The Effect of Catalytic Reaction on Hot Surface Ignition*

Hyung-Man KIM**, Hiroshi ENOMOTO***,
Hideki KATO***, Mitsuhiro TSUE***
and Michikata KONO***

The hot surface ignition of methane-air mixtures in microgravity has been studied experimentally and numerically. Experiments on the ignition of the mixtures with electrically heated nickel wires and platinum wires in microgravity have been performed. Numerical calculations, including the catalytic reaction rate for platinum, have been performed to understand the experimental results obtained in microgravity. The ignition delays and ignition temperatures for a wide range of equivalence ratios were investigated. Experimental results show that the ignition temperatures with platinum wires have a maximum near the stoichiometric mixture ratio, while those with nickel wires increase as the equivalence ratio increases. Ignition temperatures with platinum wires are higher than those with nickel wires. Numerical results show that reactants next to platinum wires are consumed by the catalytic reaction. Therefore, a higher temperature is required to ignite mixtures with platinum wires. The catalytic inhibition of hot surface ignition is simulated successfully by the numerical model.

Key Words: Ignition, Gaseous Fuel, Catalyst, Hot Surface Ignition, Microgravity, Catalytic Inhibition

1. Introduction

Hot surface ignition is a phenomenon occurring when a combustible mixture contacting with a hot solid body is ignited and flame propagation begins. Hot surface ignition is related to glow-plugs of diesel engines and knocking in internal combustion engines. Knowledge on hot surface ignition characteristics is important in a risk analysis for fire in building or explosion in mines. Moreover, it is important from a fundamental viewpoint of combustion science to elucidate the mechanism of hot surface ignition.

Numerous studies on hot surface ignition have been performed experimentally⁽¹⁾⁻⁽³⁾, theoretically^{(4),(5)}

and numerically^{(3),(6)}. However, many obscure points in the mechanism of hot surface ignition still remain. One of the complications in understanding the basic mechanism of hot surface ignition is the effect of natural convection. In the hot surface ignition of a combustible mixture, there exists time lag from the accomplishment of heating up the wire to the ignition of a mixture, which is defined as an ignition delay. Since the effect of natural convection becomes pronounced as an ignition delay becomes longer, it is difficult to analyze the phenomenon under such conditions. In the hot surface ignition using the catalyst as ignition source, there exists the additional effect that natural convection supplies reactants to the catalytic surface and promote a catalytic reaction. These experiments have been performed in normal gravity, except the experiment by Nagata et al.⁽³⁾ No mixture in a closed vessel is truly stagnant owing to buoyancy-driven convection caused by the hot surface in normal gravity.

In the present study, experimental and numerical studies have been conducted on the hot surface ignition of methane-air mixtures in a closed vessel. Hot surfaces used are nickel wires as non-catalyst and

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** Combustion and Environment Group, Power Generation Research Laboratory, Korea Electric Power Research Institute, 103-16 Munji-Dong Yuseong-Ku, Taejeon 305-380, Korea

*** Department of Aeronautics and Astronautics, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

platinum wires as catalyst. In order to define the initial condition and make the analysis simple, the following control unit was developed: which heats the wire to the predetermined temperature in a very short time, and maintains the wire temperature constant until ignition. Experiments of hot surface ignition have been performed in microgravity. The initial temperature and the initial pressure of mixtures are room temperature and atmospheric pressure, respectively. Numerical calculations, including detailed gas phase reactions, multi-component diffusion and a catalytic reaction model for platinum wires, have been performed to analyze the experimental results in microgravity.

2. Experimental Apparatus

The experimental apparatus is schematically shown in Fig. 1. The combustion chamber is a duralumin cylinder of 60 mm in diameter and 16 mm in length, fitted with parallel glass windows. The hot wires used nickel wires and platinum wires with diameter of 0.60 mm and length of 30 mm, and are supported by two copper electrodes of 5.0 mm in diameter. This hot wire is used to ignite the mixtures, to measure the temperature, and to detect the gas phase ignition. Ignition of mixtures can be determined by change in the supplied voltage due to a sudden heating of the hot wire, but it is difficult to detect this point with equivalence ratio depart from stoichiometric mixture ratio. Therefore, photodiode is also used to detect the ignition. Batteries are used as ignition energy source.

