A Study on Soot Formation in Premixed Constant-Volume Propane Combustion

(Effects of Pressure, Temperature and Equivalence Ratio)

Myung-whan Bae* and Kwang-sun Kim*

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The effects of pressure, temperature and equivalence ratio on soot formation in premixed propane-oxygen-inert gas combustion have been investigated over wide ranges of pressure (0.1 to 6 MPa), temperature (1200 to 2100 K) and equivalence ratio (1.5 to 2.7) in a specially designed disk-type constant-volume combustion chamber. To observe the soot formation under high pressure, premixtures are simultaneously ignited by eight spark plugs located on the circumference of chamber at 45 degree intervals. The eight converging flames compress the end gases to a high pressure. The soot volume fraction in the chamber center during the final stage of combustion at the highest pressure is measured by the in situ laser extinction technique and the burnt gas temperature during the same period by the two-color pyrometry method. The pressure and temperature during soot formation are varied by changing the initial charge pressure and by changing the volume fraction of inert gas in the premixture, respectively. It is found that the soot yield is dependent on the pressure, temperature and equivalence ratio, and the soot yield increases under the following conditions ; (1)decreasing temperature and increasing equivalence ratio at constant pressure, (2)increasing pressure and decreasing temperature at constant equivalence ratio, (3)increasing equivalence ratio at constant temperature and pressure.

1. Introduction

The reduction of soot emission from practical combustion devices, such as diesel engines, gas turbines and modern power stations, has become an issue of great importance. Therefore, many investigations have examined the effect of various parameters, such as fuel structure, mixture strength and temperature, on soot formation, but most of these studies have been performed at subatmospheric or atmospheric pressures. The technical combustion devices as mentioned above generally employ a diffusion controlled combus-

tion, and the combustion processes in these devices proceed at substantially above atmospheric pressure. It appears difficult, however, to investigate soot formation in diffusion flames because diffusion flames have complicated structure which features uneven mixture strength, temperature and flow velocities. Accordingly, this study focuses on the effect of various parameters on soot formation at elevated pressures to provide a fundamental data in premixed, constant-volume combustion.

Among these parameters, temperature has been found to suppress soot formation at high temperatures. Baumgärtner et al.(1983) conducted an experiment with an atmospheric ethylene-air flat flame at C/O ratio of 0.87 and showed that a 150 K increase in flame temperature reduces the soot volume fraction by one order. Takahashi et al.

* Department of Mechanical Engineering for Power, Korea Institute of Technology and Education, Cheonan, 333-860, Korea

(1984) and Harris et al.(1986) investigated the effect of temperature on the sooting limit in atmospheric premixture flames and showed that the critical equivalence ratio at which the onset of luminosity is observed shifts toward the richer side as temperature is increased.

The effect of pressure on soot formation has also been investigated by several researchers. MacFarlane et al.(1964) studied soot formation in premixed flames at pressures up to 2 MPa. They found that the soot yield (soot mass/fuel-carbon mass) increases with pressure. Recently, Mätzing et al.(1986) studied the influence of pressure on soot formation in flat premixed ethylene-air flames and showed that the increase in soot volume fraction is proportional to the second to third power of pressure in the range 0. 1~0.5 MPa. But their correlation between soot volume fraction and pressure includes the effect of temperature because the flame temperature in their experiments varies from 1100 to 1900 K. On the other hand, the present authors' previous work (Kamimoto et al., 1989) isolated the effects of pressure and temperature on soot formation. They performed time resolved measurements of soot volume fraction by the laser extinction technique for a propane-oxygen-inert gas premixed, constant-volume combustion which proceeded at an equivalence ratio of 2.1 for pressures in the range 0.4~5.8 MPa. The flame temperature was controlled by changing the volume fraction of inert gas and the concentration ratio between nitrogen and argon. According to these results, both temperature and pressure are responsible for the soot yield, which was determined from the final value of soot volume fraction. The soot yield, also, increases significantly with pressure at low temperatures, but this pressure dependence becomes weak at higher temperatures.

Although the previous experiments performed by the present authors were made only for flames with an equivalence ratio of 2.1, Baumgärtner et al.(1984) and Mätzing et al.(1986) have shown that the soot yield increases with equivalence ratio. This study, therefore, attempts to extend the previous work to a wider range of equivalence ratio.

