Effects of Benzene Addition on PAHs Formation Characteristics in a Counterflow Diffusion Flame

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To investigate polycyclic aromatic hydrocarbons (PAHs) formation characteristics in a counterflow diffusion flame of methane, the effects of benzene addition on PAHs formation are studied experimentally. Local PAHs are collected by a microprobe gas sampling system and analyzed by a gas chromatograph mass spectrometer (GC/MS). Mole fraction profiles of PAHs for the case with and without benzene addition are obtained. The responses of phenylacetyrene and cyclopentadiene formation, which are important species to the naphthalene (2 rings) formation process, to benzene addition are focused. It is found that H-abstraction- C_2H_2 -addition (HACA) mechanism, rather than Marinov's model, can be important in the 2-ring formation process. The formation of PAHs, especially the species of 1 to 3 rings, is promoted by benzene addition. Interestingly, the results show that pyrene alone decreases when benzene is added. This might be due to the consumption of pyrene during the soot formation process (e.g., the surface growth of the soot particles).

Key words: Benzene addition, HACA mechanism, GC/MS, Marinov's model, PAHs, Soot

INTRODUCTION

Soot is a pollutant from combustion. It is well known that polycyclic aromatic hydrocarbons (PAHs) play an important role in soot formation. For example, PAHs are considered to be the precursors to soot. However, the mechanisms of PAHs formation are very complicated, and the details are not revealed yet.

To this date, two main mechanisms of PAHs formation have been proposed. One is H-abstraction- C_2H_2 -addition (HACA) mechanism, which is suggested by Frenklach et al [1]. The other is the mechanism that the combination of 5membered ring radicals (e.g., cyclopentadienyl) leads to PAHs formation, which is suggested by Marinov et al [2]. The latter mechanism is often called Marinov's model. In both mechanisms, benzene is a primary source of PAHs formation. Most significant difference between these mechanisms is in the naphthalene (2 rings) formation process; naphthalene is formed through phenylacetyrene and cyclopentadiene in HACA mechanism and Marinov's model, respectively. Therefore, one can expect that focusing the 2-ring formation process might help to evaluate which mechanism would be dominant. In consideration of this, benzene is added to fuel, and the responses of both phenylacetyrene and cyclopentadiene formation to benzene addition are investigated.

In this study, to gain knowledge of PAHs formation characteristics in a methane-air diffusion flame, the effects of benzene addition in a fuel flow on PAHs formation are studied experimentally. A gas chromatograph mass spectrometer (GC/MS) is used for PAHs measurements. Possible dominant mechanism in this system is also addressed.

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EXPERIMENTAL

Burner

A schematic of the counterflow burner is shown in Fig. 1. It consists of a pair of axially symmetric nozzles. The oxidizer flow, which consists of oxygen and nitrogen, is supplied through the upper nozzle, while the fuel flow, which consists of methane, nitrogen and benzene (0~122ppm), is supplied through the lower nozzle. In each nozzle, beads and a sintered metal disk are mounted to provide a uniform exit flow profile.

A flat diffusion flame is formed close to the stagnation plane. To keep the flame flat and axially symmetric, a co-axial curtain flow of nitrogen is provided. To prevent the temperature rise of the nozzles by heat radiation from the flame, each nozzle is cooled by water flow. The two nozzles are separated by 15mm. In the figure, x represents height above the fuel (lower) burner and the origin is set at the center of the fuel burner surface.

Temperature Measurements

Temperature measurements are conducted by use of 0.10mm Pt-Pt/13%Rh thermocouple wires with a bead diameter of about 0.20mm. They are coated by silica to prevent catalysis. The measurements are performed along the x-axis every 0.5mm. Measured temperature is corrected by use of Kaskan's method [3], which takes into account the radiation heat loss.



Fig. 1. Schematic of the counterflow burner.

PAHs Measurements

PAHs measurements are conducted by use of GC/MS (SHIMADZU, GC-17A Ver.3/QP5050A) analysis system. A schematic of the gas sampling system is shown in Fig. 2. Gas sampling is performed by a quartz microprobe with a tip diameter of about 0.1mm. The gas is sucked via pressure difference induced by a vacuum pump. The sampling line from the probe to the GC/MS is maintained at 250 degrees C to prevent the condensation of PAHs in the line. Gas sampling is performed along the x-axis every 0.5mm.

GC/MS is controlled by an analysis software (SHIMADZU, CLASS-5000). In GC, the species are carried by helium flow (purity is 99.9999%), and separated by a capillary column (SHIMADZU, CBP1, 0.22mm x 25m). Identification of the species is accomplished by matching the mass spectral fragmentation patterns with the NIST/EPA/NIH Mass Spectral Database.

