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SOOT AND NO FORMATION IN A LAMINAR AXISYMMETRIC COFLOW ETHYLENE/AIR DIFFUSION FLAME

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INTRODUCTION

Understanding the mechanisms of soot and NO_X formation is of great interest due to the need to control pollutant emission. Many researchers have extensively studied the respective formation mechanisms of NO_X and soot. However, relatively little attention has been paid to the interaction between NOx and soot formation.

On the other side, it has been shown that radiative heat loss has a strong effect on NO_X formation, and soot plays an important role in radiation level of some flames. Therefore, soot may affect NO_X formation via radiation. Some researchers [1] argued that soot/soot-precursor oxidation significantly reduces OH and O concentrations in the primary reaction zone of a flame and thus may also affect the formation of NO through chemical reaction. Our previous study [2] on soot and NO formation in counterflow ethylene/oxygen/nitrogen diffusion flames showed that soot formation does affect the emission of NO through the radiation induced thermal effect and the reaction induced chemical effect.

Because of the higher soot volume fraction, the radiative heat loss from a coflow diffusion flame is much larger than from a counterflow diffusion flame. Therefore, it is anticipated that the interaction of soot and NO_X formation in the former will be much stronger than in the latter. In this paper, the formation of soot and NO, the dominant component of NO_X, in a laminar axisymmetric coflow ethylene/air diffusion flame is investigated by numerical simulation. The objective is to use the details from the numerical simulation to gain further insight into the mechanisms of soot and NO formation in a heavily sooting flame, with specific emphasis on the interaction of the two pollutants.

NUMERICAL MODEL

The studied flame is an axisymmetric coflow laminar ethylene/air diffusion flame for which the formation of soot was investigated experimentally by Gülder et al. [3].

The numerical model solved fully elliptic governing equations for conservation of mass, momentum, energy, gas species mass fractions, soot mass fraction and soot number density. Cylindrical coordinate system was used. The governing equations can be found elsewhere [4].

Similar to our previous studies [2, 4], a simplified two-equation soot model was used, since it has been proved to be able to capture the primary features of soot formation in ethylene/air diffusion flames. However, the sub-models of soot nucleation, surface growth and oxidation were modified in this paper. Soot nucleation was calculated by the reaction $C_6H_6 + C_6H_5 \Rightarrow$

$12C(S) + 5H_2 + H$, with C(S) being the carbon atoms in soot. The advantage of this approach is the possibility of predicting soot nucleation based on PAH-PAH reactions without significantly increasing the computational time and memory space, and thus appropriately including both soot and NO_X chemistry in the study. The introduction of phenyl (C_6H_5) into the nucleation step is to consider the role of hydrogen abstraction in the formation of large size PAH and soot nucleation. The soot nucleation rate was calculated by $\omega_n = 12M_s k_n [C_6H_6][C_6H_5]$ ($g \cdot cm^{-3} \cdot s^{-1}$), with M_s being the molar mass of soot (12.011 g/mole), $[C_6H_6]$ and $[C_6H_5]$ being, respectively, the mole concentrations of benzene and phenyl ($mole/cm^3$), and $k_n = 1.0E+14$.

Soot surface growth and oxidation were assumed to follow the H-abstraction and C_2H_2-addition reaction sequence given by Appel et al. [5]. However, modifications were made for the parameter α, the fraction of the reactive surface available for chemical reactions, and the reaction probability of soot oxidation due to the attack of OH. The parameter α was calculated by $\alpha = 0.0038\exp(9000/T)$. A constant 0.06 was used for the reaction probability of soot oxidation due to the attack of OH.

The computational domain covers a region from 0 to 3.0 cm in the radial direction and 0 to 11.0 cm in the axial direction. The inflow boundary (z = 0 cm) corresponds to the region immediately above the fuel nozzle. To consider the preheating effect, the velocity and temperature profiles obtained at z = 0.0 in the simulation 2 of [4] were used as inlet velocity and temperature conditions. Totally 160 (z) x 81 (r) non-uniform grids were used in the simulations, with finer grids placed in the primary reaction zone and near the fuel nozzle exit region.

