Presoot and Soot Formations in Heating of Hydrocarbon Fuels*

by

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The soluble and insoluble particles produced in heating the hydrocarbon fuel have been measured to study the sooting processes. It is shown that soluble particles called presoot in this paper can be regarded as the "precursors", composed of heavy hydrocarbon droplets, and insoluble ones are composed of soot. Methane, propane, ethylene, and acetylene were employed as the fuel. As to the methane, propane, and ethylene, it is shown that presoot are produced in endothermic reactions and the overall activation energies are determined from the Arrhenius plots of yields. In the case of acetylene, the reaction of soot formation is exothermic and presoot is not observed, because it grows into soot as soon as it forms by self-generating heat. Furthermore, it is shown that the effects of oxygen on both the presoot and soot formations are hardly detected and that the effective factors of fuel property are both the C/H ratio and the enthalpy of formation.

Key Words : Combustion, Particulate formation, Activation Energy, Dry Soot, Soluble Organic Fraction, Thermal decomposition

1. Introduction

In previous paper¹⁾ we described the "precursors" of soot in a methane-oxygen opposed jet diffusion flame. Results of light scattering measurements show that slightly upstream of a soot particle forming region, there exists a deposition region of unabsorptive particle substance, which is considered a presoot. On the other hand, Sweitzer²⁾ reported that a white smoke appeared firstly at 960 K and the higher the temperature, the darker became the color of smoke in a thermal decomposition of methane. Black smoke has some crystal structure and shows an optical absorbability in the visible range. As to the white smoke, individual particle is supposed basically to be composed of liquid heavy hydrocarbon³⁾, and to be unabsorptive.

In this paper, to study the sooting process, the amounts of the soluble and the insoluble particles which are observed as white and black smoke respectively are measured in heating a single hydrocarbon fuel or a rich fuel-air mixture as the parameter of temperature, oxygen concentration, and species of fuel.

2. Experimental Apparatus and Technique

The heating device of hydrocarbon fuel, flow reactor type, is shown in Fig.1. It comprises a heating element (Siliconit heater) attached to firebricks and a recrystallization alumina tube inserted into it. The reactor is designed to allow heating up to 2000 K at gas flow rate of 1 l/min. Methane, ethylene, propane, and acetylene (each having more than 99 % purity) were used as the fuel. Fig.2 shows an outline of the experimental apparatus. Single fuel or air-fuel mixture having equivalence ratio in the range of 5-50 which was generated by a capillary tube mixer was supplied to the flow reactor at the flow rate of 1 l/min. Except for the measuring period the air was supplied to the reactor in order to remove the deposition on the wall like

Fig.1 Flow reactor

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soot. The gross yields of presoot and soot were measured by a filtering method. The sample gas was diluted with nitrogen at the exit of the flow reactor to prevent the condensation of water during the filtering. A teflon filter employed had a $0.3\ \mu\text{m}$ nominal filtering diameter. Collection efficiency of the filter used in these experiments was measured by means of back-up filter method. It was more than 99 % under all conditions. The aging temperature and period were set at $50\ ^\circ\text{C}$ and 6 hours respectively. After the measurement of gross weight, the sample was separated into soluble and insoluble portions by Soxhlet extraction method and measured each weights. Dichloromethane was used for the solvent and extraction was made as long as 8 hours.

3. Result and Discussion

Fig.3 shows a typical result; the yields of soluble and insoluble particles obtained when a propane-air mixture having equivalence ratio $\phi=10$ is heated by the flow reactor. At first, the soluble particle begins to be observed at more than $1200\ \text{K}$. Insoluble matter appears at higher temperature than the temperature at which the soluble matter begins to be

Fig.2 Experimental apparatus

Fig.3 Example of presoot and soot yields (C_3H_8 , $\phi=10$)

observed. Though the yield of soluble particles have a maximum value, that of insoluble matter increases with the temperature in the experimental range. The color of smoke changes from white to black depending on the content of the insoluble matter.

