Effects of hydrogen addition on soot formation in pyrolysis of iso-octane behind a reflected shock wave

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Abstract
This paper discusses the effects of hydrogen addition on soot formation in iso-octane pyrolysis using a shock tube. In the experiments, 1% iso-C₈H₁₈ + 99% Ar and 1% iso-C₈H₁₈ + 1% H₂ + 98% Ar are used as a test gas in the temperature range of 1800-2600 K and in the pressure of 1.2 ± 0.1 MPa behind a reflected shock wave. Soot formation process was characterized by induction time and soot volume fraction, which is obtained from laser light extinction measurement. In addition, time history of soot particles temperature was calculated based on spectral dependence of monochromatic emissive power from thermal radiation from the soot particles. The experimental results show that soot formation had bell-shaped temperature dependence exhibiting maximum at 2000 K with and without hydrogen addition. Adding hydrogen to iso-octane, soot volume fraction reduced for T₅ = 1800 K. Additionally, induction time increased for T₅ = 1800 K and 2000 K. Soot particle temperature Tₚ was higher than T₅ by about 200-400 K except for around 1800 K. Consequently, hydrogen addition to iso-octane suppressed soot formation for T₅ = 1800 K, while no distinct effects of hydrogen addition were observed for T₅ = 2000 K and 2500 K.

Key words : Soot Formation, Soot Particle Temperature, iso-Octane Pyrolysis, Hydrogen Addition, Reflected Shock Wave

1. Introduction

From recent global-level environmental protection, demand for lower emissions from internal combustion engines and industrial burners has been increasing. To reduce emission of particulate matters (PM) such as soot particles originated from diesel engines is especially important, because it has been strictly regulated. Furthermore, emission regulation of DI spark ignition engines is introduced from the Japanese Government Regulation Policy of “Post new long term” established in 2009 (Ministry of Land, Infrastructure, Transport and Tourism in Japan, 2015). It is essential, therefore, to develop methods of PM suppression.

The soot formation process in pyrolysis of acetylene and other hydrocarbons has been studied experimentally and theoretically in many papers during about last five decades (Knorre, et al., 1996; Krestinin, 2000; Woiki, et al., 2000). Wang et al. have proposed HACA (hydrogen abstraction – carbon addition) soot growth model, which is the detailed kinetic mechanism both for pyrolysis initiation and soot growth (Wang, et al., 1997). According to HACA, hydrogen and acetylene play the essential role in soot formation. HACA in benzene which is one of the aromatic hydrocarbons produces soot precursor PAH (polycyclic aromatic hydrocarbon) with reiterating cyclization reaction. Thereafter, PAH becomes kernels of soot particles during their growth and then primary particles are generated by addition reaction of PAH and acetylene etc.

From this proposal, some of experiments were performed regarding the effects of hydrogen addition on soot formation in pyrolysis of acetylene in order to suppress soot particles. Eremin et al. have investigated the effects of hydrogen addition on soot formation in acetylene pyrolysis using a shock tube (Eremin, et al., 2012). They have reported that the hydrogen addition causes significant increase in induction time of soot formation and decrease of soot particle size. This is due to decrease in reaction rate of acetylene pyrolysis resulting from change of pyrolysis reaction path and increase of...
activation energy. The reaction path of acetylene pyrolysis is (R1)-(R4) shown below:

\[
\begin{align*}
    & H + C_2H_2 = C_2H + H_2 & (R1) \\
    & C_2H + C_2H_2 = C_4H_2 + H & (R2) \\
    & 2C_2H_2 = C_4H_3 + H & (R3) \\
    & C_4H_3 = C_4H_2 + H & (R4)
\end{align*}
\]

The main channel of acetylene pyrolysis is the reaction (R3). However, the bottleneck of this chain is the reaction (R1). Hydrogen addition suppresses the reaction (R1) by shift equilibrium. From these results, the reactions (R3) and (R4) are the main path of acetylene pyrolysis and C4H2 formation, which is main species for particle formation. Similarly, Knorre et al. have obtained the same effects of hydrogen addition on soot formation from acetylene and ethylene, and found that hydrogen affects soot precursors formation at the beginning of the pyrolysis process (Knorre, et al., 1996).

However, because gasoline, whose main component is iso-octane, is used in actual SI engines, it is necessary to study the effects of hydrogen addition on soot formation in pyrolysis of iso-octane. In the present work, based on these past studies, hydrogen has been added to iso-octane in a shock tube study. Soot formation process behind a reflected shock wave has been experimentally studied with optical measurements.