2. Experimental Apparatus and Procedures

Figure 1 shows the schematic diagram of the experimental apparatus, which includes a constant-volume combustion chamber, the optical arrangement, and data acquisition system. The disk-type combustion chamber is 100 mm in diameter and 14 mm thick. The premixed fuel rich propane (99.5%)-oxygen-inert gas mixture is drawn into the initially evacuated chamber from a high pressure mixing reservoir. The premixed reactants charged in the chamber are ignited simultaneously by eight spark plugs located on the circumference of the combustion chamber with 45 degree intervals. Then the eight laminar flames force the end gases to the center of the chamber as the flames themselves propagate to the center. Thus the combustion ends at the center of the chamber where the pressure reaches a maximum. Glass windows, 10 mm in diameter, are mounted at opposing sides of the chamber to permit optical access to the observation field.

The soot volume fraction in the observation field is measured by the in situ laser extinction technique. In this technique, the soot volume fraction is correlated to the attenuation of the laser beam ; this attenuation is caused directly by soot particles. A 1 mW He-Ne laser is used as the light source. A narrow band-pass filter (2.5 nm FWHM band-pass, central wavelength 633.2 nm) is placed in front of a photomultiplier tube (Toshiba PM55) to minimize the effect of the continuum self-emission from the luminous soot particles on the measurements. In each experiment, the
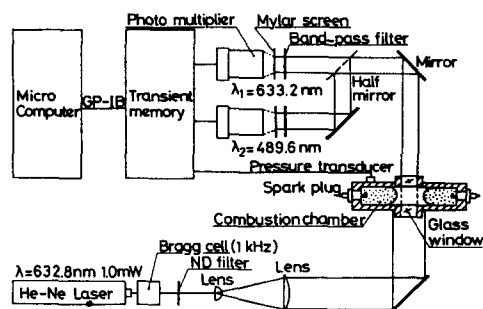

Fig. 1 Schematic diagram of the experimental arrangement

temperature of chamber walls is held 420 K to avoid the condensation of water on the observation windows. The transmissivity(τ_λ) at wavelength(λ_1) through a pathlength(L) of particle is related to the soot volume fraction, fv, by Lambert-Beer's law and the Rayleigh theory :

$$\tau_\lambda = \exp[6\pi L/\lambda_1 \cdot Im\{(m^2-1)/(m^2+2)\} \cdot fv] \quad (1)$$

In this study complex refractive index(m) measured by Dalzell and Sarofim(1969), $m = 1.56 - 0.52i$, is used.

The soot volume fraction, fv, depends on not only the extent of soot formation but also the amount of charged fuel. Therefore, the soot formation ratio, Cs, which is defined in terms of a percentage of the soot to the carbon content of the original fuel in the mixture, is more appropriate for evaluating the sooting tendency. Cs in normal paraffins, C_nH_{2n+2}, is calculated by the following expression :

$$Cs = (7n+1)/6n \cdot \{1 + 1/(\phi \cdot fst)\} \cdot \{1/(1-DRm)\} \cdot (\rho_s/\rho_{bg}) \cdot fv \quad (2)$$

where ϕ is the equivalence ratio of the premixture, fst is the stoichiometric fuel-oxygen ratio, DRm is the volume fraction of the inert gas to the total mixture, ρ_s is the density of the soot particles, 1.8 g/cm^3, and ρ_{bg} is the density of burnt gas at the observation field where fv is measured.

The flame temperature is measured by the two-color pyrometry method which is based on the continuous emission from high temperature soot particles. The temperature, T_{bg}, can be calculated from the radiation intensities E_1 and E_2, which are measured at wavelengths λ_1 and λ_2 respectively, by the following equation :

$$T_{bg} = \frac{C_2(1/\lambda_1 - 1/\lambda_2)}{ln\{\alpha_1/\alpha_2 \cdot \varepsilon_1/\varepsilon_2 \cdot E_2/E_1 \cdot (\lambda_2/\lambda_1)^5\}} \quad (3)$$

where C_2 is the second radiation constant, λ is effective wavelength, and ε is emissivity. The subscripts 1 and 2 indicate values at wavelength λ_1 and λ_2, respectively. The constants α_1 and α_2, which are characteristic of the optical device employed, are determined by a calibration using a black body furnace which has an emissivity of 0.981. ε_2 in the above equation is calculated from the measured value of ε_1 using Hottel's equa-

tion(1967), as follows :

$$\varepsilon_2 = 1 - (1 - \varepsilon_1)^{(\lambda_1/\lambda_2)^{1.38(Matsui\ et\ al.,\ 1988)}} \quad (4)$$