In previous paper¹⁾, we reported that unabsorptive particles composed of heavy hydrocarbon droplets formed preceding the soot formation. On the other hand, the white smoke is basically supposed to be unabsorptive particle even the particle size effects the color of particulate clouds. Further, heavy hydrocarbon droplets are, of course, soluble fraction. Therefore, the white smoke or soluble fraction observed in this experiment is considered to be the same matter as the presoot reported ref.(1). As to the soot particle, it has some crystal structure and it does not dissolve into solvent. So that insoluble fraction observed in this experiment is soot. In this paper, we call soluble and insoluble particles presoot and soot respectively.

As to acetylene, the behavior of

Fig.4 Temperature change in heating methane mixture

Fig.5 Temperature change in heating propane mixture

thermal decomposition is different from the other three fuels. Because of this, it is discussed in 3.5.

3.1 The temperature of pyrolysis

Figs.4-6 show the temperature changes in flow reactor when the methane, ethylene, propane mixtures are supplied respectively at 1 l/min. In those figures, boundaries indicated by oblique lines show the beginnings of presoot and soot formations. Further, the temperatures at $\phi=0$ indicate the temperature of supplying air at 1 l/min (T_a). The temperature of flow reactor is decreased from initial state in almost all cases when the fuel gas is supplied to the reactor. The degree of temperature drop changes with the mixing ratio, initial temperature, and fuel. There are two factor to be considered. One is the heat capacity of fuel gas much higher than that of air. The other is the formation enthalpy of system. The temperature shown in Figs.4-6 is the temperature of products. But for example, activation energy should be evaluated with the temperature of reactants. So that it is

Fig.6 Temperature change in heating ethylene mixture

Fig.7 Temperature drop in flow reactor

much better for analysis to take the mixture temperature before reactions as the parameter. For this the temperature before reaction, in other words the temperature of mixture when the enthalpy supplied from flow reactor is being stored into sensible heat of mixture, must be estimated.

Fig.7 shows the temperature drop in several gases in the flow reactor when T_s is 1000 K where no presoot nor soot is formed. T_s is the temperature of the flow reactor when stagnant air is present inside it and T_g is the observed temperature during measurement. As to methane, $(T_s - T_g)$ is almost equal to that of air so that the initial temperature of mixture is assumed as T_a . As to ethylene, the tendency of $(T_s - T_g)$ is close to that of carbon dioxide. Further the ratio of $(T_s - T_g)$ of ethylene to that of carbon dioxide is 1.2. Therefore the initial temperature of ethylene mixture is estimated at 1.2 times the temperature drop in the carbon dioxide-air mixture having the same concentration of ethylene (Fig.8). In case of propane, the variation of temperature drop is very complex, with a maximum value as shown in Fig.9. The peak moves to higher flow rate

Fig.8 Temperature drop in heating carbon dioxide-air mixture

Fig.9 Temperature drop in heating propane mixture

side with temperature. Further, at temperatures below 1100 K, the particulate matter is not observed. Therefore, the reaction for temperature drop occurs in gas phase and it can be easily supposed as a slow reaction. Moreover, in the region of higher fuel flow rate than peak value, where no gas phase reaction occurs, $(T_s - T_g)$ is almost coincident with that of carbon dioxide. For these reasons, the initial temperature of propane mixtures is made equal to that of carbon dioxide-air mixture (Fig.8) by assuming the gas phase reactions to be included in sooting reactions.

To verify whether the those estimated initial temperature is correct or not, the soot yields were measured under various mixture flow rates and temperatures of the flow reactor. Fig.10 shows the result against the initial temperature estimated. From this, the yields are well explained with a single curve for each fuel, which means that the estimation is proper. Further, it is easily supposed that the yields of presoot and soot are unique function of the enthalpy supplied to the mixture from reactor. In other words, the residence time in the flow reactor has an

Fig.10 Soot yields against the assessed initial temperature

effect only on the enthalpy exchange between mixture and reactor in the flow rate range from 0.5 to 1.0 l/min, where the residence time may be much longer than the reaction time for particulate formation.

