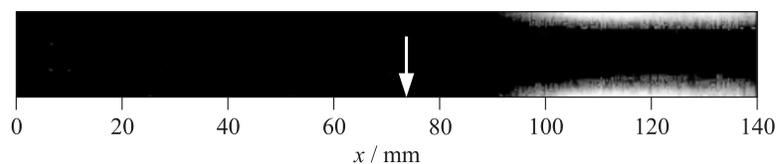


Figure 3 Measured OH concentrations (luminescence at $x > 90$ mm [11]) and predicted homogeneous–heterogeneous ignition distance (shown by arrow) in the flow of fuel-lean hydrogen–air mixture in channel reactor with Pt-covered ceramic walls

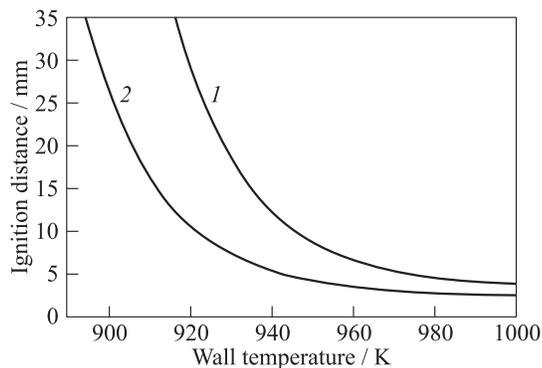


Figure 4 Ignition distances of the stoichiometric hydrogen–air mixture at the Pt-covered plate vs. plate temperature predicted with solely homogeneous (1) and homogeneous–heterogeneous (2) reaction mechanism

temperatures of interest (below 1000 K) at atmospheric pressure. From now on, the ignition delay is defined as the time taken for the temperature to attain the inflection point at the temperature curve. The results of measurements were taken from [7–10].

Figure 3 compares predicted and measured [11] ignition distances for the flow of fuel-lean hydrogen–air mixture with the equivalence ratio 0.32 (flow velocity is 2 m/s, flow Reynolds number 1370, and mixture temperature 312 K) in the straight channel reactor 7 mm wide with Pt-covered flat ceramic walls. In the calculation, the wall surface temperature distribution in the streamwise direction obtained by thermocouples was used. The site density was taken equal $\Gamma = 2.72 \cdot 10^{-9}$ mol/cm² [5]. In general, the agreement of predicted and measured ignition delay times and distances can be treated as satisfactory.

Figure 4 shows predicted ignition distances in the flow configuration of Fig. 1 with solely homogeneous (curve 1) and with homogeneous–heterogeneous (curve 2) reaction kinetics in the flow of stoichiometric hydrogen–air mixture over the Pt-covered plate 35 mm long heated to different temperatures. The flow parameters are $U_{\text{in}} = 5$ m/s, $T_{\text{in}} = 298$ K, and $p_{\text{in}} = 0.1$ MPa. The site density in the calculations with heterogeneous reaction kinetics was taken equal to

$\Gamma = 2.72 \cdot 10^{-9}$ mol/cm² [5]. Clearly, the catalytic effect of the plate surface manifests itself in the consistently decreasing ignition distance (and time). For example, at plate temperature $T_w = 920$ K, the ignition distance at the catalytic surface decreases by a factor of 3: from 30 to 10 mm. Moreover, a hot catalytic plate can ensure ignition of hydrogen–air mixture under conditions when ignition at a hot noncatalytic plate of the same length is impossible. For example, a noncatalytic plate 35 mm long considered herein cannot ignite the stoichiometric hydrogen–air mixture at $T_w < 917$ K whereas a catalytic plate of the same length ignites the mixture at $T_w > 894$ K. The effect of catalytic surface on the ignition distance is visible even at $T_w = 1000$ K despite very low gas-phase ignition delays in homogeneous temperature conditions (see Fig. 2).

Note that ignition at the plate surface in the flow configuration of Fig. 1 is affected by the adopted initial conditions implying displacement of pure air flow by the flow of reactive hydrogen–air mixture. In addition to mixing and viscous effects in the vicinity to plate tip, this implies that oxygen atoms are already adsorbed at the catalytic surface which stimulates heterogeneous chemistry.

Concluding Remarks

Catalytic ignition of hydrogen–air mixtures over a Platinum-covered plate has been studied computationally using a detailed homogeneous–heterogeneous kinetic mechanism. Heterogeneous reactions on the catalytic plate surface were shown to consistently decrease the ignition distance and time as compared with the noncatalytic plate surface. However, the effect of heterogeneous reactions on hydrogen ignition depends on the initial conditions, in particular, on the concentration of atomic oxygen preliminarily adsorbed by the surface. In view of it, further studies are required to elucidate the influence of various flow-control measures affecting the surface properties governing the ignition distance.

Acknowledgments

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