# Soot Formation in Hydrocarbon Pyrolysis behind Reflected Shock Waves

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## 1 Introduction

Soot formation is one of the important subjects in combustion research, in particular for reduction of soot emitted from diesel engines and industrial burners. It is known that soot yield in hydrocarbon pyrolysis starts at about 1300 K, passes through a maximum near 1700-1800 K, and decreases toward higher temperatures [1]. This behavior of the soot yield is presented by a bell-shaped curve as a function of temperature [2]. However, in shock-tube experiments the ambient gas temperature can be changed owing to heat release through soot formation process [3], which leads to necessity of consideration of the real soot particles temperature.

In the present work pyrolysis of acetylene, n-hexane, and benzene has been studied using a shock tube at various temperatures and fuel concentrations. The soot yield was obtained from the laser extinction measurement, while the soot particles temperature was estimated from spectral measurement of thermal radiation from soot.

## 2 Experimental

The experiments were performed behind reflected shock waves in a 100-mm i.d. aluminum shock tube with a 3795mm long driven section and a 1700mm long driver section. Speed of the incident shock wave was measured by three piezoelectric pressure transducers. In the present study two kinds of optical measurements were conducted as shown in Fig. 1. One is laser extinction method using He-Ne laser with wavelength of 632.8 nm for measurement of soot concentration. Intensity of the transmitted laser power was detected by a photomultiplier. Based on the assumption that the soot particle is much smaller as compared to the wavelength of the laser light, volumetric concentration of soot particles can be calculated from the ratio of intensity of the incident and transmitted laser light. In the calculation the real and imaginary part of complex index of soot particles were 1.57 and 0.44, respectively [4]. The other is spectral measurement of thermal radiation from soot particles for estimation of the soot particles temperature. Using Hottel-Broughton equation [5], monochromatic emissive power of soot particles $E_\lambda$ is given as

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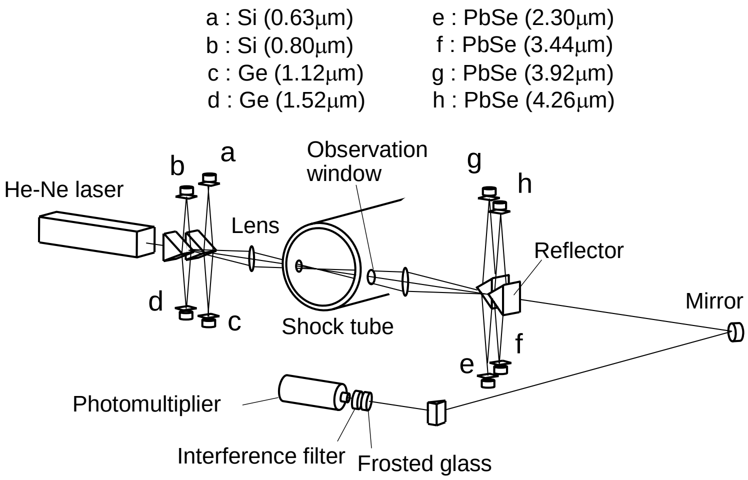


Figure 1. Optical setup of laser extinction measurement and spectral measurement of thermal radiation from soot particles.

$$E_{\lambda} = \left\{1 - \exp\left(-\frac{kcl}{\lambda^{0.95}}\right)\right\} \times \frac{C_1}{\lambda^5\left\{\exp\left(\frac{C_2}{T_p\lambda}\right) - 1\right\}}, \tag{1}$$

where, $C_1$, $C_2$, $kcl$, $\lambda$, $T_p$ denote the first and the second radiation constant, optical thickness, wavelength, and soot particles temperature, respectively. In the present study the monochromatic emissive power of soot particles was detected at eight wavelengths of 0.630, 0.804, 1.12, 1.52, 2.30, 3.32, 3.39, and 4.26 μm. Then the combination of $T_p$ and $kcl$ which satisfies Eq. 1 was obtained from the least squares fitting.