3.2 Yields of presoot and soot

Figs.11 and 12 show the yields of presoot and soot respectively by thermal decompositions of methane, propane, and ethylene. Experimental range of equivalence ratios for methane and propane mixture is from 5 to infinite. As for ethylene, from 10 to infinite. Since the yield per unit carbon in fuel does not change with equivalence ratio, it is not effective for presoot and soot formation. As for the fuel species, ethylene has the greatest sooting capability of the three fuels, and methane the least.

The presoot begins to form at lower temperature than soot and has a maximum value. About the ratio of presoot to total particulate matter, the sum of presoot and soot yields, continuously decreases as shown in Fig.13. It is, therefore, supposed that the soot is made from presoot by carbonization. As to this, detailed discussion is made in 3.3.

Fig.12 Soot yields

Fig.11 Presoot yields

Fig.13 The ratio of presoot to gross yields

3.3 Activation energy

Arrhenius temperature dependence shows the ratio of reactive molecule to total at given temperature. In other words, it shows the ability to form products. In the case of exothermic reaction, the ability of reaction becomes higher with progress of reactions or with an increase of temperature. However, the sooting processes of methane, propane and ethylene are recognized as endothermic reaction from the temperature drop of reaction and heat capacity of reactants shown in Figs.4-6 and 7-9. By assuming that no product activates and deactivates the reactants, the Arrhenius temperature dependence of presoot and soot can be estimated from their yields.

Figs.14 and 15 show the Arrhenius plots of presoot and soot respectively. About presoot, the yields are plotted in the range where the formation of soot can be neglected in comparison with that of presoot. In addition, datum below 1 mg/g of carbon in fuel are also omitted because of poor accuracy in logarithm scale. It is clear that the yields well coincide in a straight line for each fuel about both presoot and soot and that the graphic inclinations of each line show the overall activation energies of presoot and soot. Moreover, each line is relatively steep, hence the reaction is frozen by a slight drop of temperature. Therefore, it is concluded that the assumption what the products have no ability as an exciter for reactants is justified in these cases. Arrhenius rate law is, however, usually discussed in kinetic manner, then the activation energy obtained in this study may be an expedient one. The activation energy for each fuel about both of presoot and soot is shown in Table 1. The activation energy of presoot is lower than that of soot so that presoot is formed preceding the soot formation. As to the

effects of fuel property, the possibility of presoot and soot formations becomes higher in order of ethylene, propane, methane.

Representing the presoot yields as

$$f_p \exp(-E_p/RT) \dots \dots \dots (1)$$

and the soot yields as

$$f_s \exp(-E_s/RT) \dots \dots \dots (2)$$

we find the ratio of soot to total particulate matter R_s as follows:

$$\begin{aligned} R_s &= \frac{f_p \exp(-E_p/RT) - f_s \exp(-E_s/RT)}{f_p \exp(-E_p/RT)} \\ &= 1 - f_s/f_p \exp(-(E_s - E_p)/RT) \\ &= 1 - f_s/f_p \exp(-E_{sp}/RT) \dots \dots \dots (3) \end{aligned}$$

where, E_{sp} is $(E_s - E_p)$, E_s is the total activation energy of soot, and E_p is that of presoot. Fig.16 shows the Arrhenius plots of $(1 - R_s)$. For this, the graphic inclination gives E_{sp} shown in Table 2. E_{sp} is roughly consistent with $(E_s - E_p)$ obtained from Figs.14 and 15: E_p is determined in the range where soot yields are relatively negligible. Consequently, it is concluded that presoot does not decrease, but forms and grows into soot even when soot mainly yields. Furthermore it is supposed that propriety of E_p is

Table 1 Activation energies of presoot and soot

fuel	activation energy E	
	KJ·mol ⁻¹	
CH ₄	presoot	330
	soot	420
C ₃ H ₈	presoot	240
	soot	320
C ₂ H ₄	presoot	200
	soot	270

Fig.14 Arrhenius plots of presoot yields

Fig.15 Arrhenius plots of soot yields

still retained in that region. In comparison with soot, the activation energy of presoot is not so small and the proportion of E_p to E_s is about 1.3 to 1.4 for each fuel. Further the degree of temperature drop in the presoot forming region is greater than that of soot, so that it is assumed that the potential energy of presoot is higher than that of soot.