2. Experimental

Schematic of a double-diaphragm-type shock tube used in the present work is shown in Fig. 1. It has an inner diameter of 100 mm and consists of a 4380 mm long low pressure section, a 200 mm long middle pressure section, and a 2000 mm long high pressure section. A shock tube was used to obtain high temperature and high pressure field where iso-octane pyrolysis was induced, because temperature and pressure behind a reflected shock wave can be assumed constant for a certain period. Shock speed and the pressure history of the incident shock wave were measured with four piezo-electric pressure transducers. The diaphragm made of PET was ruptured by pressure difference between the driver section and driven section. This diaphragm rupture was triggered by evacuating the middle pressure section. Temperature behind a reflected shock wave were calculated from the shock speed of the incident shock wave and were ranged from 1800 K to 2600 K, while the pressure was kept 1.2 ± 0.1 MPa. The test gas mixture, which is composed of iso-octane, hydrogen and argon in volume was prepared manometrically in a mixture cylinder. In the experiments, 1% iso-C8H18 + 99% Ar and 1% iso-C8H18 + 1% H2 + 98% Ar were used as a test gas. The ratio of hydrogen addition to iso-octane was determined to be 1% which means the same amount of hydrogen towards iso-octane (Eremin, et al., 2012).

Soot formation was observed by using two optical methods: (1) Laser extinction method, (2) Spectral measurement of thermal radiation from soot particles.
2.1 Laser extinction measurement

To measure soot volume fraction laser extinction measurement was conducted. Selected laser wavelength was 632.8 nm (He-Ne laser; NEC, GLG-5000, 0.5 mW) and intensity of the transmitted laser was measured by a photomultiplier (Hamamatsu R457) as shown in Fig. 2. Extinction of monochromatic light at wavelength $\lambda$ is based on Beer-Lambert law as follows (Mathieu, et al., 2009):

$$\frac{I}{I_0} = \exp(-C_{ext}N_sL), \quad (1)$$

where, $I_0$ is intensity of the incident light and $I$ is intensity of the transmitted light through the column $L$ including absorbing species with concentration of $N_s$, and $C_{ext}$ is the extinction cross section. On the assumption that the soot particle diameter is much smaller than the wavelength of the light source $\lambda$, Eq. (1) can be formulated,

$$\ln\left(\frac{I}{I_0}\right) = -36\pi \frac{n^2 \kappa L}{Z} N_s V_s, \quad (2)$$

$$Z = (n^2 + n^2 \kappa^2)^2 + 4\left(n^2 - n^2 \kappa^2\right) + 4. \quad (3)$$

The variables $n$ and $nk$ are the real and imaginary part of complex index of soot particles, respectively. In this work, $n = 1.57$ and $nk = 0.44$ at 632.8 nm were used (Dalzel and Sarofim, 1969). The time history of total soot volume $N_sV_s$ is obtained using Eq. (2). Typical temporal profile of laser light extinction for iso-octane pyrolysis is shown in Fig. 3.

![Fig. 2. Optical setup of laser extinction measurement and spectral measurement of thermal radiation from soot particles.](image)

![Fig. 3. Temporal profile of laser light extinction at 632 nm for iso-octane pyrolysis for $T_3 = 2030$ K.](image)
2.2 Spectral measurement of thermal radiation from soot particles

The monochromatic emissive power of the soot particles were measured at the eight wavelengths of 0.630, 0.804, 1.12, 1.52, 2.30, 3.32, 3.39 and 4.26 μm using interference filters. From Hottel-Broughton equation, the spectral intensity of soot particles is described as follows (Hottel and Broughton, 1932):

\[
E_\lambda = \left\{1 - \exp\left(-\frac{k c L}{\lambda^{0.95}}\right)\right\} \cdot \frac{C_1}{\lambda^5 \left\{\exp\left(\frac{C_2}{T_p \cdot \lambda}\right) - 1\right\}},
\]

where, \(C_1\) and \(C_2\) are Planck’s first and second constant, respectively. Soot particles temperature \(T_p\) and the value of optical density \(k c L\) were calculated from the least squares fitting of monochromatic emissive power as shown in Fig. 4.

