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### NUMERICAL MODELING OF SOOT FORMATION IN AN AXISYMMETRIC TWO-DIMENSIONAL LAMINAR ETHYLENE/AIR COFLOW DIFFUSION FLAME

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#### ABSTRACT

Soot formation from a two-dimensional laminar ethylene/air diffusion flame was modeled by relatively detailed chemical kinetics and dynamics model. The gas phase chemistry used was a mechanism including the formation and growth of PAH up to four ring aromatics. The soot particle dynamics was described by the moments model, which can account for the effect of particle size distribution. The result was compared with the measured data. It was found that the simulation captured the primary features of soot in the studied flame. The predicted soot distribution and peak soot volume fraction were close to the measured. Although the predicted maximum flame temperature was slightly lower than the experimental data, the error was acceptable. The paper further analyzed the mechanism of soot formation based on the numerical results, and found that most results were consistent with the current understanding of soot formation mechanism

#### **INTRODUCTION**

Studying pollutant emissions is an essential aspect of combustion research. Soot is one of primary pollutants emitted during the combustion of fossil fuels. Emission of soot not only has a detrimental effect on human health, but also contributes significantly to global warming. Therefore, various restrictions are being placed on soot emission today. Strategies are needed to control and reduce the emission of soot.

Quantitative understanding of soot formation mechanism is crucial to the development of strategies for the reduction of soot emission. Understanding the mechanism of soot formation needs both experimental and numerical studies. In the earlier time, scientists and engineers modeled soot formation based on local fuel concentration in a combustor. This kind of models is crude, since soot particles are not formed directly from parent fuel. Later, researchers realized that acetylene is an important precursor of soot, and therefore many soot formation models were set up based on local concentration of acetylene. Particle dynamics was usually modeled by solving two equations for soot mass fraction and number density, respectively. These acetylene based models were successful to explain many fundamental and practical phenomena, such as in [1-6]. However, the effect of hydrogen abstraction cannot be accounted for and thus some phenomena in soot formation cannot be captured by these models [7], since hydrogen abstraction plays important role during soot formation [8].

Significant progress has been made in understanding the mechanism of soot formation in the last decade. Some relatively detailed chemical kinetics for soot formation have been developed, such as [9-11]. Meanwhile, more accurate aerosol models started to be employed in modeling soot particle dynamics [10,11]. However, most of these detailed kinetics and accurate particle dynamics model were only applied to simple flame configurations, like onedimensional premixed and counterflow flames. In applications, real almost all flames are multidimensional. The applicability of these models to multidimensional flames is still questionable.

The purpose of this paper is to model soot formation by a relatively detailed chemical reaction scheme and an accurate particle dynamic model for a twodimensional coflow laminar diffusion flame, one with most characteristics of multidimensional flames but relatively simple geometry. We first describe the particle dynamics model and chemical kinetics used. The numerical result presentation follows. The modeling results are compared with measured data. Finally we briefly analyze the mechanism of soot formation in the studied flame.

#### NUMERICAL AND SOOT MODELS

Flame Configuration: The flame studied is a twodimensional axisymmetric laminar coflow ethylene/air diffusion flame, which has been experimentally studied in [12,13]. The flame was generated at atmosphere pressure with a burner in which the fuel issued from a 10.9-mm inner diameter vertical tube, and the oxidant (air) from the annular region between the fuel tube and a 100-mm diameter concentric tube. The wall thickness of the fuel tube was 0.95 mm. The fuel was ethylene. The volume flow rates of air and ethylene were, respectively, 284 1/min and 194 ml/min at room temperature (298 K) and atmosphere pressure condition.

The numerical model solved fully elliptic governing equations for conservation of mass, momentum, energy, gas species mass fractions and soot moments. Cylindrical coordinate system was employed. The governing equations for gas phase can be found elsewhere [14].

**Soot Model:** The formation and evolution of soot particles was modeled by the method of moments [15]. Compared to the simplified two-equation model used in our previous studies [5,7,14], this model can account for the effect of particle size distribution. Meanwhile, not many extra governing equations are needed to describe particle dynamics by this model. The soot particle moments were defined as

$$M_r = \sum_{i=1}^{\infty} m_i^r N_i \tag{1}$$

where  $M_r$  is the *rth* moment of soot particle distribution, and  $m_i$  and  $N_i$  are the mass and the particle number density, respectively, of the soot particles of size class *i*. The soot particle mass was represented by the number of carbon atoms. In this paper, six concentration moments (i.e.  $M_r = M_1, M_2, M_3, M_4, M_5, M_6$ ) were used.