The numerical scheme and the methods are the same as those used in our previous study [4]. The chemical reaction mechanism used is a combination of an optimized chemistry developed by Qin et al. [6] and the nitrogen chemistry of Gri-Mech 3.0 [7]. The resulted mechanism contains 87 species and 569 elementary reactions.

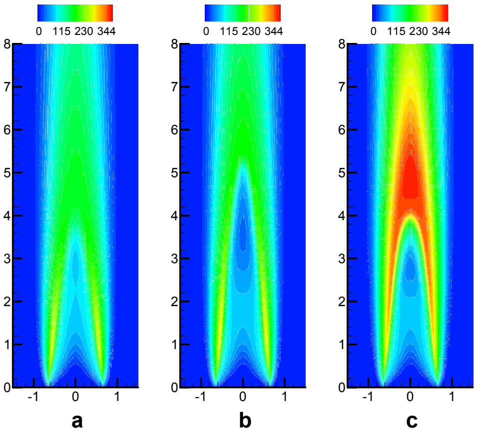
RESULTS AND DISCUSSION

The simulation was first carried out for soot formation by two reaction schemes: the full chemistry and its revised version obtained by removing all the reactions and species (except N_2) related to NO_X formation. It was found that there is almost no discernable difference in the predicted soot volume fraction profiles between the results obtained by the two reaction schemes. Accordingly, we conclude that the formation of NO_X has little influence on the production and oxidation of soot in the flame. Therefore, we concentrate on the influence of soot on the formation of NO in this paper. Hereafter all the results presented were obtained by the full reaction scheme.

Soot may affect NO formation through the thermal and chemical effects. With the former, the existence of soot causes a flame temperature reduction mainly due to radiation heat loss, whereas the latter results from the competition for some species by both soot and NO formation. To identify these two effects, three simulations were conducted. The first simulation (SIM1) was conducted by including both NO_X and soot in the model, while the nucleation and surface growth rates of soot were set as zero in the second (SIM2) and third (SIM3) simulations. The temperature of SIM2 was kept the same as that in the first simulation, whereas the temperature was calculated in SIM3. Therefore, the difference in results between SIM1 and SIM2 is caused by the chemical effect of soot, while the difference between SIM2 and SIM3 is primarily caused by the thermal effect.

To verify the soot mode, the predicted soot volume fraction distribution by SIM1 was compared with that obtained by Gülder et al. [3]. It was found that the simulation captured the general features of soot in the flame. Therefore, the used soot model is reasonable.

Figure 1 shows the predicted NO concentrations by the three simulations. It illustrates that soot in the flame suppresses the formation of NO. The peak NO concentrations and NO emission indices from the three simulations are, respectively, 266 (SIM1), 276 (SIM2), 370 (SIM3) ppm and 2.73 (SIM1), 3.14 (SIM2), 5.08 (SIM3) g-NO/kg-C_2H_4. Therefore, the influence of soot on NO formation is caused by both the thermal and the chemical effects. Relatively, the thermal effect is more significant.



a b c

Fig. 1 Predicted NO concentration (ppm) by the three simulations. a. SIM1; b. SIM2, c. SIM3.