When the equivalence ratio is below 1.9, soot is generated only if the temperature is low and the amount of soot formed, furthermore, is very small. The faint radiation intensity at this condition prohibits the employment of the two-color method. Therefore, temperature is calculated based on a simple thermodynamic model for cases in which the equivalence ratio is below 1.9. If one assumes that both the specific heat and gas constant do not change before and after combustion occurs, one can calculate the density of burnt gas, ρ_{bg}, from the measured gas pressure, P, using the following expression :

$$\rho_{bg} = \frac{X}{\{1-(1-X)(P_i/P)^{1/n}\}} \cdot \rho_i \quad (5)$$

where $X = (P-P_i)/(P_m-P_i)$ is the mass fraction of burnt gas, P_i is the initial pressure, P_m is the maximum pressure, n is polytropic index, and ρ_i is the density of initial premixture. The burnt gas temperature, T_{bg}, is calculated from ρ_{bg} and P using the gas state equation. The polytropic index, n, is assumed to be 1.3, but its effect on ρ_{bg} is quite small because X is close to one in the final stage of combustion.

Figure 2 shows a set of typical time records of the total intensity (emitted+transmitted), emission intensity, pressure, soot volume fraction, and burnt gas temperature. The calculated burnt gas temperature is found to be in good agreement with the temperature measured by the two-color method. Since the pressure and temperature change with time during soot formation, the pressure and temperature which identify the gas state during soot formation are defined as the chamber pressure and temperature at the time when the value of fv becomes $(1/2) \cdot fv^*$. The data of this paper for the final soot volume fraction, fv^*, are obtained by the mean value of fv during 50 ms after fv comes to a plateau value. As an example, the mean value of fv between 301 ms and 350 ms is represented in Fig. 2 by fv^*. These values are denoted by P^* and T_{bg}^* respectively. The final soot formation ratio, i.e. soot yield, Cs^*, is calculated from the final soot volume
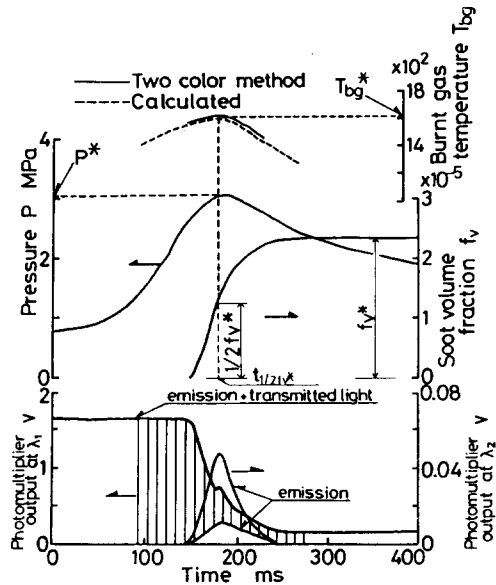
Fig. 2 Typical data of emissions, emitted + transmitted light, pressure P, soot volume fraction fv and burnt gas temperature T_{bg} as a function of time. Conditions : laminar combustion, 8 points ignition, equivalence ratio $\phi=2.2$ and initial pressure $P_i=0.81$ MPa

Fig. 3 Burnt gas temperature T_{bg}^* versus pressure P^* at equivalence ratio $\phi=2.2$ and 2.3

fraction in Fig. 2.

Some data of soot yield and burnt gas temperature at lower pressures($P^* < 0.2$ MPa) have been obtained with the extrapolation. These data, however, are of little significance for qualitative analysis because the main objective of this paper is about the soot formation at higher pressures.

