Improvement of Lean Hydrocarbon Mixtures Combustion Performance by Hydrogen Addition and Its Mechanisms

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Abstract

To apply the lean-burn technique to real engines two problems must solved; these are the substantial decrease in the burning velocity and the great increase in misfires as the mixture is thinned to the required extent which is near or beyond the flammability limit of the mixture. This paper shows that adding a small amount of hydrogen to the lean hydrocarbon/air mixture can increase its turbulent burning velocity substantially and extend its quenching limit greatly, thus being able to solve the above two problems at the same time. Improvement in the combustion performance by hydrogen addition is attributed to the preferential diffusion of hydrogen to the flamelets convex to the unburned side to increase their local heat release rate by enriching the local mixture. Without extra-supply of hydrogen by preferential diffusion, convex flamelets of lean mixture would be quenched most readily because heat loses from them is more than from other flamelets.

Introduction

Recently, lean burn was extensively studied as a future technique to reduce the exhaust emissions as well as to improve the fuel economy of SI engines. However, two problems are protecting this technique from its application to real engines; they are the substantial decrease in the burning velocity and the remarkable increase in misfires as the mixture becomes as lean as required (about 0.6 or lower in fuel/air equivalence ratio, which is near or beyond the flammability limit of hydrocarbon mixture). In order to solve these two problems, various methods[1]~[4] have been attempted, such as increasing the ignition energy, stratifying the mixture, or intensifying the turbulence, etc. Although these methods truly improve the lean mixture combustion performance to some extent, to burn even leaner mixtures at even higher burning velocity requires other methods.

The method investigated in this work is different from the above ones, which improves the lean mixture combustion performance by adding a small amount of hydrogen to the mixture. Because hydrogen mixture has the lowest fuel/air equivalence ratio of flammability limit and the highest burning velocity[5], by doing so, it can be expected

to solve the above two problems, and to burn even leaner mixtures beyond the hydrocarbon flammability limit. In this study, we first investigated the laminar burning velocity and flammability limit of each mixture, making the hydrogen addition amount and equivalence ratio varied independently. With such basic data, we then measured the turbulent burning velocity and quenching limit (which was identified with the highest turbulence intensity that a flame can withstand) of mixtures near the flammability limit. Experimental results show that hydrogen addition can increase the turbulent burning velocity substantially and extend the quenching limit of lean hydrocarbon mixtures greatly. Mechanisms for such effects are discussed on the basis of the effects of reactant preferential diffusions on the local mixture composition, flame structure and burning velocity of local flamelets.

Experimental

Combustion Chamber and Turbulence

The combustion chamber used is a nearly spherical vessel with an equivalent inner diameter of 120mm. It is fixed with two glass windows of 80mm diameter in two opposite directions for flame observation, and four perforated plates of 100mm diameter in the other four directions. Behind each perforated plate, a fan is equipped to mix gases and generate nearly isotropic turbulence in the center region of the chamber. Turbulence intensity can be controlled to vary up to 3.76m/s with the turbulence integral length scale being about 3.6mm over the whole range of turbulence intensity. Details of the vessel are available in Ref.(5). To conduct laminar combustion, the mixture with desired composition was set static for about 1 minute after mixing and then ignited at the vessel center. To conduct turbulent combustion, turbulence intensity was controlled by the fan speed, whose relative error was within 1%.

Measurement of Burning Velocity

The laminar burning velocity, S_L, was measured by the pressure history of spherical flame in closed vessel[6] in the early stage of combustion when the pressure rise was 0.1 to 0.2 atm to satisfy the assumption of the flame

being spherical. As this method requires the final pressure of constant volume adiabatic combustion, which is difficult to obtain experimentally, we used the theoretical value. Moreover, the turbulent burning velocity, S_T, was approximated by relation[7] $S_T/S_L \approx (dp/dt)_T/(dp/dt)_L$, where dp/dt is the pressure rise rate, and subscripts T and L designate turbulent and laminar combustions, respectively. Moreover, each experiment was repeated 10 times to increase the precision of measurements, with the initial pressure and temperature being 1atm and 298K, respectively.