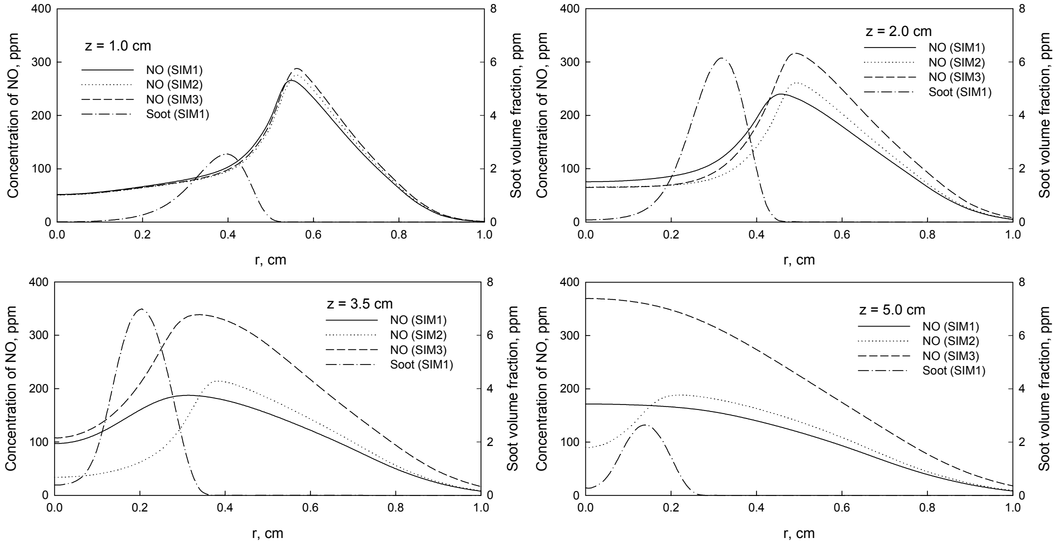


Fig. 2 Radial profiles of soot and NO at four axial heights.

The radial profiles of soot, NO and temperature at four axial heights are shown in Figs. 2 and 3. It is demonstrated that the regions of peak soot and NO at radial direction are separated. The peak soot volume fraction positions are located near the centerline (fuel side), while the peak NO concentration positions are further away from the centerline, except at axial height of z = 5.0 cm. The positions of peak NO are close to or the same as those of the peak temperatures. Therefore, the formation of NO is more sensitive to temperature.

At z = 1.0 cm, the effect of soot on NO formation is relatively small, and the thermal and chemical effects play similar roles. However, with the rise of z, the influence of soot on NO formation gradually increases. The thermal effect of soot becomes more and more significant than the chemical effect, when z is increased.

At z = 3.5 and 5.0 cm, NO concentration in the centerline region of SIM2 is significantly lower than that of SIM1. This phenomenon also exists at z = 1.0 and 2.0 cm, but it is not as significant as in the upper flame region. This means that the chemical effect of soot actually lowers the formation rate of NO in the centerline region.

Figures 2 and 3 further show that, at z = 1.0 cm, the lower soot volume fractions causes that the temperature variation due to soot is smaller. With z being increased to 2.0 and 3.5 cm, soot volume fraction is significantly increased, resulting in the greater radiative heat loss and temperature variation. The greater temperature variations at z = 2.0 and 3.5 cm leads to the bigger temperature difference between SIM1 and SIM3 at z = 5.0 cm due to convection, although soot volume fraction is small here.

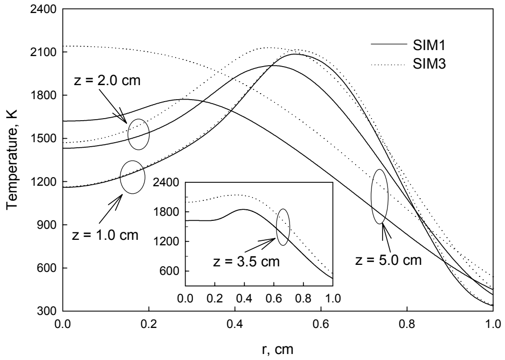


Fig. 3 Radial temperature profiles at four axial heights.