Hot wire in the combustion chamber is heated electrically up to the desired temperature in a short period (about 10 ms) and maintained at constant temperature thereafter by the feedback control circuit, as shown in Fig. 2. Hot wire functions as one resistor for the wheatstone bridge: The electric potential difference between R_A - R_B and R_C - R_{HW} drives the operational amplifier, whose output current is amplified by transistors. Therefore, the change in the resistance of hot wire yields desired feedback effect so that the temperature of hot wires maintains constant. The constant value can be adjusted by varying resistance R_C that is made of constantan with diameter of 1.0 mm.

Experiments have been performed with the equivalence ratio of methane-air mixtures and the predetermined temperature of the hot wire changing. The experimental apparatus and the drag shield were hung by a wire. Immediately after the wire is cut, the control unit is operated by using the microgravity switch, which is turned on when it detects microgravity condition in experimental apparatus. It takes

Fig. 1 Schematic of the experimental apparatus

Fig. 2 Schematic of the control circuit

some moments from the accomplishment of heating up the wire until the mixture ignites. Histories of the supplied voltage to the wire and the photodiode output voltage are recorded by a storage oscilloscope. Microgravity conditions were attained by free fall method in the drop tower at the University of Tokyo, which provides about 0.6 s microgravity conditions (G level, less than 10^{-3} times that of normal gravity).

3. Numerical Model

Numerical calculations have been carried out to simulate the hot surface ignition experiments in microgravity. A cylindrical heat source, or a hot wire, is surrounded with a mixture and its length is assumed to be infinite. Axial symmetry, zero azimuthal velocity, and no gradient along the axis are assumed. Because of low Mach numbers, constant pressure is assumed, therefore, momentum equation is not used. The conservation equations in one dimensional cylindrical coordinate for continuity, energy, and chemical species are written, respectively⁽⁷⁾:

$$\frac{\partial \rho}{\partial t} + \frac{1}{r} \frac{\partial (\rho V r)}{\partial r} = 0 \quad (1)$$

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p V \frac{\partial T}{\partial r} = -\frac{p}{r} \frac{\partial (Vr)}{\partial r} + \frac{1}{r} \frac{\partial (\sigma_{rr} Vr)}{\partial r} - \frac{\lambda}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) - \sum_{k=1}^{29} \dot{\omega}_k H_k \quad (2)$$

$$\rho \frac{\partial Y_k}{\partial t} + \rho V \frac{\partial Y_k}{\partial r} = \frac{1}{r} \frac{\partial}{\partial r} \left[\rho D_k r \frac{\partial Y_k}{\partial r} \right] + \dot{\omega}_k \quad (k=1, \dots, 29) \quad (3)$$

where $\dot{\omega}_k$, H_k , and σ_{rr} are the mass production rate of species k by gas phase reactions, the specific enthalpy of formation, and the viscous stress tensor. The transport properties such as viscosity μ , thermal conductivity λ , and diffusion coefficient D_k are given in a multicomponent formulation^{(7),(8)}. The elementary reaction mechanism taken from Kee et al.⁽⁷⁾ involves 134 reactions and 29 species.

The boundary conditions are given by

$$r = r_w: T = T_{HW}, V = 0, \rho D_k r \frac{\partial Y_k}{\partial r} = \frac{v_k}{v_F} \dot{r}_{SR} \quad (4)$$

$$r = \infty: \frac{\partial T}{\partial r} = 0, \frac{\partial V}{\partial r} = 0, \frac{\partial Y_k}{\partial r} = 0 \quad (5)$$

where v_k , v_F , and $\dot{r}_{SR}$ are the stoichiometric coefficients of species k and fuel in the catalytic reaction and the reaction rate of the catalytic reaction, respectively. For an inert surface, $\dot{r}_{SR} = 0$. Positions of the wire surface and infinite boundary in the present numerical calculation are 0.3 mm and 25 mm, respectively.