Quantification of benzene is accomplished by use of a standard gas of benzene (NIPPON SANSO, 499ppm). Mole fraction of benzene in the sampling gas is calculated by

$$X_{C6H6} = \frac{S_{C6H6}}{\alpha_{C6H6}} \times \left(499 \times 10^{-6}\right) \quad (1)$$

where X_{C6H6} is the mole fraction of benzene. S_{C6H6} and α_{C6H6} represent the gas



Fig. 2. Schematic of the sampling system.

chromatograph peak area of benzene for the sampling gas and the standard gas, respectively. For quantification of the species except for benzene, the Total Ionization Cross Section Method [4] is used. According to this method, mole fraction of the species in the sampling gas is given by

$$X_{i} = \frac{Q_{C6H6}}{Q_{i}} \times \frac{S_{i}}{\alpha_{C6H6}} \times (499 \times 10^{-6}) \quad (2)$$

where X_i and S_i are the mole fraction and the gas chromatograph peak area of the species *i*, respectively. Q_i is the total ionization cross section, a constant for the species *i* [4].

Experimental Conditions

In this study, the mole fraction of methane/oxygen in the fuel/oxidizer flow is selected at 0.75/0.20. Under this conditions, the flame shows a yellow color, indicating great deal of soot is produced. For both the fuel and the oxidizer flow, nozzle exit flow rates are maintained at 7.5cm/s at room temperature. It is noted that they increase by 1 to 2cm/s because the nozzles are heated up by the flame.

In this study, two types of fuels are used. One is the fuel with benzene addition (122ppm). The other is the fuel without benzene addition.

RESULTS AND DISCUSSION

Temperature Measurements

Temperature profiles for the case with/without benzene addition are shown in Fig. 3. Both profiles have the peaks at x=10.5mm. They have gentle gradient in the fuel side, and steep in the oxidizer side. Any significant difference in the maximum temperature between them is not observed. It is concluded that 122ppm benzene addition has no effect on temperature profile.



Fig. 3. Temperature profiles for the case with/without benzene addition.

PAHs Measurements

Mole fraction profiles of PAHs for the case with/without benzene addition are shown in Fig. 4. When benzene is added to the fuel flow, mole fractions of the species except for pyrene (4 rings) increase in the fuel side. This indicates that the formation of PAHs, especially the species of 1 to 3 rings, is promoted by benzene addition. All the species have the peaks in the region of x=5.5~7.0mm for both conditions.

Without benzene addition, the mole fraction profile of phenylacetyrene is in good agreement with that of naphthalene (2 rings). With benzene addition, the profiles of these two species are also similar. On the other hand, the mole fraction of cyclopentadiene in the oxidizer side is relatively high, and the profile of it is not similar to that of naphthalene irrespective of benzene addition. By this comparison, one can suggests that naphthalene has relatively stronger correlation with phenylacetyrene than with cyclopentadiene. This result shows that HACA mechanism can be important in the 2-ring formation process.

Increase rates of PAHs by benzene addition are shown in Fig. 5. The increase rate of the species $i(I_i)$ introduced here is defined as follows;

$$I_i = \frac{A_i - B_i}{B_i} \times 100 \quad (3)$$

where A_i and B_i are the average mole fraction of the species *i* for the case with and without benzene addition, respectively. As shown in the figure, the species with 1 to 3 rings increase with the benzene addition. On the other hand, pyrene (4 rings) alone is not varied, rather, slightly decreases. This result shows that the PAHs up to 3 rings would be influenced by benzene addition, in other words, the effects of benzene addition might not affect 4-ring formation. One hypothesis to explain this behavior is that the primary particles of soot increase when benzene is added. Since pyrene is known as an interactive species with the soot particles [5], the decrease would be expected by the consumption of it



Height above the burner x [initi]

Fig. 4. Mole fraction profiles for the case with/without benzene addition.

during the soot formation process (e.g., the surface growth of the soot particles). In order to convince this hypothesis, a precise soot measurement in the flame is required.

CONCLUSIONS

In this study, the effects of benzene addition (122ppm) on PAHs formation characteristics in a counterflow diffusion flame of methane are studied experimentally. This study has brought the following concluding remarks;

- 1. 122ppm benzene addition has no significant effect on temperature profile.
- 2. When benzene is added to fuel, PAHs formation is promoted in the fuel side, especially the species of 1 to 3 rings.
- 3. Similarity of the mole fraction profiles of phenylacetyrene and naphthalene (2 rings) suggests the importance of HACA mechanism in the 2-ring formation process.

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Fig. 5. Increase rates of PAHs by benzene addition.