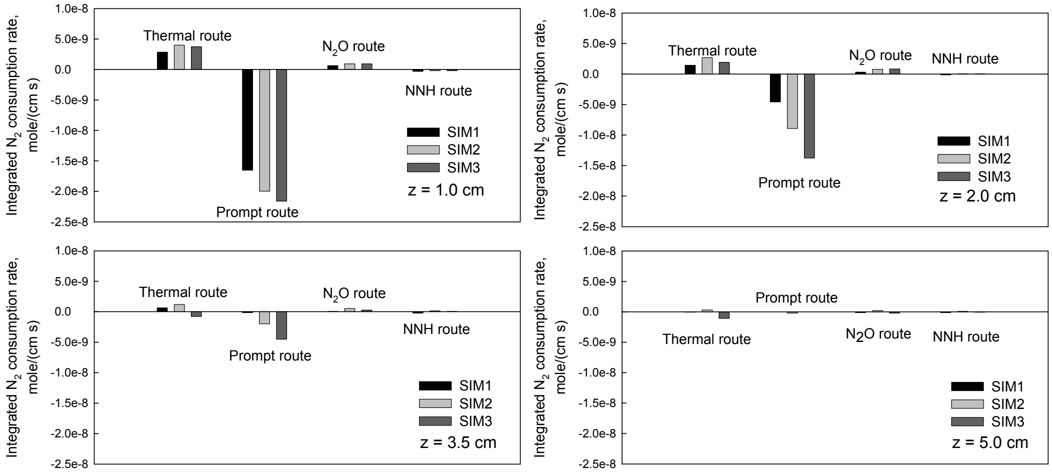


Fig. 4 Integrated nitrogen consumption rates from different routes at four axial heights.

To figure out how soot affects the formation of NO, we first analyze the mechanism of NO formation. It is well know that NO can be formed by four routes, the thermal, the prompt, the N_2O and the NNH intermediate routes, based on the initiation reactions converting molecular nitrogen to atom nitrogen or species containing element nitrogen. It should be pointed out that the thermal route of NO formation should not be confused with the thermal effect of soot. The thermal effect of soot can cause the variation of NO formation rates from all the four routes. Figure 4 displays the integrated nitrogen consumption rates at four axial heights. It is first observed that most nitrogen consumption occurs at z = 1.0 to 3.5 cm. Secondly, most nitrogen consumption at z = 1.0 to 3.5 cm is through the prompt route. It implies that the prompt route dominates the formation of NO in this flame. The thermal route actually forms molecular nitrogen at z = 1.0 to 3.5 cm, except in SIM3. It is because significant atom nitrogen is formed by the prompt route, which leads to that the forward rate of the reaction $N + NO = N_2 + O$ exceeds the reverse rate. However, the thermal route consumes nitrogen at z = 3.5 and 5.0 cm in SIM3. The reason is that the significantly high temperature at z = 3.5 and 5.0 cm in SIM3 causes that the thermal route starts to play role in NO formation there. Overall, nitrogen consumption at z = 3.5 and 5.0 cm is much smaller than that at z = 1.0 and 2.0 cm.

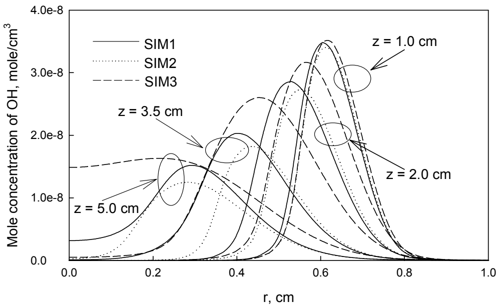


Fig. 5 Radial profile of OH at four axial heights.

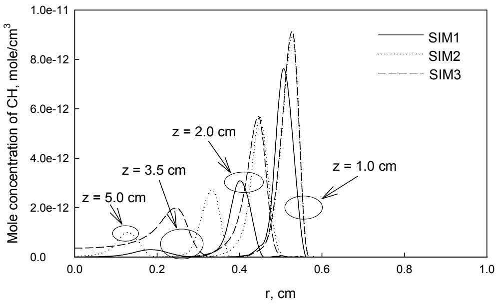


Fig. 6 Radial profiles of CH at four axial heights.

A pathway analysis indicates that in the prompt route, molecular nitrogen is converted to atom nitrogen and species containing element nitrogen mainly by the reaction CH + N_2 = HCN + N. Then the formed N is converted to NO by reaction N + OH = NO + H, and other reaction sequences. Atreya et al. [1] argued that soot/soot-precursor oxidation significantly reduced OH concentration in the primary reaction zone and contributed to the reduction of NO formation, since OH affects NO formation through the reaction OH + N = NO + H. To verify this viewpoint, we check the concentrations of OH, as shown in Fig. 5. It is noted that although the concentration of OH in SIM3 is higher, it is lower in SIM2 than in SIM1. This means that the chemical effect of soot formation actually intensifies the formation of OH. The reason is that the formation of soot reduces the concentration of CO in the flame, and CO is a species consuming OH. An important formation reaction of CO is O + C_2H_2 = CO + CH_2. In SIM1, the formation of soot consumes acetylene, and thus less CO is formed. Consequently, less OH is needed by the reaction CO + OH = H + CO_2 in SIM1. Although the oxidation of soot also consumes OH, its effect is much less than that of the reaction CO + OH = H + CO_2, especially at lower flame region. This causes that more OH exists in SIM1. Therefore, we conclude that OH is not a species that chemically suppresses the formation of NO when soot is taken into account in the simulation.