Mixture Composition

The composition of mixture was varied by two parameters: the total fuel/air equivalence ratio, Φ, and the molar fraction of the added hydrogen in the whole fuel gases, δ. It can be expressed as $(1 - \delta)C_xH_y + \delta H_2 + X_O(O_2 + 3.762N_2)$. Thus, Φ is calculated by

$$\Phi = [(x + y/4)(1 - \delta) + \delta/2]/X_O, \qquad (1)$$

where x and y are the numbers of carbon and hydrogen atoms in a molecule of the hydrocarbon fuel, and X_O is the mole numbers of oxygen. In order to investigate the dependence of hydrogen preferential diffusion on the molecular weights of hydrocarbon fuels, three hydrocarbon fuels, CH_4, C_2H_6 and C_3H_8 were used.

Results and Discussion

Validation of Measurements

The burning velocity data have been validated[8] by the agreement of the obtained laminar burning velocities of propane/air mixtures over a wide range of equivalence ratio with those by Metghalchi et al.[9] using a similar method. Although the former shows a little higher than the latter, probably owing to some small systematic errors, they agreed well in tendency. In comparing the burning velocities of different mixtures, such systematic errors are unlikely to affect the comparison results because all data were measured with the same method.

Laminar Burning Velocity and Flammability Limit

Figure 1 shows the laminar burning velocities and flammability limits of methane/air mixtures with different amounts of hydrogen additions. As the mixture composition is determined by two parameters: Φ and δ, the data of laminar burning velocity, after smoothening, are equivalently plotted in Fig.2 with Φ and δ being the coordinates (contours for ethane and propane mixtures are omitted for short). Data in this form are useful, as it will be used latter, in discussing the influences of mixture composition on laminar burning velocities.

The measured flammability limits on the lean side are as follows: Without hydrogen addition, such limits of methane, ethane and propane mixtures are about 0.6, 0.6 and 0.7 (Φ), respectively. With a hydrogen addition amount of δ=0.2, these are extended to about 0.5, 0.5, and 0.6, respectively. Although hydrogen addition is found to extend the flammability limit to the lean side and increase

the laminar burning velocity in all cases investigated, such effects usually are insignificant when δ is small.

Turbulent Burning Velocity and Quenching Limit

While flammability limit refers to the fuel concentration limit beyond which a flame cannot propagates by itself in a laminar mixture, quenching limit indicates the severest turbulence conditions that a flame can withstand. For a certain combustion chamber, such conditions can be identified with a turbulence intensity. Therefore, quenching limit indicates, indirectly, the highest speed at which an engine can run without misfires.

Figure 3 shows experimental results on the turbulent burning velocity and quenching limit of lean mixtures near
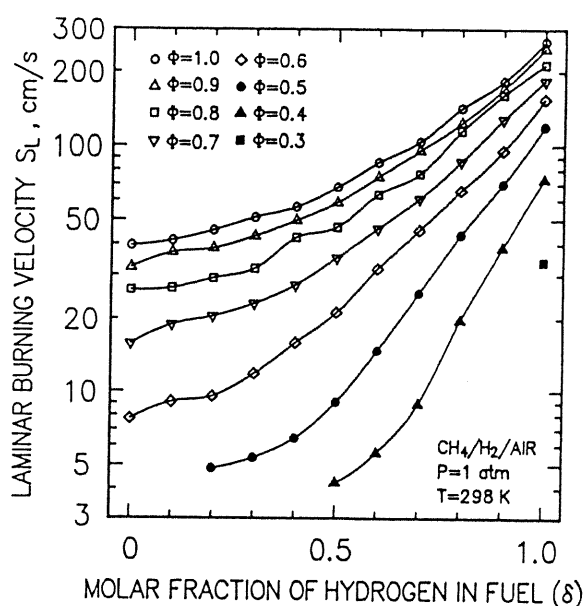

