Effect of Hydrogen addition on ignition of methanehydrogen-air mixtures over a hot surface

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1 Introduction

The study of ignition of flammable mixtures is of particular importance from an industrial perspective. It enables the engineers to develop a safer operating environment and also reduce accidental fires. Combustion characteristics related to ignition such as flammability limits[1], ignition energy [2-9], and ignition threshold for various heating sources have been studied in last few decades.

Methane hydrogen ignition has been studied with a focus on the emissions and combustion efficiency in spark ignition processes[10-13]. Cheng et.al [14] experimentally determined the induction time and ignition limits for 11 different mixtures of methane-hydrogen-oxygen. They also proposed a formula for induction time which consists of a term for the ratio of methane-hydrogen concentrations. Zhang et.al [1] studied the ignition delays of lean methane-hydrogen mixtures and found that the ignition delay increases with increasing temperatures. It also showed the effect of free radicals on the process.

Gavilanes [4] provided more insight into the ignition location and the role of flow separation in the creation of zones prone to ignition in a stoichiometric hydrogen-air mixture. In the same study, it was also shown that the ignition process was essentially driven by chain branching reactions involving OH radical.

The present work aims at studying the ignition thresholds of CH_4 - H_2 -air mixtures with varying equivalence ratios. Additionally, the effect of variation of hydrogen percentage has also been investigated. The local mixture equivalence ratio and temperature just before ignition threshold of mixtures have been studied to understand the role of preferential diffusion on ignition. Ignition of the hydrogen/air mixtures is achieved using a cylindrical, uniformly heated hot surface, modelled as a commercially available glow plug [4].

2 Numerical Model

The numerical conditions are similar to [4]. The governing equations account for mass, momentum, energy and species conservation. Laminar flow conditions have been modelled, and a buoyancy dominated flow field is expected.

The diffusion coefficients are modelled using multicomponent diffusion based on the Maxwell-Stefan equations. The Soret effect has also been considered due to the expected formation of strong temperature gradients caused by the combustion of hydrogen [15]. All simulations have been carried out using the general purpose CFD code Fluent.

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3 Computational grid and boundary conditions

The domain used in the present studies is shown in Fig. 1. It corresponds to a cylindrical combustion chamber of diameter 114.3 mm and height 165.1 mm used in the studies conducted by Gavilanes [16]. The glow plug with a height 9.3 mm, and a diameter 5.1 mm, is located in the center of the bottom plane. The 2D axisymmetric mesh consists of 41901 cells generated using GAMBIT as shown in Fig. 1. The meshing is such that the mesh density is higher in the proximity of the glow plug, with a minimum cell size of $25\mu m \times 25\mu m$ to accurately resolve the various transients related to ignition phenomenon at the surface of the plug [17-19].



Figure 1 Computational domain and boundary conditions. (all dimensions in m)

No slip and constant temperature boundary conditions are imposed on the boundary walls as shown in Fig. 1. The glow plug surface has a temperature ramp condition given by $T_{plug} = T_0 + H(t)$ where H gives the rate of heating in K/s.

The initial conditions are $P_0 = 101$ kPa, $T_0 = 300$ K, $U_0 = (0, 0, 0)$ m/s. Mass fractions of the species H₂, N₂ and O₂ are calculated based on the equivalence ratios of the mixtures used.

4 Reaction Mechanism

GRI-Mech 3.0 has been used to model the chemical kinetics in the simulations. Previously, this reaction mechanism has shown good agreement with experimental values for predictions of laminar flame speeds, extinction strain rates and major species profiles of methane-hydrogen mixtures [20, 21]. As the present study does not focus upon the formation of the nitrogen oxides (NO_x), a modified version of the mechanism is used by assuming that N_2 remains inert during the ignition process.

5 Effect of Hydrogen addition on Ignition Phenomenon

Simulations have been performed for varying concentrations, Figure 2: Left shows the ignition temperatures obtained. The ignition temperature is determined by monitoring the plug surface temperature and the maximum temperature of the mixture. The mixture is considered to have ignited when the difference between the plug surface temperature and the maximum temperature of the mixture is ≈ 150 K [4].

Figure 4.1 shows the change in ignition temperature with the percentage of methane. As the percentage of hydrogen in the mixture decreases from 100 % to 0% the ignition temperatures are observed to steadily increase, with the mixture having 100% hydrogen igniting at the lowest temperature of 977K and the mixture with 100% Methane igniting at 1392K. This increase in ignition temperatures indicates that the presence of hydrogen in the mixture tends to lower the ignition threshold of a higher hydrocarbon such as methane.



Figure 2: Left: Variation of ignition threshold with mixture composition. Right: Pre-ignition and point of ignition contour plots with velocity vectors for stoichiometric mixtures of 50% methane at heating rate of 180 K/s.