3. Results and Discussions

Results for the cases of equivalence ratio $\phi=2.2$ and 2.3 are presented first. In this experiment, the inert gas volume fraction composed of nitrogen and argon was fixed to be 0.79, the same as in air, and the concentration ratio between nitrogen and argon was varied to control the burnt gas temperature. The temperature measured by the two-color method is shown against pressure P^* for the cases of $\phi=2.2$ and 2.3 in Fig. 3. It is seen from the figure that combustion at higher pressures results in higher burnt gas temperature because of the relative reduction of heat losses at higher gas
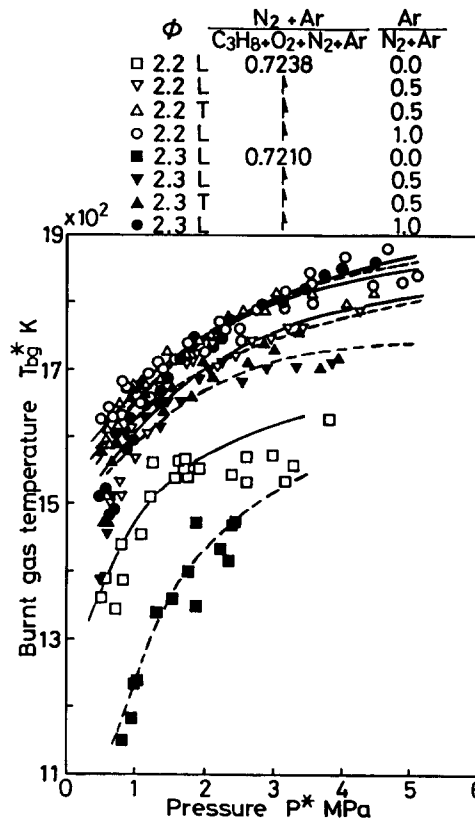
density conditions. In addition, it is also seen that T_{bg}^* increases as the volume fraction of argon is increased because the specific heat of argon is lower compared to that of nitrogen. The letter L in the figure denotes laminar combustion, while the letter T represents turbulent combustion. Turbulent combustion was generated by a turbulence generating ring, which has an inner diameter of 50 mm, an outer diameter of 52 mm, and a height of 14 mm. 27 holes(15.4% of the total area) with 4 mm diameter were drilled through the wall of the ring to allow for the passage of gas. The ring is oriented such that its center coincides with that of the chamber. As can be seen in the figure, T_{bg}^* for the turbulent combustion case is higher than that of the laminar combustion case under the same conditions because the heat loss for turbulent combustion is lower due to the short combustion period.

Figure 4 shows the correlation between the final soot yield Cs^* and P^* for the same conditions as in Fig. 3. A comparison of data between Figs. 3 and 4 indicates that the set with the higher T_{bg}^* will have a lower Cs^* from the given two sets of data. In addition, for a given data set, both Cs^* and T_{bg}^* increase proportionally with P^*. Accordingly, in order to separate the 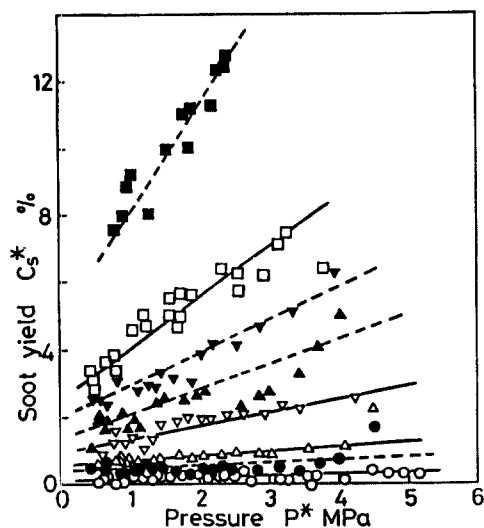effects of pressure and temperature on soot formation, it is necessary to replot Cs^* against P^* with T_{bg}^* as a parameter from the data of Figs. 3 and 4.
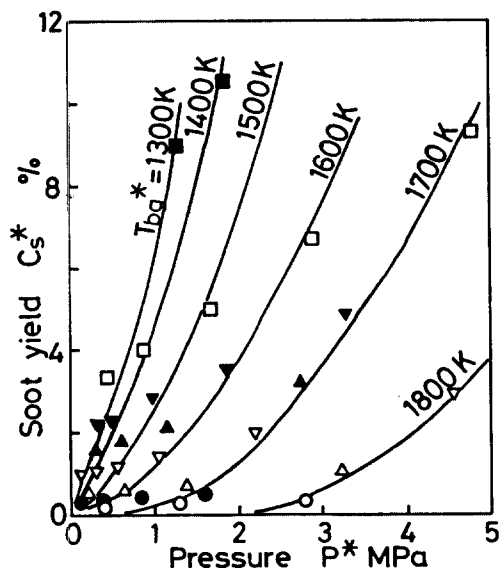
Figure 5 shows the replotted data at the equivalence ratio of 2.2 and 2.3 over the pressure range of $0.1 \sim 5$ MPa. This figure illustrates the very important result that Cs^* increases sharply with P^* at lower temperatures, but the effect of pressure is weak and Cs^* decreases as the temperature is increased. Figure 5 includes data at higher pressures than those in previous papers. Nevertheless this trend of the pressure dependence on soot yield is qualitatively consistent with the results obtained in the previous flame studies (MacFarlane et al., 1964 ; Mätzing et al., 1986 ; Kamimoto et al., 1989). On the other hand, this trend in the shock tube study is contradictory to that of flame studies. In shock tube experiments, the soot yield at high temperatures decreases with pressure because the increase in pressure promotes the fragmentation process at high temperatures. Soot formation in shock tube experiments proceeds similarly to that in premixed flames. In many of shock tube studies, however, the process of soot formation can not be completely achieved because the measuring time is limited.