Fig.1: Measurements of laminar burning velocities and flammability limits of methane/air mixtures with hydrogen addition
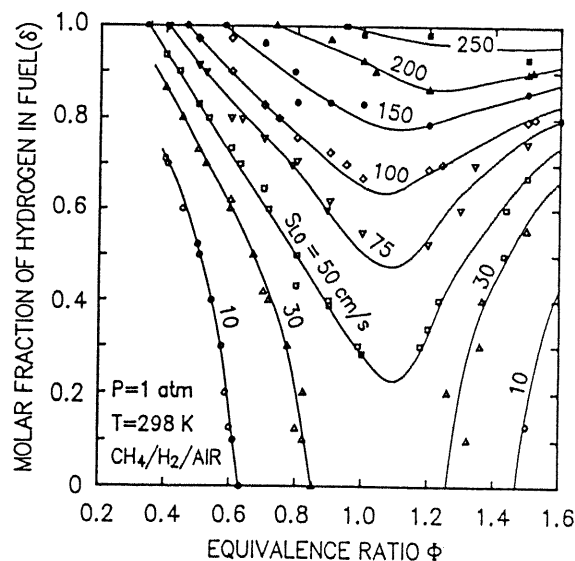

Fig.2: Effects of hydrogen addition amount δ and equivalence ratio Φ on laminar burning velocity of methane/air/hydrogen mixture

flammability limit. From these results, we concluded:

First, adding a small amount of hydrogen to a lean hydrocarbon mixture can substantially increases its turbulent burning velocity and largely extend its quenching limit. For instance, the highest turbulent burning velocity of a lean methane/air mixture ($\Phi=0.6$) is about 0.5m/s with its quenching limit being about 1.5m/s without hydrogen addition, which is increased up to about 1.2m/s with its quenching limit being extended to about 4m/s with a hydrogen addition of $\delta=0.2$.

Second, the more the hydrogen addition, the more the turbulent burning velocity is increased, and so is the quenching limit extended. For practical uses, a hydrogen addition of $\delta=0.2$ to methane/air lean mixture is enough to increase its burning velocity and to extend its quenching limit, which makes the hydrogen weight about 3% of the total fuel when the equivalence ratio is 0.6.

Finally, both the increase in the turbulent burning velocity and the extension in the quenching limit by hydrogen addition depend on the molecular weight of the hydrocarbon fuel involved. With the same hydrogen addition (δ), the smaller the hydrocarbon molecules, the more the turbulent burning velocity is increased, and so is the quenching limit extended. Mechanisms for such phenomena will be discussed latter.

The turbulent burning velocity increase and quenching limit extension of lean mixture are very important to a lean-burn engine. First, the increased turbulent burning velocity can not only offset its power output lowered by the low burning velocity of lean mixture, but also improve its thermal efficiency by decreasing the combustion duration. Second, the extended quenching limit enables it to burn even leaner mixtures without misfires.

Mechanisms of Combustion Improvement by Hydrogen Addition

Although hydrogen addition has no significant effects in increasing the laminar burning velocities of lean mixtures when δ is small as shown in Figure 1, it can substantially increase the turbulent burning velocities as shown in Fig.3. This indicates that turbulence plays an important role in helping the added hydrogen to increase the burning velocity. Moreover, Fig.3 shows the turbulent burning velocity increased by hydrogen addition to depend on the hydrocarbon involved, which implies that hydrocarbon diffusion plays another important role. Here we focus our discussion on how the turbulence and hydrocarbon diffusion affect the thermal diffusion, hydrogen diffusion and mixture composition at the local flamelets of a turbulent flame.