The test gas mixture composed of a hydrocarbon fuel and argon was prepared manometrically in a mixing vessel. As for the hydrocarbon fuel, benzene, n-hexane, and acetylene were used. Test ranges of fuel concentration, temperature, pressure, and total density behind the reflected shock wave were summarized in Table 1.

Table 1: Experimental conditions.

| Fuel | Volumetric percentage of fuel | $T_5$ (K) | $P_5$ (bar) | $\rho_5 \times 10^{-5}$ (mol/cm$^3$) |
|---|---|---|---|---|
| benzene | 0.5 | 1710 - 2340 | 4.1 - 8.0 | 2.29 - 5.74 |
| | 1.0 | 1600 - 2690 | 1.6 - 8.8 | 0.87 - 6.39 |
| n-hexane | 1.0 | 1910 - 2520 | 3.9 - 8.3 | 2.06 - 8.36 |
| | 2.0 | 2130 - 2600 | 1.4 - 2.2 | 1.47 - 2.25 |
| acetylene | 1.0 | 1680 - 2370 | 4.9 - 10.0 | 2.76 - 5.63 |
| | 2.0 | 1760 - 2080 | 2.5 - 3.3 | 2.54 - 3.32 |

# 3 Results and discussion

## 3.1 Soot yield

From the volumetric soot concentration obtained from the laser extinction measurement, soot yield was estimated as conversion ratio of carbon contained in the fuel to soot particles. Figure 2 shows

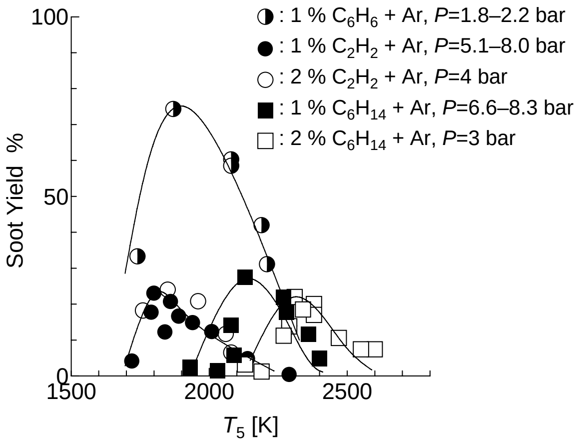


Figure 2. Temperature dependence of soot yield for benzene, n-hexane, and acetylene pyrolysis.

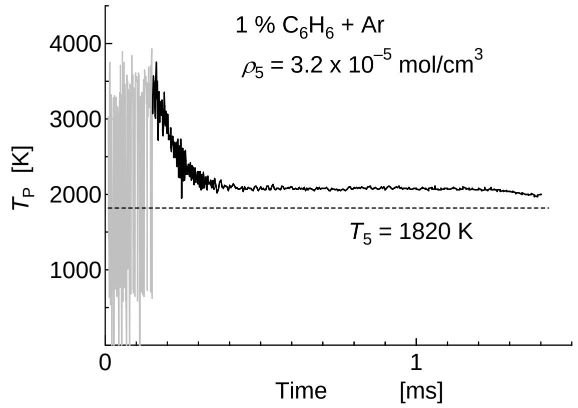


Figure 3. Typical temporal profile of soot particles temperature for benzene pyrolysis.

effects of temperature on the soot yield for various hydrocarbon fuels. It is confirmed that the soot yield displays the well-known bell-shaped temperature dependence [1, 2 ]. Maximum value of the soot yield is obtained at about 1800 K for acetylene, 1900 K for benzene. As for n-hexane, increase in fuel concentration causes shift of the temperature giving the maximum soot yield from 2100 to 2300 K.

