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THE EFFECT OF CO ADDITION ON SOOT FORMATION IN A LAMINAR ETHYLENE/AIR COFLOW DIFFUSION FLAME

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INTRODUCTION

Recent development in fuel enrichment combustion stimulates our interest in the effect of carbon monoxide (CO) addition on various flame properties, since CO is a primary component of a reformat gas - an effective and practical enrichment additive [1]. One of these flame properties is sooting propensity of diffusion flames of various fossil fuels in air.

Although the effect of the addition of various additives on soot formation has been investigated extensively, surprisingly there is not much information available in the literature on the effect of CO addition, especially on the chemical effect of CO addition on soot formation. CO contains carbon element, but is a soot-free burning component. Therefore, the addition of CO to a hydrocarbon fuel flame has a dilution effect in terms of soot formation. In addition, CO participates in chemical reactions that may influence soot formation rate. Consequently, the addition of CO may have complex effect on soot formation. Arthur and Napier [2] noted that the addition of CO had a weakly suppressive effect on soot formation in methane flames but did not offer any explanation for the behavior. Du et al. [3] observed that the addition of CO caused a linear decrease in soot formation in an ethylene diffusion flame, and a complicated behavior in a propane diffusion flame. They argued that the addition of CO could chemically promote soot inception chemistry, but did not provide any discussion on the variation in the chemistry of surface growth, another important sub-process of soot formation that contributes the most to the formation in terms of the total mass. Therefore, further study is needed to investigate the detailed mechanism of the effect of CO addition on soot formation in diffusion flames.

This paper investigates the effect of CO addition on soot formation in a coflow ethylene/air diffusion flame by both experiment and numerical simulation. Specifically, we are interested in the chemical effect of CO addition on soot formation. To isolate the chemical effect from others, the paper also investigates the addition of nitrogen (N_2).

EXPERIMENTAL METHODOLOGY

The experiment is conducted in a coflow laminar diffusion flame burner. The fuel stream issues from a 10.9 mm inner diameter vertical tube, and the air from the annular region between the fuel tube and a 100 mm diameter concentric tube. The wall thickness of the fuel tube is 0.95 mm. The base flame is a pure ethylene/air diffusion flame. During the experiment, the volume flow rates of air and ethylene are kept as 284 l/min and 194 ml/min (1 atm, 20 °C), respectively, while CO or N_2 is added to the center fuel tube. All experiments are carried out at room temperature and atmosphere pressure condition. To keep all the studied flames as attached flames, the investigated volume fraction of CO or N_2 (α_{CO} or α_{N_2}) in the fuel stream is limited to less than 0.8.

The soot volume fraction is measured using diffuse-light two-dimensional line-of-sight attenuation (LOSA) optical diagnostic method developed by Thomson et al. [4]. The light source for the experiments is a mercury arc lamp diffused by an integrating sphere and imaged to the flame center with a pair of lens doublets. The flame center is imaged by a second pair of lens doublets onto a CCD array filtered with a 450 nm narrow band filter.

NUMERICAL MODEL

The formation and evolution of soot particles is simulated by the method of moments [5]. Six concentration moments are used.

The nucleation of soot particles is assumed to be due to the coalescence of two large size PAH, pyrene (A4), into a dimer. Then the particle size increases or decreases due to the particle coagulation, surface growth and oxidation. The gas phase chemistry and the calculation methods for the particle nucleation, coagulation, surface growth and oxidation are basically those developed by Appel et al. [6] with some modifications.

The first modification is the gas phase chemistry. More routes and reactions, which have been shown to be important in PAH formation and growth by other researchers [7-11] are added. The complete set of gas phase reaction scheme consists of 580 reactions and 108 species.

The second modification is the calculation of coagulation. The free molecular regime is employed. However, we limit the particle coagulation by setting the coagulation rate as zero when the mean particle diameter is greater than 25 nm. This is based on the experimental observation that generally the maximum diameter of a primary particle is about 25 ~ 30 nm.

Finally, we increase the surface growth rate by raising the parameter α , the fraction of surface sites available for surface reactions, to close to unity.

The governing equations for conservation of mass, momentum, energy and gas species mass fractions can be found elsewhere [12]. The SIMPLE numerical scheme [13] is used to handle the pressure and velocity coupling. The diffusion terms in the conservation equations are discretized by the central difference method and the convective terms are discretized by the power law method [13]. The discretized governing equations of gas species and soot moments are, respectively, solved in a fully coupled fashion at each control volume. Those of momentum, energy and pressure correction are solved using the tri-diagonal matrix algorithm.