The catalytic reaction rate of methane and oxygen on platinum surface used in the numerical calculations is as follows⁽⁶⁾:

$$\dot{r}_{SR} = A \exp\left(\frac{-E_{SR}}{RT}\right) C_{CH_4} C_{O_2}^{0.5} \quad (6)$$

where C_{CH_4} and C_{O_2} are the mole fractions of methane and oxygen on the surface of platinum wires, respectively. Activation energy, $E_{SR} = 134.7$ [KJ/mol] and pre-exponential factor, $A = 1.3 \times 10^{11}$ in Eq. (6) are drawn from Trimm et al.⁽¹⁰⁾

Ignition occurrence is defined as the time that the place, where the heat release rate due to the gas phase reaction takes the local maximum value with time, appears. Ignition delay and ignition position are defined the time lag from the start of numerical calculation to the ignition and the cell location of maximum temperature, respectively.

4. Results and Discussion

4.1 Dependence of the ignition delay on the predetermined temperature

Ignition delay is used as the estimating parameter of the capability of hot surface ignition. Figure 3 shows typical histories of the supplied voltage to the hot wire and of the photodiode output voltage recorded by a storage oscilloscope, when a stoichiometric mixture was ignited with the platinum wire at the predetermined temperature. When the mixture is

ignited, the supplied voltage decreases quickly because the wire is heated. The photodiode output increases rapidly and levels off by the heating of wires as the electric voltage is supplied. At the moment of ignition, there is a sudden jump in the photodiode output. Thus, it is found that the ignition occurrence can be determined successfully. The time lag from the accomplishment of the heating hot wire to the ignition occurrence is defined as the ignition delay (t_{ig}) as shown in Fig. 3.

In order to investigate the influences of nickel oxidation on the ignition delay, we experimented using several states of nickel oxide (NiO). A NiO wire was made by a heating nickel wire at the predetermined temperature of 1422 K in oxygen during the heating time for oxidation (t_{ox}). Figure 4 shows the variations of the ignition delay with t_{ox} for the stoichiometric mixture in microgravity. Ignition delays decrease with t_{ox} , and this is considered to be because the consumption of oxygen due to nickel oxidation decreases. Generally, variations of ignition delays are negligibly small over t_{ox} of 10 s. In order to

Fig. 3 Histories of supplied voltage to hot wire and photodiode output voltage: $f=1.0$, Platinum, $T_s=1751$ K

Fig. 4 Variations of ignition delay with the heating time for nickel oxidation: $f=1.0$

investigate the oxidation state moved to the inside, the oxygen concentration in the cross section of NiO was measured by X-ray diffraction analyzer.

Figure 5 shows the distributions of oxygen concentration in the cross section of NiO. Oxygen concentration was measured in the fixed position from the surface. The amount of oxygen is abundant in the surface and dwindles away into nothing inside. Oxide layer becomes thicker with t_{ox} . Oxygen concentration in the surface increases until t_{ox} of 10 s, but thereafter, becomes saturated and the diffusion of oxygen occurs only inside. From these distributions, the amount, which is integrated in a radial distance and divided by t_{ox} , becomes the oxygen consumption rate, that is, the amount of oxygen adsorbed into a nickel wire per unit area and time. Figure 6 shows the variation of oxygen consumption rate with t_{ox} . Oxygen consumption rate decreases with t_{ox} , and is negligibly small over t_{ox} of 10 s. This means that NiO over t_{ox} of 10 s approaches to the inert surface in which nickel oxidation does not occur. Since NiO becomes easier to break mechanically with t_{ox} , NiO at t_{ox} of 10 s is adopted as the inert surface in the present experiment.

In the present experiment, the upper and lower limits of ignition delay obtained were made 0.5 s in microgravity and almost ten times as long as the time which is taken to heat up the hot wire to the predetermined temperature, respectively. Figure 7 shows the dependence of ignition delay on the predetermined temperature obtained with NiO (inert) wires and Pt (catalytic) wires for the stoichiometric mixture experimentally and numerically. From the computational results, ignition delay varies non-linearly with the predetermined temperature. As ignition delay approaches 0 s, infinite predetermined temperature is needed. This means that there exist the transition period for transferring heat to the mixture before sufficient gas phase reaction for ignition occurs.