### 3.2 Soot particles temperature

Figure 3 shows the typical result of soot particles temperature in benzene pyrolysis obtained from the spectral measurement of thermal radiation. At the early stage of the soot formation process, the soot particle temperature $T_p$ is remarkably higher than the ambient temperature at pyrolysis starting behind the reflected shock wave $T_5$, which may be accounted for release of latent heat in the phase change process from a gas to a solid of soot. Then the heat transfer between the soot particles and the ambient gas causes gradual decrease of $T_p$. However, it is shown in Fig. 3 that $T_p$ is not consistent with $T_5$ at the late stage of soot formation process and still shows higher value. It is unlikely that the soot particles temperature differs from temperature of the ambient gas even at 1 ms, since, for instance, in laser-induced incandescence measurements the soot particles temperature reaches the ambient temperature

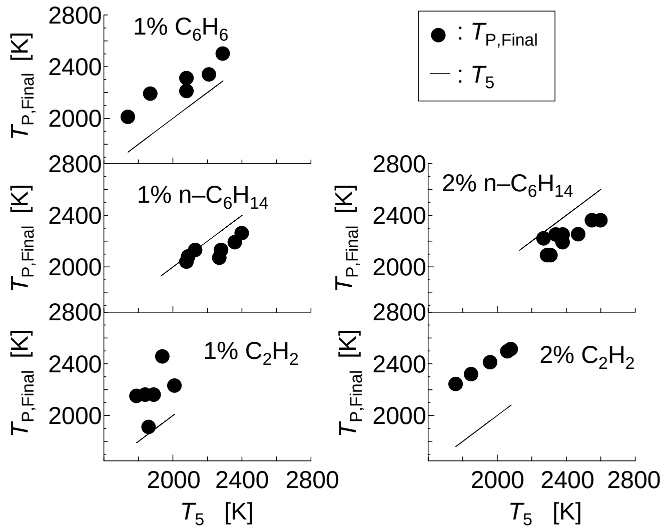


Fig. 4. Relation between $T_5$ and $T_{p,final}$ in hydrocarbon pyrolysis.

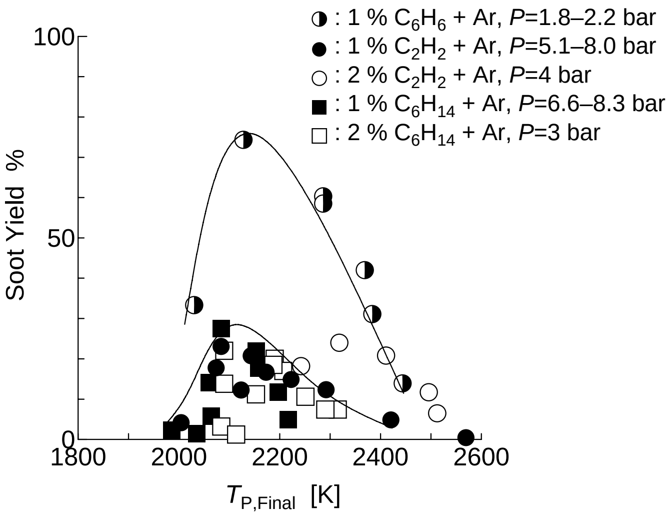


Figure 5. Soot yield versus final soot particles temperature for benzene, n-hexane, and acetylene pyrolysis.

in a few microseconds after laser heating. From the discrepancy between $T_p$ and $T_5$, final soot particles temperature $T_{p,final}$ was defined as the measured soot particle temperature at 1 ms. As shown in Fig. 4, behavior of $T_{p,final}$ is dependent on the type of hydrocarbon fuel. In pyrolysis of benzene and acetylene, the fact that $T_{p,final}$ is higher than $T_5$ indicates that exothermic reactions are dominant in soot formation process, while endothermic reactions occurs in pyrolysis of n-hexane. Since soot growth reactions proceed on the surface of the soot particles, these results suggest that the soot yield should be related to the soot particle temperature [3]. From this, temperature dependence of the soot yield has been rearranged as shown in Fig. 5. It is found that the temperature showing the maximum soot yield is about 2100 K and is independent of the type of hydrocarbon fuel, pressure, and fuel concentration.

## 4 Summary

The pyrolysis of hydrocarbon fuels behind the reflected shock wave was experimentally studied using optical methods. The results show that the soot particle temperature, which differs substantially from the ambient temperature at pyrolysis starting behind the reflected shock wave, governs the final soot yield.

## References

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