As for the pressure dependence on soot yield, Mätzing et al.(1986) measured the size and number density of soot particles in flat premixed ethylene-air flames by both the scattering and extinction methods, and showed that the increase in soot volume fraction at higher pressures is mainly caused by an increase in particle size.

Figure 6 shows the relationship between Cs^* and P^* with T_{bg}^* as a parameter for equivalence ratios $\phi = 2.5$ and $\phi 2.7$. The inert gas fractions in the premixture were fixed at 0.596 and 0.464 for $\phi = 2.5$ and 2.7, respectively. The burnt gas temperature was controlled by changing the volume fraction of argon in the $Ar + N_2$. Comparing the result in Fig. 6 with that in Fig. 5, one may note that the pressure dependence of Cs^*, i.e. the gradient of each curve, is larger for the cases of $\phi = 2.5$ and 2.7 for a given T_{bg}^*.

The critical equivalence ratio, ϕ_c, which is the equivalence ratio at the onset of soot formation for atmospheric flames was found to be 1.9 for propane-air premixed flames (Olson et al., 1984).
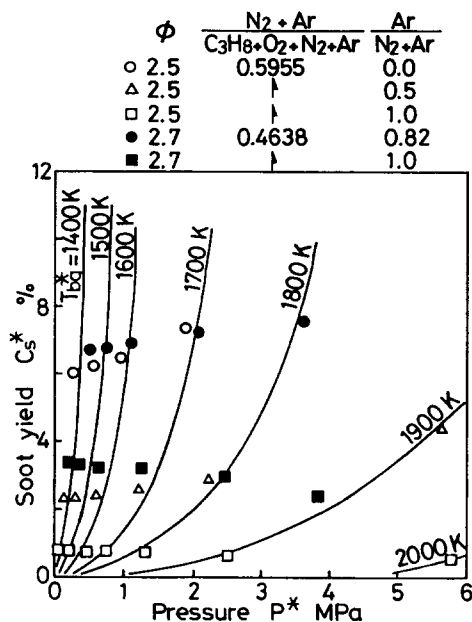

Fig. 4   Soot yield C_s^* versus P^* at $\phi = 2.2$ and 2.3

Fig. 5   Correlation between C_s^* and P^* with T_{bg}^* as a parameter at $\phi = 2.2$ and 2.3

φ	$\frac{N_2+Ar}{C_3H_8+O_2+N_2+Ar}$	$\frac{Ar}{N_2+Ar}$
o 2.5	0.5955	0.0
△ 2.5	↑	0.5
□ 2.5	↑	1.0
● 2.7	0.4638	0.82
■ 2.7	↑	1.0

φ	$\frac{N_2}{C_3H_8+O_2+N_2}$		
o 1.5	0.804	▲ 1.8	0.783
● 1.5	0.821	□ 1.9	0.768
△ 1.7	0.797		

Fig. 6 Correlation between C_s^* and P^* with T_{bg}^* as a parameter at $\phi=2.5$ and 2.7
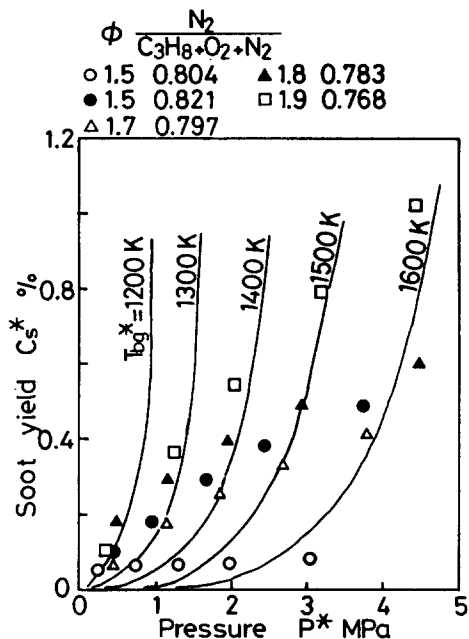
Fig. 7 Correlation between C_s^* and P^* with T_{bg}^* as a parameter at $\phi=1.5$, 1.7, 1.8 and 1.9