The computational domain covers an area from 0 to 3.0 cm in the radial (r) direction and 0 to 11.0 cm in the axial (z) direction. The inflow boundary ($z = 0$ cm) corresponds to the region immediately above the fuel nozzle. Totally 160 (z) \times 95 (r) non-uniform grids are used in the simulations, with finer grids placed in the primary reaction zone and near the fuel nozzle exit region. Other details of the numerical methods can be found from our previous publication [12].

RESULTS AND DISCUSSION

Figure 1 displays the predicted and measured soot volume fraction distribution in the base flame, i.e. the pure ethylene/air flame. It is observed that although soot volume fraction in the lower centreline region is slightly underpredicted, the simulation has basically captured the primary features of soot field. The peak soot volume fraction and the distribution of soot are reasonably predicted.

Figure 2 shows the variation of the normalized maximum integrated soot volume fraction ($F_{v,max}/F_{v,max_base}$) against the fraction of CO/N₂ in the fuel stream, with $F_{v,max}$ being the maximum

integrated soot volume fraction of a diluted flame, and F_{v, max_base} being that of the base flame. Integrated soot volume fraction is obtained by $F_v = \int 2\pi r f_v dr$, with f_v being the local soot volume fraction. It is revealed that the addition of either CO or N₂ monotonically reduces the formation of soot in the ethylene/air diffusion flame. This is consistent with the study of Du et al. [3].

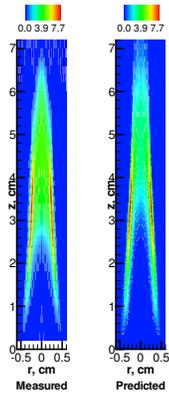


Fig. 1 Measured and calculated soot volume fraction (ppm) of pure ethylene/air flame.

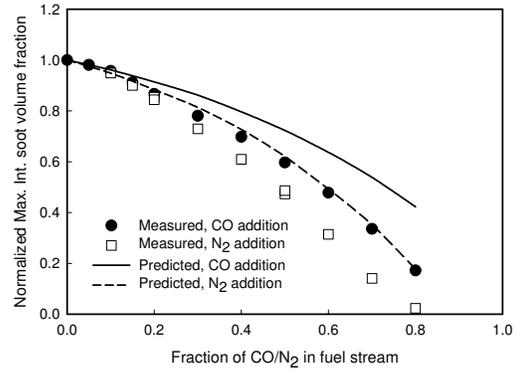


Fig. 2 Normalized maximum integrated soot volume fraction.

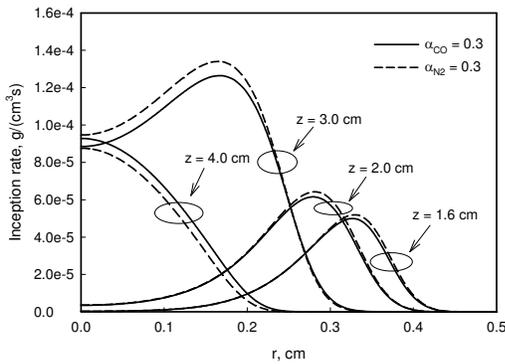


Fig. 3 Particle inception rate.

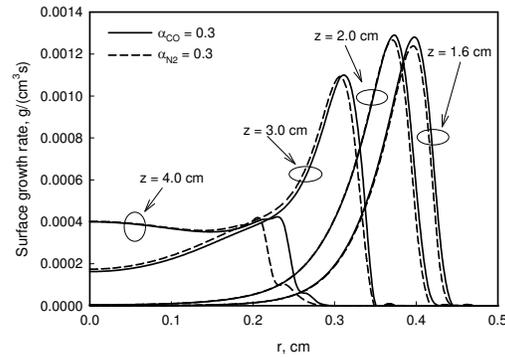


Fig. 4 Surface growth rate.

A specific feature is observed from both experimental and numerical results in Fig. 2, i.e. the addition of N₂ is more effective than that of CO in suppressing soot formation. As for other gaseous additives, the suppression of CO or N₂ addition on soot formation is caused by the thermal, dilution and chemical effects. Since CO and N₂ have similar thermal and transport properties, the addition of them has similar thermal and dilution effects in terms of soot formation. However, N₂ is basically inert for soot formation, but CO actively participates in chemical reactions. Therefore, the difference between the CO and N₂ diluted flames reflects the chemical effect of CO addition. Accordingly, Fig. 2 implies that the chemical effect of CO addition actually promotes the formation of soot in an ethylene/air diffusion flame. This is opposite to the chemical effect of carbon dioxide addition on soot formation [14].