Effects of Turbulence on Hydrogen Diffusion and Thermal Diffusion

In a spherical laminar flame, the flame curvature is the same everywhere, therefore, both the local fluxes of heat and reactant diffusions are uniform over the whole flame surface. Consequently, the temperature or concentration of reactants along the flame surface is the same everywhere. However, in a turbulent flame, the local cur-
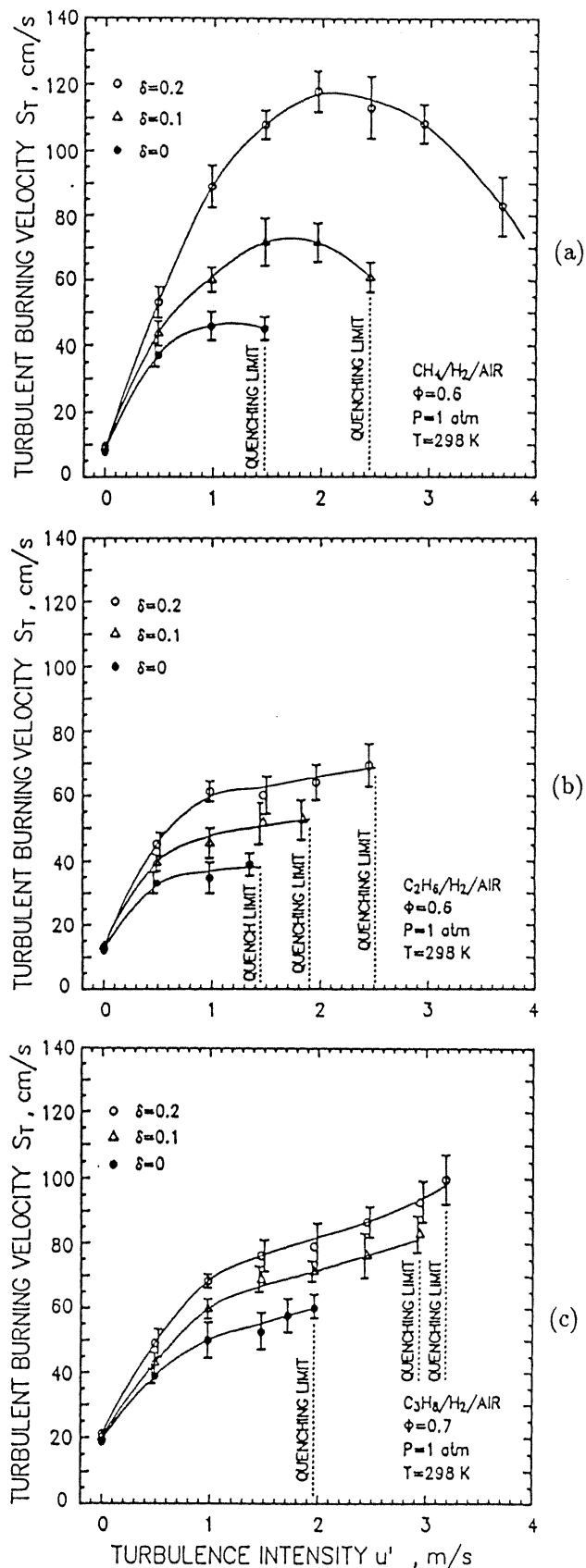

Fig.3: Effects of hydrogen addition on the turbulent burning velocity and quenching limit of lean mixtures near flammability limit

vature is varied by turbulence, which can change the temperature and concentration of reactants in the reaction zone as illustrated in Fig.4. For convenience, a flamelet convex toward the unburned mixture is referred to as a convex flamelet and that convex toward the burned mixture a concave flamelet.

As shown in Fig.4, the flamelet above the x axis is a convex flamelet, where reactant diffusions to the flamelet are convergent. As the diffusion coefficient of hydrogen is much larger than that of other components, it diffuses faster to the convex flamelet than other components and thus, a zone containing more hydrogen is formed before the convex flamelet.

On the other hand, thermal diffusions from the convex flamelet are divergent toward the unburned mixture, therefore heat lost from this part is more than from other parts, tending to decrease the reaction zone temperature. According to Arrherius' formula, reaction rate is governed by the temperature and concentration of reactants (here mainly the fuel gases), therefore, any change in local burning velocity depends on the quantity of hydrogen excessively diffused into the reaction zone and the heat excessively lost to the unburned mixture. When the former dominates over the latter, the local burning velocity increases and the flamelet becomes even more convex (which increases the flame area), thus increasing the turbulent burning velocity substantially, or, the convex flamelet is flattened and the turbulent burning velocity decreased.