Both experimental and numerical results show that higher surface temperatures are required to ignite the mixture with Pt wires than with NiO wires. In order to understand the effects of catalytic reaction on ignition temperature in detail, numerical calculations were performed using the catalytic reaction model of methane and oxygen on Pt surface. Figure 8 shows typical distributions of mole fractions of methane for the stoichiometric mixture calculated with the inert wire and the catalytic wire. In the computational result with the inert wire, methane concentration keeps nearly constant before ignition and decreases suddenly at the moment of ignition. In case of the catalytic wire, methane concentration decreases from the beginning of numerical calculation

Fig. 5 Distributions of oxygen concentration in the cross section of nickel oxide

Fig. 6 Variation of oxygen consumption rate with the heating time for nickel oxidation

Fig. 7 Variations of ignition delay with the setting temperature: $f=1.0$

to ignition, which shows the depletion of methane near the wire by the catalytic reaction. Thus, there is a catalytic inhibition of ignition due to the reactant depletion.

4.2 Dependence of the ignition temperature on equivalence ratio

The ignition of a combustible mixture by hot surface depends not only on the surface temperature

Fig. 8 Typical distributions of CH_4 mole fraction: $f=1.0$

Fig. 9 Dependence of the ignition temperature in an ignition delay of 0.3 s on equivalence ratio

but also on the length of time during which the mixture is exposed to it. Thus in the present study, the ignition temperature is defined as the predetermined temperature at which the mixture is ignited in a fixed ignition delay.

Figure 9 shows dependence of the ignition temperature in an ignition delay of 0.3 s on equivalence ratio obtained experimentally and numerically. The ignition temperatures were calculated from the relations between the predetermined temperature and ignition

Fig. 10 Histories of catalytic reaction rate calculated with catalytic wire

delay, as shown in Fig. 8. Generally, ignition temperatures obtained experimentally are higher than those obtained numerically. The reasons are regarded as follows: In the present numerical study, one-dimensional cylindrical coordinate is used and no gradient along the axis is assumed. However in the present experiment, temperature gradient along the axis arises from the cooling effect of two copper electrodes. Longitudinal heat losses in the mixture make ignition temperature higher in the experiment. The predetermined temperature is set beforehand numerically, however, it takes time to heat the wire up to the predetermined temperature experimentally and reactants are consumed during the time. Hence, initial concentrations of reactants in the experiment are lower than those in the numerical calculation. Therefore, consumption of reactants in the experiment make ignition temperature much higher.

Experimental results show that the ignition temperatures with Pt wires are highest near the stoichiometric mixture ratio and decrease with equivalence ratio depart from the stoichiometric mixture ratio, while those with NiO wires have a minimum near the stoichiometric mixture ratio. Figure 10 shows typical histories of catalytic reaction rates calculated with catalytic wires at 1650 K. Catalytic reaction rates decrease gradually subsequent to a rapid decrease at the beginning of numerical calculation and decrease suddenly at the moment of ignition. Quantitative comparison of catalytic reaction rates shows the strength of the catalytic inhibition of ignition due to the reactant depletion on the surface of the wire. A catalytic reaction rate for the stoichiometric mixture is the highest in all equivalence ratios calculated, which accounts for the fact that the ignition temperatures with Pt wires have a maximum at the stoichiometric mixture ratio in the results shown in Fig. 9.

5. Conclusion

Experimental and numerical studies have been performed on the hot surface ignition of methane-air mixtures. Hot surfaces used are inert NiO wires and catalytic Pt wires. The main conclusion are as follows;

1) The ignition delays obtained with inert NiO wires are shorter than those obtained with catalytic Pt wires.

2) Higher surface temperatures are required to ignite the mixture with catalytic Pt wires than inert NiO wires. Hence, there is a catalytic inhibition of hot surface ignition due to the reactant depletion on the surface of the wire.

3) Ignition temperatures with catalytic Pt wires are highest near the stoichiometric mixture ratio and decrease with equivalence ratio depart from the stoichiometric mixture ratio, while those with inert NiO wires increase with equivalence ratio increase.

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