There has been extensive discussion on the thermal and dilution effects on soot formation in a diffusion flame. Therefore, we focus on the chemical effect in this paper. We'll do this by

comparing the numerical details of CO and N₂ diluted flames, taking the 30%CO and 30%N₂ flames as examples.

Soot formation consists of three sub-processes: inception, surface growth and oxidation. We first check inception. Figure 3 displays radial profile of the inception rate at four axial heights for the 30%CO and 30%N₂ diluted flames. The selected four axial heights cover the primary soot formation regions. It shows that in most regions the inception rate in the CO diluted flame is lower than in the N₂ diluted flame, except at $z = 4.0$ cm. Therefore, over all the chemical effect of CO addition, which promotes the formation of soot, is not through inception in most regions.

Figure 4 displays surface growth rate at the four axial heights. It is noted that the surface growth rate in the CO diluted flame is higher than in the N₂ diluted flame, meaning that surface growth is one sub-process through which the addition of CO chemically promotes soot formation. Surface growth includes PAH condensation and acetylene (C₂H₂) addition. However, the simulation indicates that C₂H₂ addition dominates, and the higher surface growth rate in the CO diluted flame is primarily because of C₂H₂ addition. Therefore, we will examine how the addition of CO chemically affects C₂H₂ addition. In our numerical model, the rate of C₂H₂ addition is calculated by the mechanism of H-abstraction-carbon-addition (HACA) [5,6], which suggests that the factors affecting the rate of C₂H₂ addition include temperature, particle surface area and concentrations of C₂H₂ and H radical.

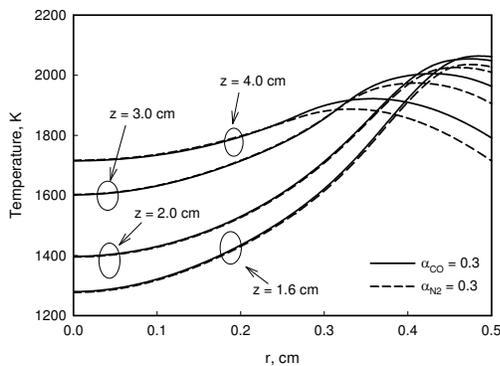


Fig. 5 Flame temperature distribution.

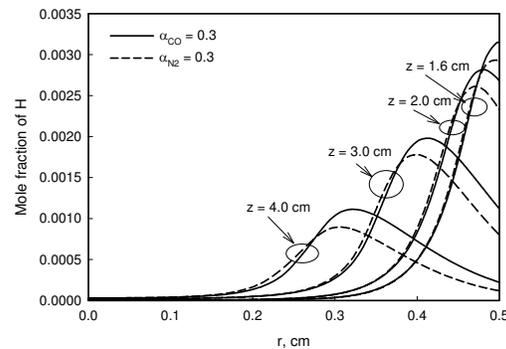


Fig. 6 Concentration of H radical.

Figure 5 displays the temperature distributions at the four axial heights. Temperature in the CO diluted flame is higher than in the N₂ diluted flame, which tends to increase the rate of C₂H₂ addition. This is as expected, since CO actively participates in chemical reactions and releases heat, while N₂ does not. Therefore, the higher temperature is a factor that causes the higher surface growth rate in the CO diluted flame.

Particle surface area is closely related to particle number density and thus inception rate. Because of the lower inception rate, as shown in Fig. 3, particle surface area is also lower in most regions of the CO diluted flame than in the N₂ diluted flame. Although the inception rate of the CO diluted flame is higher at $z = 4.0$ cm, the absolute value of surface growth rate there is very small. Therefore, surface area should not be a factor resulting in the higher C₂H₂ addition rate in the CO diluted flame.

The third factor that may influence the rate of C₂H₂ addition is the concentration of H radical, which controls the formation rate of active site for C₂H₂ addition. Although [3] suggested that the concentration of H in the CO diluted flame might be higher due to the reaction $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$, Fig. 6 shows that the difference in the concentration of H between the two flames in the

surface growth region (see Fig. 4) is negligible. This is because the consumption rate of H radical by other reactions, such as the chain branching reaction $H + O_2 = OH + O$ and those for fuel pyrolysis, also increases owing to the addition of CO. Accordingly, H radical is not a primary factor either causing the higher rate of C_2H_2 addition in the CO diluted flame.

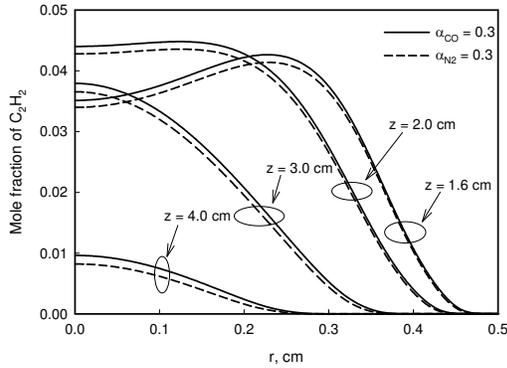


Fig. 7 Concentration of acetylene (C_2H_2).