In the left half of the contour plots, the temperature around the glow plug is shown, with contours beginning at 400 K to 1300 K taken at every 100 K. The thermal boundary layer formation can be clearly seen in these plots. The mixture around the plug is rapidly heated up and the resulting temperature gradients set up a convective current in the vicinity of the plug. Two such currents rise along the sides of the plug and meet at the top to form the stagnation region.

The ignition occurs at the top of the glow plug in all the cases. Before ignition, the OH concentrations begin to increase above the glow plug, where the formation of a semi-circular stagnation region is clearly indicated. The rate of heat release by chemical reaction in the stagnation region, is greater than the heat diffused to the wall, leading to the formation of the ignition kernel.

6 Effect of Equivalence ratio on Ignition Phenomenon

Simulations were performed for the equivalence ratios of 0.4, 1 and 2. Each of these equivalence ratios were tested with mixtures composed of 20%, 50% and 80% methane. Based on the mole fractions of hydrogen and methane in each composition, stoichiometric moles of air was calculated. Corresponding to

each equivalence ratio, actual number of moles of hydrogen, methane and air were calculated for defining equivalence ratio in numerical computations performed.

In the case of the mixture with 80% methane, ignition was found to occur only at a maximum equivalence ratio of 1.75. The results of the simulations have been shown in Figure 3: Left.



Figure 3: Left: Variation of ignition temperature with equivalence ratio Right: Variation of local equivalence ratios with calculated equivalence ratios.

It is observed that the ignition temperatures rise with increasing equivalence ratios. The rich mixtures have a higher ignition threshold indicating that the leaner mixtures are more volatile and tend to ignite at lower temperatures. To study the chemistry in the stagnation region, a sector has been defined in the region above the glow plug. This region is chosen due to the formation of the stagnation region and the presence of high temperature gradients before ignition. From the Figure 3: Right it is observed that the local equivalence ratios have an increasing trend. This behavior is particularly visible in the case of the mixture with 50 % hydrogen. The marked increase in equivalence ratios can be attributed to the higher diffusivity of hydrogen that is present in larger amounts in the rich mixtures. Fluent allows to calculate mole fractions of each element locally. The local equivalence ratio is calculated in the similar way as calculating the ordinary equivalence ratio, based on the mole fractions of fuel and oxidizer obtained locally at each point, from fluent ((XCH₄+XH₂)/XO₂). Local equivalence ratios obtained are leaner in the case of mixtures with 80% and 100% methane concentrations. However, the mixtures with 20% and 50% methane exhibit relatively rich equivalence ratios.

7 Effect of critical reactions on Ignition Phenomenon

Among the reactions occurring during ignition, the reactions shown in Figure 4 are found to be prominent during the combustion. Among the above reactions, the reactions R3, R37 and R83 are chain reaction steps involving the O, H and OH radicals and R33 generates the hydroperoxy radical. In Figure 3.11 the reaction rates of R97, resulting in the formation of CH_3 and H_2O , are the highest except in the case of 20% methane ignition. In the ignition of the mixture with 20% methane, R52 has the highest reaction rates and

results in the formation of H_2 and CH_3 . With increasing percentage of methane all the reactions in Figure 4.10 exhibit higher reaction rates. The reactions R97 and R166 were found to contribute significantly in combustion of methane-hydrogen-air mixtures by performing sensitivity analysis. The effect of R97 and R166 are particularly interesting while also the increased production of H_2 from R52.



Figure 4: Reaction rates for (Left) hydrogen combustion and (Right) methane combustion at $\phi = 1$.

7 Conclusion

Two dimensional transient axi-symmetric simulations of $CH_4/H_2/air$ mixture ignition using a glow plug have been performed. Variation of ignition temperature with equivalence ratio and heating rates has been studied. Ignition temperature of the mixtures is significantly lowered by addition of H₂. Lower ignition thresholds are observed in mixtures with high concentration of H₂. Higher ignition thresholds have been observed in mixtures having higher CH₄ concentrations. The local equivalence ratios developed have been calculated. Increased local equivalence ratios were observed prior to ignition for every equivalence ratio with rich mixtures exhibiting a relatively greater increase in local equivalence ratios. The location of ignition is similar for rich and lean mixtures with both stoichiometric and leaner mixtures igniting at the top of the heated surface. The development of the ignition kernel starting at the pre-ignition mixture and progressing to the point of ignition was plotted for every case. It exhibits the nature of the flame front developed and the composition of the mixture prior to ignition and during the ignition process. The mixtures with lower CH₄ concentration have a more rapidly developing flame front. Critical reactions at the point of ignition in both CH₄ and H₂ combustion have been identified and plotted.

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