Since ϕ_c is known to be a function of temperature, soot formation can be observed even at leaner equivalence ratios than 1.9 if the burnt gas temperature is lowered. Hence experiments were performed over a range of equivalence ratio $\phi=$ 1.5~1.9 ; the inert gas fraction was increased to a value larger than that for the propane-air mixture experiments in order to reduce the burnt gas temperature. The results are shown in Fig. 7. A comparison of C_S^* in Fig. 7 with those in Figs. 5 and 6 indicates that at a given temperature, the magnitude of C_S^* for $\phi=1.5\sim1.9$ is approximately one-tenth of that for richer equivalence ratios. This means that the equivalence ratio has a large influence on soot formation.

From the data obtained in this study, one can express C_S^* as a function of pressure, temperature and equivalence ratio. Figure 8 illustrates the variation of C_S^* with T_{bg}^* and ϕ for each pressure. Note that temperature increases from right to left on an abscissa. The figure shows clearly that the soot yield increases with decreasing temperature and increasing equivalence ratio if pressure is kept constant, with increasing pressure if temperature and equivalence ratio are kept con-
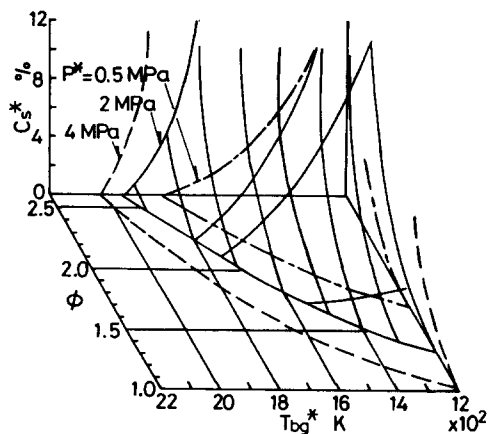
Fig. 8 C_s^* as a function of, T_{bg}^* and P^* and sooting limit.

stant, and with increasing equivalence ratio if temperature and pressure are kept constant.

A curved line is formed for each pressure on ϕ-T_{bg}^* plane along the intersection with the curved surface in Fig. 8, which expresses C_S^* as a function of ϕ and T_{bg}^*. Although the definition is different from that of the ordinary soot threshold, this curve can be regarded as a kind of sooting limit, i.e. a relationship between critical equiva-

lence ratio ϕ_c and temperature. It is obvious from the dependence of this curve with pressure that the soot formation region on the ϕ-T_{bg}^* plane expands with an increase in pressure. When the relationship between ϕ_c and T_{bg}^* with P^* as a parameter in the figure is considered as a relationship between ϕ_c and P^* with T_{bg}^* as a parameter, one may note that ϕ_c decreases with pressure at a given temperature. This trend appears to be contradictory to the result by MacFarlane et al. (1964), who stated that the critical equivalence ratio is independent on pressure. In their experiments, however, for a fixed equivalence ratio, the flame temperature increases by about 200 K when the pressure is increased from 0.58 to 1.56 MPa. Consequently, the result shown in Fig. 8 can be considered to be in quantitative agreement with that given by MacFarlane et al.(1964).

4. Conclusions

The effects of equivalence ratio, pressure and temperature on soot formation were investigated over wide ranges of equivalence ratio(1.5 to 2.7), pressure(0.1 to 6 MPa) and temperature(1200 to 2100 K) by the in situ laser extinction technique for premixed propane-oxygen-inert gas combustion in a constant-volume chamber. The experimental results obtained are as follows:

(1) The soot yield and soot threshold are dependent on the equivalence ratio, temperature and pressure.

(2) The soot yield increases with decreasing temperature and increasing pressure for the case of constant equivalence ratio.

(3) The soot yield increases as the equivalence ratio is increased if the temperature and pressure are constant. This tendency is more pronounced at higher pressures and lower temperatures.

(4) The sooting region on the ϕ-T_{bg}^* diagram expands with increases in pressure.

Acknowledgment

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