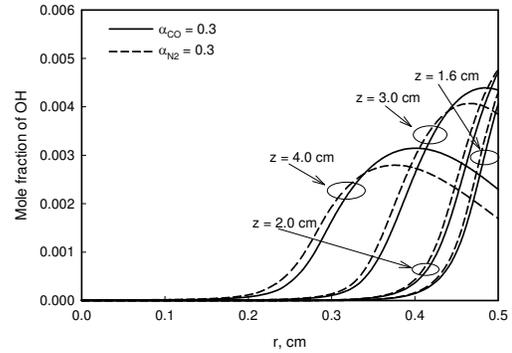


Fig. 8 Concentration of OH.

The last factor that may affect the rate of C_2H_2 addition is the concentration of C_2H_2 , as shown in Fig. 7. Apparently, the concentration of C_2H_2 is higher in the CO diluted flame than in the N_2 diluted flame, which results in the higher rates of C_2H_2 addition and surface growth in the CO diluted flame. Therefore, higher C_2H_2 concentration is a factor that causes the effect of CO addition which chemically promotes the formation of soot. The pathway analysis indicates that the higher concentration of C_2H_2 in the CO diluted flame is because of the reaction $C_2H_2 + O = CO + CH_2$, which is the primary destruction reaction of C_2H_2 . When CO is added, the reverse rate of this reaction is intensified, resulting in the lower C_2H_2 destruction rate and thus higher concentration of C_2H_2 . Therefore, the reaction $C_2H_2 + O = CO + CH_2$ is an important factor that causes the chemical effect of CO addition which promotes the surface growth rate. To our knowledge, this observation has never been reported in the literature.

Now we examine how the addition of CO influences soot oxidation. Being consistent with the current understanding on soot oxidation, the simulation indicates that the oxidation of soot is primarily due to the attack of OH on soot particles. Figure 8 displays the concentration of OH radical in the near centerline region at the four axial heights. It is observed that the concentration of OH radical in the near centerline region, where soot exists, is lower in the CO diluted flame than in the N_2 diluted flame. As mentioned before, this is due to the reaction $CO + OH = CO_2 + H$, which intensifies the consumption rate of OH when CO is added. The lower concentration of OH tends to slow the oxidation rate of soot in the CO diluted flame and to increase the net soot formation rate. This is another factor that causes the chemical effect of CO addition on soot formation. This is similar to the suggestion of Du et al. [3], and consistent with the viewpoint of Puri and Santoro [15] who indicated that soot and CO oxidation competed with each other for OH. However, we point out that this factor may be weakened in certain extent by the higher temperature in the CO diluted flame, as shown in Fig. 6, since higher temperature tends to increase the oxidation rate.

Therefore, we can conclude that the chemical effect of CO addition that promotes the formation of soot in the ethylene/air diffusion flame is through surface growth and oxidation. It is because of the temperature increase resulted from chemical reactions, and the variations in the concentrations of C_2H_2 and OH radical owing to the reactions $C_2H_2 + O = CO + CH_2$ and $OH + CO = CO_2 + H$.

CONCLUSIONS

An experimental and numerical study has been conducted on the effect of CO addition on soot formation in an ethylene/air diffusion flame, with special emphasis on the chemical effect. The chemical effect is isolated from the thermal and dilution effects by comparing the results of CO and N₂ diluted flames. Both experiment and simulation show that the addition of both CO and N₂ monotonically reduces the formation of soot. However, the addition of N₂ is more effective than that of CO in suppressing soot formation, implying that the addition of CO chemically promotes the formation of soot, which is different from the chemical effect of carbon dioxide or hydrogen addition. The further analysis of the details from numerical simulation indicates that the chemical effect of CO addition that promotes the formation of soot is through oxidation and surface growth. Firstly, when CO is added, flame temperature is increased compared to the N₂ diluted flame, leading to the higher surface growth rate. Secondly, the concentration of acetylene (C₂H₂, a main soot precursor) is increased due to the reduced forward rate of the reaction $C_2H_2 + O = CO + CH_2$, which also results in the higher surface growth rate for soot formation in the CO diluted flame. Finally, the addition of CO reduces the concentration of OH radical owing to the reaction $OH + CO = CO_2 + H$, and consequently slows the oxidation rates of soot in the CO diluted flame. These three factors cause the chemical effect of CO addition that promotes the formation of soot.

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