The activation energies obtained in this study for methane, propane, and ethylene are supposed to be useful in many cases of sooting problem. But it is necessary to take account of the circumstance that they are determined by the conversion ratio from fuel to presoot or soot.

3.4 The effects of oxygen

Obvious effects of oxygen on both the presoot and soot formations are hardly observed in this study, as shown in Fig.17 for example. There are two other kinds of effects of oxygen to be considered. One is the oxygen-catalysed pyrolysis. It is said that the decomposition of hydrocarbons is greatly accelerated by addition of oxygen⁴⁾. Indeed oxygen is effective for decomposition, but for sooting it is not so effective because the sooting mechanisms include some polymerization processes. The other is the exothermic reaction or oxidation. In this study, however, experiments are carried out in the range of equivalence ratios from 5 to infinite to avoid the flammable range. Thus the partial oxidation does not occur.

3.5 Sooting process of acetylene

Unlike pyrolysis of methane, propane, ethylene, presoot is not observed under any conditions of temperature and equivalence ratio in the thermal

Table 2 The difference of activation energies between presoot and soot

fuel	E_{sp} $\text{KJ}\cdot\text{mol}^{-1}$	$E_s - E_p$ $\text{KJ}\cdot\text{mol}^{-1}$
CH_4	180	90
C_3H_8	150	80
C_2H_4	120	70

Fig.16 Arrhenius plots of $(1-R_s)$

decomposition of acetylene. In comparison with the other three fuels, acetylene has much higher enthalpy of formation, and decomposition proceeds under exothermic condition. Therefore, as soon as it forms, presoot grows into soot by self-generating heat. In addition, acetylene yields the greatest volume of soot, of all the fuels employed in this study.

The starting temperature of soot formation for acetylene varies in steps as shown in Fig.18. In this figure, longitudinal axis is the initial temperature of air (T_a). The starting temperatures of soot formation under $\phi > 48$ and $\phi < 48$ are about 1000 K and 700 K respectively. So, it is considered that the heat is generated by partial oxidation in the case of $\phi < 48$.

3.6 Effect of fuel property

The capability of sooting becomes higher in order of acetylene, ethylene, propane, methane. This order coincides with the order of carbon to hydrogen ratio and that of formation enthalpy of fuel. Hence, it is supposed that the effective factors of fuel property for sooting are both the C/H

Fig.17 Example of oxygen effects on presoot formation

Fig.18 Starting temperature of soot formation of acetylene mixture

Fig.19 Starting temperatures of presoot and soot formations

ratio and the formation enthalpy.

Fig.19 shows the beginning temperature of presoot and soot formations against the C/H ratio of fuel. The starting temperatures of presoot and soot become low with C/H ratio. It can be said that the starting temperature is one of the indexes for presumption of capability of sooting.

4. Conclusions

The soluble and insoluble particles generated in heating a single hydrocarbon fuel or a rich fuel-air mixture have been measured to study the sooting process. The soluble particle is recognized as

white smoke, and insoluble as black smoke. It is shown that white smoke called presoot can be regarded as the "precursors" and black smoke is composed of soot.

As to methane, propane, and ethylene, it is shown that presoot and soot yield under endothermic reaction. The overall activation energies can be determined from the Arrhenius plots of their yields. In the case of acetylene, presoot is not yielded because of the rapid growth of presoot to soot based on the exothermic reaction. The effects of oxygen on both the presoot and soot formations are hardly detected. The effective factors of fuel property are both the C/H ratio and the enthalpy of formation. Further, the beginning temperature is one of the indexes for presumption of capability of sooting.

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References

- (1) Takeuchi, K., et al., Proc. ASME-JSME Thermal Eng. Conf., (1983), P. 355.
- (2) Sweizer, C. W. and Heller, G. L., Rubber World, No. 134 (1956), P. 855.
- (3) Takeuchi, K., et al., J. Marine Eng. Soci. Japan (in Japanese), Vol. 19 No. 3 (1984-3), P. 19.
- (4) Mincoff, C. and Tipper, F., "Chemistry of Combustion Reactions", (1962), P. 253, Butter Worths.