For the concave flamelet below the x axis, as thermal diffusions to the unburned mixture are convergent while the hydrogen diffusions to the flamelet are divergent, the reaction zone temperature is increased but the hydrogen concentration is decreased. As temperature increase and hydrogen concentration decrease have opposite effects on the local burning velocity, these effects are largely canceled. Moreover, even if either effect dominates over the other, as any increase in the local burning veloc-
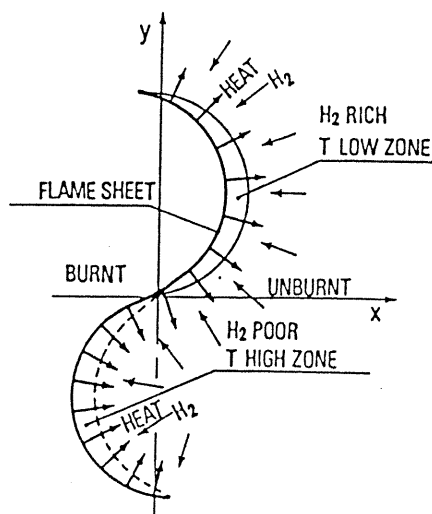
ity of a concave flamelet will flatten the flamelet and thus decreases its area, the contribution by concave flamelets to the turbulent burning velocity is hardly varied.

Although convex and concave flamelets are roughly equal in numbers in a turbulent flame, as analyzed above, the turbulent burning velocity is mainly determined by the convex ones. Furthermore, as convex flamelets are always exposed to severer thermal conditions because of convergent thermal diffusions, without extra supply of hydrogen, they would be more readily extinguished, leading to the flame quenching. This explains why flames of lean mixtures with hydrogen addition not only have much higher burning velocities, but also withstand much higher turbulence intensities than those without (see Fig.3).

Although the amount of hydrogen addition is different, mixtures with the same fuel and the same equivalence ratio have nearly the same laminar burning velocity as shown in Fig.1, therefore, under the same turbulence conditions, flames of such mixtures can be expected to have roughly the same flame area. Therefore, increase in the turbulent burning velocity can be attributed to the local (laminar) burning velocity of the turbulent flame. In order to investigate the effects of hydrogen addition on the turbulent flame structure, the flame structure of four methane/air mixtures with different amounts of hydrogen addition but with the same fuel/air equivalence ratio ($\Phi=0.6$) and the same turbulence intensity ($u'=1.47$m/s) was visualized using schlieren photography as shown in Fig.5. The disconnection of a schlieren fringe can be considered to be a local quenching of the flamelet. Such disconnection can be observed everywhere in Fig.5(a), the flame without hydrogen addition, it can also be seen somewhere in Fig.5(b), the flame with only an $\delta = 0.1$ hydrogen addition, but it can hardly be found in Fig.5(c) and (d) because of more hydrogen addition. This explains why the more the hydrogen addition, the higher turbulence intensity the flame can withstand without being quenched. Moreover, Fig.5 also shows that the more the hydrogen addition, the narrower the schlieren fringes. This suggests that the local burning velocity of the flamelets increase with the amount of hydrogen addition, because the flamelet thickness is in reverse proportion to the local (laminar) burning velocity.

Effects of Hydrocarbon Diffusion on Composition of Local Mixture

We have analyzed how turbulence affects the hydrogen diffusion and thermal diffusion at local flamelets. Here we discuss how the diffusion of hydrocarbon changes the composition of local mixture at a convex flamelet. Firstly, we rewrite the mixture composition in a general form: $\alpha C_x H_y + \beta H_2 + X_O(O_2 + 3.76N_2)$. Thus, the equivalence ratio, Φ, and the volume fraction of hydrogen in the fuel gases, δ, are

$$\Phi = [\alpha(x + y/4) + \beta/2]/X_O; \qquad (2)$$

$$\delta = \beta/(\alpha + \beta), \qquad (3)$$

respectively. Where there are no preferential diffusions, $\alpha=(1 - \delta)$, $\beta=\delta$; where there are any, let $\Delta\alpha$ and $\Delta\beta$ be

Fig.4: Variation in hydrogen concentration and temperature of local mixture caused by difference in flamelet curvature

the changes in α and β, respectively, which causes the changes in Φ and δ as follows:

$$\Delta\Phi = (\partial\Phi/\partial\alpha)\Delta\alpha + (\partial\Phi/\partial\beta)\Delta\beta; \qquad (4)$$

$$\Delta\delta = (\partial\delta/\partial\alpha)\Delta\alpha + (\partial\delta/\partial\beta)\Delta\beta. \qquad (5)$$