![Image of monochromatic emissive powers for iso-octane pyrolysis](image)

**Fig. 4.** Monochromatic emissive powers for iso-octane pyrolysis: \(T = 2030\) K, \(P = 1.23\) MPa. Solid circles denotes monochromatic emissive powers and solid lines indicate the best-fit curve based on the least square method.

3. Results and Discussion

3.1 Definition of symbols characterizing soot formation

Figure 5 shows a typical temporal profile of \(NsVs\) and \(k c L\) for iso-octane pyrolysis. The moment at which a reflected shock wave passed the observation window is time zero \((t = 0)\). Here, induction time \(\tau\) is defined as the time between the moment of reflected shock wave passage and the intersection of \(NsVs\) and \(k c L\) tangent with the time axis as shown in Fig. 5. After the induction time, \(N s V s\) begins to increase and reaches the maximum value. \(N s V s|t = 1.0\) is defined as the value of \(N s V s\) at \(t = 1.0\) ms corresponding to almost available test time in all the test condition. Soot growth rate \(d N s V s/dt\) is calculated from temporal gradient of \(N s V s\).

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3.2 Soot formation

3.2.1 Temperature dependence of $N_{sVs_{t}} = 1.0$

Figure 6 shows temperature dependence of $N_{sVs_{t}} = 1.0$ with and without hydrogen addition to iso-octane. Plots of $N_{sVs_{t}} = 1.0$ show the so-called bell-shaped temperature dependence reported in previous papers (Ohashi, et al., 2009; Hong, et al., 2009; Douce, et al., 2000). $N_{sVs_{t}} = 1.0$ plots exhibit a pronounced maximum at 2000 K. Additionally, $N_{sVs_{t}} = 1.0$ increases steeply in the low temperature range from 1800 K to 2000 K, and decreases gently in the high temperature range over 2000 K. This trend has been indicated by Akihama et al. (Akihama, et al., 2001). They report that steep increase in $N_{sVs_{t}} = 1.0$ in the low temperature range results from less soot formation due to inhibition of PAH formation and soot surface growth around 1800 K. Conversely, gradual decrease in $N_{sVs_{t}} = 1.0$ in the high temperature range is accounted for by less temperature dependence of soot decomposition reaction. These results indicate hydrogen addition suppresses $N_{sVs_{t}} = 1.0$ around 1800 K. Additionally, no effect of hydrogen addition on $N_{sVs_{t}} = 1.0$ and soot growth rate over 2000 K was observed.
3.2.2 Temporal profile of $N_sV_s$

Figure 7 (a) and (b) show temporal profile of $N_sV_s$ at 1800 ± 50 K and 2000 ± 50 K, respectively. At 1800 ± 50 K as shown in Fig. 7 (a), addition of hydrogen clearly reduces $N_sV_s$ and increases the induction time. This is because the reaction rate of acetylene pyrolysis decreases, which is due to the change of acetylene reaction path in PAH formation at the beginning of soot formation process. At 2000 ± 50 K as shown in Fig. 7 (b), little effects of hydrogen addition on $N_sV_s$ was observed. However, adding hydrogen to iso-octane leads to increase in the induction time obviously. At 2500 ± 50 K, significant change of soot formation is not detected with and without hydrogen addition. In contrast, the soot growth rate decreases at 1800 ± 50 K with hydrogen addition and unchanged over the bell peak of 2000 K.

Mathieu et al. have found that soot volume fraction in hydrogen addition to heavy hydrocarbon C$_9$H$_{18}$ (propyl-cyclohexane) decreases at low temperatures in regard to the bell peak owing to the decrease of PAH (Mathieu, et al., 2009). They reported that the suppression effect of hydrogen addition is partly due to the decrease in the rate of soot inception and in the rate of surface growth via PAHs. Reduction of the surface growth, regardless of the considered species (i.e., C$_2$H$_2$, PAHs), was also observed. This reduction has been found to be due to the deactivation of active surface sites by hydrogen radical additions. In contrast, soot volume fraction is almost unchanged at high temperatures. This trend coincide well with the experimental results as shown in Fig. 7.

![Graph showing temporal profile of $N_sV_s$](image)

**Fig. 7.** Temporal profile of $N_sV_s$ with and without H$_2$ addition to iso-octane.

3.2.3 Temperature dependence of induction time

Figure 8 shows temperature dependence of induction time $\tau$ in the Arrhenius plot. The induction time decreases with increase in the ambient temperature regardless of hydrogen addition. Adding hydrogen prolongs the induction time both in the low temperatures and around the bell peak, as shown in Fig. 7 (a), (b) and Fig. 8. It is also shown that the difference in the induction time between with and without hydrogen addition decreases with increase in the ambient temperature. This difference is approximately 0.15 ms at 1800 ± 50 K and 0.05 ms at 2000 ± 50 K. In the high temperature around 2500 K, no effect of hydrogen addition on induction time can be found.