The rate limiting step for the prompt NO formation is the reaction CH + N_2 = HCN + N. Therefore, radical CH is an important species affecting the formation of NO through the prompt route. Figure 6 displays the profiles of CH at the four axial heights. It is observed that the concentrations of CH in SIM2 and SIM3 are higher than in SIM1 at z = 1.0 to 3.5 cm, where soot nucleation and surface growth happen. A sensitivity analysis shows that the dominant reaction for CH formation is the reverse reaction of CH + H_2 = H + CH_2, and an important CH_2 generation reaction is O + C_2H_2 = CO + CH_2. Accordingly, the formation of radical CH is closely related to acetylene (C_2H_2). Meanwhile, acetylene is also the most important precursor of soot. At z = 1.0 to 3.5 cm, the formation of soot consumes acetylene and thus less CH is formed in SIM1. This is the reason that CH concentration in SIM1 is lower than in SIM2 and SIM3 at z = 1.0 to 3.5 cm.

As a result of less CH in SIM1, the rate of the reaction CH + N_2 = HCN + N is smaller at z = 1.0 to 3.5 cm, which results in lower NO formation rate in SIM1 than in SIM2, although the flame temperature was kept the same in these two simulations. Therefore, the chemical suppression effect of soot on NO formation is through radical CH. When soot is considered in the simulation, the lower concentration of CH is because soot consumes acetylene (C_2H_2). So we can conclude that it is the competition of soot and NO for acetylene that causes the chemical suppression effect of soot on NO formation in the flame.

At z = 5.0 cm, the concentrations of CH in SIM1 and SIM3 are negligible, compared to in SIM2. In SIM1, it is because some acetylene is consumed to form soot at lower flame region and thus less acetylene is transported to z = 5.0 cm. Differently, in SIM3, it is caused by the fact that acetylene is quickly converted to combustion products and other intermediate species at lower flame region due to the higher temperature.

The significantly lower NO concentration in the centerline region in SIM2 than in SIM1 is caused by the reburn of NO. Since soot is not included in SIM2, more hydrocarbon radicals appear in the centerline region. This leads to the consumption of NO by the reactions with these hydrocarbons. The most significant reburn reaction of NO in this region is HCCO + NO = HCNO + CO. In SIM3, these hydrocarbon radicals are quickly converted to final combustion products due to the higher temperature, and the reburn rate of NO is reduced. Therefore, the NO concentration in the upper centerline region of SIM3 becomes higher than in SIM1.

The thermal effect of soot on NO formation is relatively easy to understand. Although the prompt mechanism dominates the formation of NO in the studied flame, the higher temperature in SIM3 intensifies the conversion rates of most reactions. Therefore, the NO formation rate in SIM3 is much higher than in SIM1 and SIM2. The thermal effect depends on the temperature variation.

CONCLUSIONS

The interaction of soot and NO_X formation in a laminar axisymmetric coflow ethylene/air diffusion flame has been investigated by numerical simulation. The results indicate that the formation of NO_X has little effect on the formation of soot. However, the formation of soot in the flame significantly affects the formation of NO. Soot in the flame suppresses the formation rate of NO. In the studied flame, the peak NO concentration and NO emission index are reduced by 104 ppm and 2.25 g-NO/kg-C_2H_4, respectively, due to the formation of soot. The influence of soot on NO formation is caused by both the radiation induced thermal effect and reaction induced chemical effect, with the former being more significant than the latter. The chemical effect is caused by the competition of acetylene (C_2H_2) between soot and NO. The formation of soot consumes acetylene in the flame, and thus lowers the concentration of radical CH. This finally reduces the rate of the reaction CH + N_2 = HCN + N that is the limiting step of the prompt NO formation route, the dominant one in the studied flame.

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