Since $\Delta\alpha$ and $\Delta\beta$ are small as usual, we can obtain $\partial\Phi/\partial\alpha = (x + y/4)/X_O$; $\partial\Phi/\partial\beta = (1/2)/X_O$; $\partial\delta/\partial\alpha \approx -\delta$; $\partial\delta/\partial\beta \approx 1 - \delta$. Thus,

$$\Delta\Phi \approx \frac{(x + y/4)}{X_O}\Delta\alpha + \frac{1/2}{X_O}\Delta\beta; \qquad (6)$$

$$\Delta\delta \approx \Delta\beta - \delta(\Delta\alpha + \Delta\beta). \qquad (7)$$

As is known, the diffusion coefficient of a component in a multicomponent mixture is roughly in reverse proportion to the square-root of its molecular weight. Because the molecular weight of hydrogen, M_H, is far smaller than that of any other component in the mixture, it always diffuses excessively (more than its molar fraction) to the convex flamelet; therefore, $\Delta\beta$ is always positive, tending to increase both Φ and δ according to Eqs.(6) and (7). However, the sign of $\Delta\alpha$ and its influence on $\Delta\Phi$ depends on the molecular weight of the hydrocarbon gas, M_{CH}. As the molecular weight of oxygen (32) is close to that of nitrogen (28), they can be regarded as a single gas (air) having a molecular weight, M_A, of about 29. Therefore,

when $M_{CH} \ll M_A$ (e.g. CH_4), $\Delta\alpha$ is positive, tending to further increase Φ; when $M_{CH} \gg M_A$ (e.g. C_3H_8), $\Delta\alpha<0$, tending to decrease Φ. In order to see the sign of $\Delta\Phi$ in Eq.(6), let

$$S = (2x + y/2)|\Delta\alpha|/\Delta\beta. \qquad (8)$$

According to Eq.(6), $\Delta\Phi$ can be positive, zero or negative, depending on whether $S<1$, $S=1$, or $S>1$. Finally, when M_{CH} is close to M_A (e.g. C_2H_6), $\Delta\alpha$ is negligible, and $\Delta\Phi$ only depends on $\Delta\beta$.

Hydrocarbon diffusion also affects the value of $\Delta\delta$ according to Eq.(7), which takes the following forms according to the value of $\Delta\alpha$:

$$\Delta\alpha < 0: \quad \Delta\delta \approx (1 - \delta)\Delta\beta + \delta|\Delta\alpha| > 0; \qquad (9)$$

$$\Delta\alpha = 0: \quad \Delta\delta \approx (1 - \delta)\Delta\beta > 0; \qquad (10)$$

$$\Delta\alpha > 0: \quad \Delta\delta \approx (1 - \delta)\Delta\beta - \delta\Delta\alpha. \qquad (11)$$

In order to know the sign of $\Delta\delta$ in Eq.(11), $\Delta\beta$ and $\Delta\alpha$ are such estimated that they are, respectively, proportional to the respective molar fractions and diffusion coefficients of hydrogen and hydrocarbon gases. Thus,

$$\Delta\beta/\Delta\alpha \approx (D_H\delta)/[D_{CH}(1 - \delta)], \qquad (12)$$

where D_H and D_{CH} are the diffusion coefficients of hydrogen and hydrocarbon, respectively. Substituting Eq.(12) into Eq.(11) yields

$$\Delta\delta \approx \delta\Delta\alpha(D_H/D_{CH} - 1). \qquad (13)$$

As D_H (about 7.1×10^{-3} m^2/s) is far greater than D_{CH} ($1.6 \sim 2\times10^{-3}$ m^2/s), considering $\Delta\alpha>0$, we obtain $\Delta\delta>0$ from Eq.(13), i.e. $\Delta\delta>0$ in all cases.