These results correspond well with a previous paper (Eremin, et al., 2012). Hydrogen addition changes the temperature dependence of the induction time. From these results it is found that hydrogen addition increases activation energy $E_a$, which indicates, therefore, that reaction rate of acetylene pyrolysis and formation rate of PAH are suppressed.
3.3 Soot particle temperature

Figure 9 (a) and (b) show temporal profiles of soot particle temperature $T_P$ at $1800 \pm 20$ K and $2000 \pm 50$ K, respectively. The strong oscillation of $T_P$ observed in the early stage of soot formation process is caused by insufficient detection of soot particles because of low soot volume fraction as shown in Fig. 7. Thus the soot particle temperature in this oscillation period is not applicable. It is shown that $T_P$ is higher than the initial ambient temperature $T_5$ by about 200-400 K except for considerable small soot formation around 1800 K. This is due to heat release during the soot particle formation process. This result that the soot particle temperatures differs from the initial ambient temperature has been reported by Emelianov et al. (Emelianov, et al., 2005). At $1800 \pm 20$ K as shown in Fig. 9 (a), $T_P$ increases until the end of observation time with and without hydrogen addition. It must be noted that hydrogen addition decreases $T_P$, which is due to the suppression of soot particle formation around 1800 K. At $2000 \pm 50$ K as shown in Fig. 9 (b), hydrogen addition delays of the rise of $T_P$, which is coincide with the delay of the induction time. As in the case of $N_sV_s$, no effect of hydrogen addition on $T_P$ was observed.
4. Conclusion

Soot formation in pyrolysis of iso-octane with and without hydrogen addition behind a reflected shock wave have been studied using the laser extinction method and spectral measurement of thermal radiation from soot particles. The following conclusions have been obtained.

1. Temperature dependence of soot formation in pyrolysis of iso-octane shows the bell shape exhibiting a pronounced maximum at 2000 K.
2. Around 1800 K, hydrogen addition clearly suppresses soot formation, while in contrast, soot volume fraction is almost unchanged around 2000 K and 2500 K.
3. The induction time decreases with increase in the ambient temperature with and without hydrogen addition. Additionally, hydrogen addition prolongs the induction time in the low temperatures and around the bell peak temperature.
4. The soot particle temperature is higher than the ambient temperature by about 200-400 K except for the considerable small soot formation around 1800 K in the case of hydrogen addition.
5. Around 2000 K, hydrogen addition delays the rise of the soot particle temperature similar to the delay of the induction time.

Nomenclature

\begin{align*}
C_{ext} & \quad \text{extinction cross section} \ [m^2] \\
C_1 & \quad \text{Plank’s first radiation constant} (=3.74\times10^5 \ [kW \ \mu m^4/m^2]) \\
C_2 & \quad \text{Plank’s second radiation constant} (=1.44\times10^4 \ [\mu m^4 \ K]) \\
c & \quad \text{volume concentration of soot particles} \\
E_a & \quad \text{activation energy} \ [kJ/mol] \\
E_\lambda & \quad \text{monochromatic light emissivity} \ [kW/m^2 \ \mu m] \\
I & \quad \text{intensity of transmitted laser light} \\
I_0 & \quad \text{intensity of incident laser light} \\
k & \quad \text{arbitrary constant} \\
L & \quad \text{optical path length of absorbing laser light} \ [m] \\
N_s & \quad \text{number density of particles} \ [\text{number of particles/m}^3] \\
n & \quad \text{real part of complex refractive index of soot particles} \\
n_k & \quad \text{imaginary part of complex refractive index of soot particles} \\
P_5 & \quad \text{pressure behind a reflected shock wave} \ [Pa] \\
T_p & \quad \text{temperature of soot particles} \ [K] \\
T_s & \quad \text{temperature behind a reflected shock wave} \ [K] \\
V_s & \quad \text{volume of particle} \ [m^3/\text{number of particles}]
\end{align*}

Greek symbols

\begin{align*}
\lambda & \quad \text{wavelength} \ [m]
\end{align*}

References