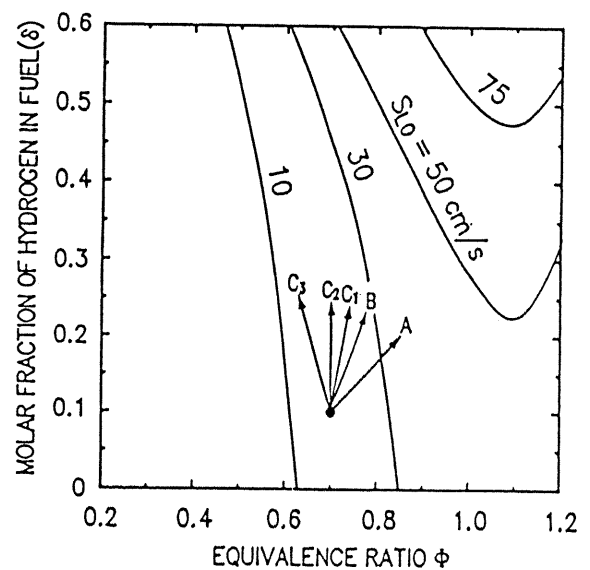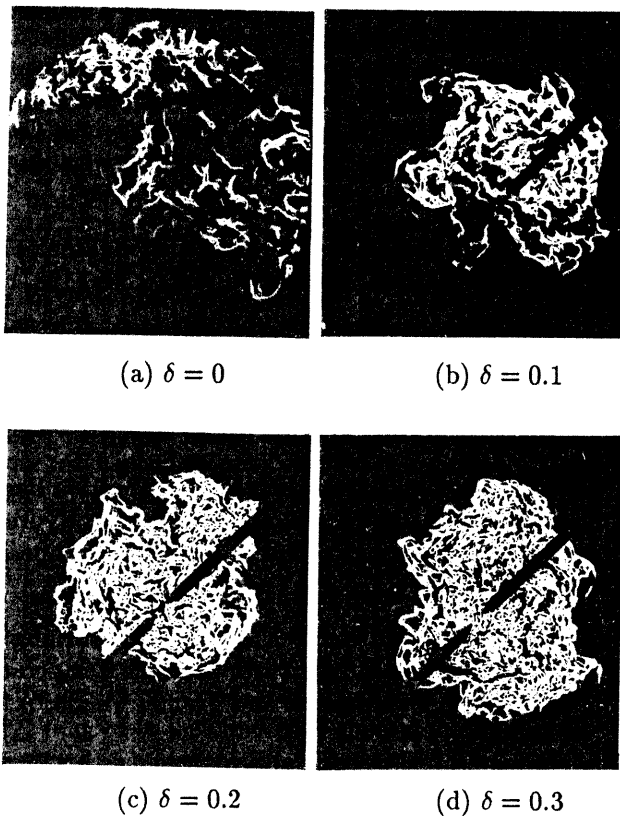With the above results, we can discuss the respective influences of methane, ethane and propane diffusions

(a) $\delta = 0$ (b) $\delta = 0.1$

(c) $\delta = 0.2$ (d) $\delta = 0.3$

Fig.5: Schlieren photographs of turbulent flames of methane/air mixtures with different amounts of hydrogen addition. u'=1.47m/s in all cases

Fig.6: Changes in composition and laminar burning velocity of local mixture because of preferential diffusions of limiting reactants. A: CH_4; B: C_2H_6; C_1: C_3H_8 ($S<1$); C_2: C_3H_8 ($S=1$); C_3: C_3H_8 ($S>1$)

on the local mixture composition of convex flamelets as follows:

Methane: In a $CH_4/H_2/AIR$ mixture, as $M_H \ll M_A$ and $M_{CH} \ll M_A$, the proportions of hydrogen and methane diffusing to the convex flamelets are greater than their respective molar fractions in the mixture. Therefore, $\Delta\beta > 0$ and $\Delta\alpha > 0$, thus $\Delta\Phi > 0$ from Eq.(6) and $\Delta\delta > 0$ from Eq.(13). The change in the local mixture composition is shown by vector **A** in Fig.6.

Ethane: In a $C_2H_6/H_2/AIR$ mixture, $M_H \ll M_A$ and $M_{CH} \approx M_A$, therefore, $\Delta\beta > 0$ and $\Delta\alpha \approx 0$. Consequently, $\Delta\Phi > 0$ from Eq.(6) and $\Delta\delta > 0$ from Eq.(10). The change in the local mixture composition is shown in Fig.6 by vector **B**.

Propane: In a $C_3H_8/H_2/AIR$ mixture, as $M_H \ll M_A$ and $M_{CH} \gg M_A$, therefore, $\Delta\beta > 0$ and $\Delta\alpha < 0$. Thus $\Delta\delta > 0$ from Eq.(9), but $\Delta\Phi$ can be negative, zero, or positive as analyzed above. The changes in the composition of the local mixture is shown in Fig.6 by 3 vectors C_1, C_2, and C_3, which represent when $\Delta\Phi$ is positive, zero and negative, respectively.

Note that the contour data in Fig.6 are cited from Fig.2, the data of methane mixture, as the contour shape is similar to that of ethane or propane mixture[8], we here use the same contours to discuss ethane and propane mixtures to save space. Comparing vectors **A**, **B** and **C** (including C_1, C_2 and C_3) in Fig.6, it is obvious that, the increase in the laminar burning velocity becomes less steeper from the direction of vector **A** to that of vector **C**. As the increase in the convex flamelet local burning velocity makes significant contributions to the turbulent burning velocity, this explains why the increases in the turbulent burning velocity depend on the hydrocarbon in the mixture; the smaller the hydrocarbon molecules, the more significant such increases (see Fig.3).

We have mainly discussed the change in the composition of the local mixture at the convex flamelets, caused by the preferential diffusions of hydrogen and hydrocarbon gases, and its effect on the local laminar burning velocity. As preferential diffusions should have also changed the local temperature that is another important factor affecting both the local laminar burning velocity and the quenching limit, in order to understand thoroughly the combustion of lean mixture with hydrogen addition, such temperature changes should be analyzed in the future work.

Conclusions

(1) Adding a small amount of hydrogen to a lean hydrocarbon mixture can substantially increases its turbulent burning velocity and largely extend its quenching limit; therefore the lean burn engines can operate at much higher speed without misfires.

(2) The more the hydrogen addition, the more the quenching limit is extended, and so is the turbulent burning velocity increased. For practical uses, adding about 3% of hydrogen (weight percentage in total fuel) to lean methane/air mixture is considered enough to increase its burning velocity and extend its quenching limit.

(3) The effects of extending the quenching limit and increasing the turbulent burning velocity by hydrogen addition depend on the molecular weight of the hydrocarbon; the lesser the molecular weight of the hydrocarbon involved in the lean mixture, the more significant such effects are. Moreover, such effects can be qualitatively explained by the effect of preferential diffusions of limiting reactants (fuel gases) of the mixture.

References

1. Iguchi, S. Current Status and Problem of Efficiency Improvement with Lean Burn, Journal of JSAE (in Japanese with English summary). Vol.45, No.8, p.18-24 (1991)

2. Akishino, K. On Lean Burning with Barrel Stratified Charge, Pre-print of 69th JSME Spring Annual Meeting (in Japanese) Vol.D, p.220-222 (1992)

3. Horie, K. Development of a Low Fuel Consumption, High Output 4-Valve Lean Burn Engine, Pre-print of 69th JSME Spring Annual Meeting (in Japanese), Vol.D, p.223-226 (1992)

4. Nakanishi, K. Development of Lean Burn Engines in TOYOTA, Pre-print of 69th JSME Spring Annual Meeting (in Japanese), Vol.D, p.227-231 (1992)

5. Kido, H. et al. Experimental Studies on the Turbulent Burning Velocities of Premixed Mixtures in a Closed Bomb, Transactions of JSME (in Japanese with English summary), Vol.52, No.480, p.3084-3090 (1986)

6. Lewis, B. and von Eble, G. F. Combustion, Flames and Explosions, 3rd Ed., Academic Press, p.389 (1987)

7. Babkin, V. S., Babushok, V. I. and Suyushev, V. A. Dynamics of Turbulent Gas Combustion in a Closed Volume, Combustion, Explosion, and Shock Waves, Vol.13, No.3, p.291-295 (1978)

8. Kido, H., Huang, S., and Nitta, T. Combustion Performance of Lean Hydrocarbon Mixture with Hydrogen Addition, Proceedings of 30th (Japanese) Symposium on Combustion, p.112-114 (1992)

9. Metghalchi, M. and Keck, J. C. Laminar Burning Velocity of Propane-Air Mixtures at High Temperature and Pressure, Combustion and Flame, Vol.38, p.143-154 (1980)