The governing equation for each soot concentration moment is

$$\rho u \frac{\partial (M_r / \rho)}{\partial z} + \rho v \frac{\partial (M_r / \rho)}{\partial r} = \frac{\partial}{\partial z} \left( \rho D_{p,1} \frac{\partial}{\partial z} \left( \frac{M_{r-2/3}}{\rho} \right) \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r \rho D_{p,1} \frac{\partial}{\partial r} \left( \frac{M_{r-2/3}}{\rho} \right) \right) - \frac{\partial}{\partial z} (V_{T,z} M_r) - \frac{1}{r} \frac{\partial}{\partial r} (r V_{T,r} M_r) + Q_r$$

$$(2)$$

where  $\rho$  is density (g/cm<sup>3</sup>), *u* and *v* the axial (*z*) and radial (*r*) direction velocities (cm/s), respectively.  $V_{T,x_i}$  is the thermal diffusion velocity of soot in *z* (axial) or *r* (radial) direction, and was calculated by

$$V_{T,x_i} = -0.55 \frac{\upsilon}{T} \frac{\partial T}{\partial x_i} \qquad (x_i = z \text{ or } r)$$
(3)

Quantity  $D_{p,1}$  is the diffusion rate of the smallest soot particles, and was given by

$$D_{p,1} = \frac{3}{2\rho} \sqrt{\frac{mk_B T}{2\pi}} \left(1 + \frac{\pi\alpha_T}{8}\right)^{-1} \frac{1}{d_1^2}$$
(4)

with *m* being the mean mass of the gas (g),  $K_B$  the Boltzmann's constant (erg mol<sup>-1</sup> K<sup>-1</sup>), *T* the temperature (K),  $\alpha_T$  the thermal accommodation coefficient (0.9), and  $d_I$  the diameter of the smallest soot particle (cm).

The source term  $Q_r$  in each moment equation accounts for particle nucleation, coagulation, surface growth and oxidation of soot particles. The nucleation was assumed to be due to the coalescence of two large size PAH, pyrene (A4), into a dimer. Then the particle size increases due to the particle coagulation, surface growth and oxidation. The gas phase reaction scheme and the calculation methods for the particle nucleation, coagulation, surface growth and oxidation were basically those developed by Appel et al. [16]. Several modifications were made, since the original model underpredicted soot volume fraction.

The first modification was to limit the particle coagulation by setting the coagulation rate as zero when the mean particle diameter is greater than 25 nm. This was based on the experimental observation that generally the maximum diameter of a primary particle is about  $25 \sim 30$  nm. Then we increased the surface growth rate by changing the acetylene addition rate (S4 in the table 3 of [16]) and the parameter  $\alpha$  – the fraction of surface sites available for surface reactions. The reaction rate of acetylene

addition provided in [16] was increased by five times in this paper. The parameter  $\alpha$  was still calculated by Eq. 1 of [16], but the parameter *a* in the equation was increased by 3 times and the parameter b was modified to  $b=-1.38+1.02\times10^{-3}\times T$ .

After above modifications, the predicted peak soot volume fraction was improved. However, soot volume fraction in centerline region was still significantly underpredicted. Realizing that the chemistry developed in [16] underpredicted the concentration of pyrene in some flames, we reduced the scrubbing factor of pyrene  $\alpha_{44}$  to 0.0005, i.e. the reaction rate of pyrene was calculated by  $r_{A4} = r_{g,A4} + \alpha_{A4} \cdot r_{s,A4}$ , with  $r_{A4}$ ,  $r_{g,A4}$ ,  $r_{s,A4}$  and  $\alpha_{A4}$ being, respectively, the net rate, the rate due to gas phase reactions, the rate due to soot formation and the scrubbing factor of pyrene. This treatment was an ad hoc one. The final solution should be the improvement of chemical reaction scheme. The scrubbing factors for all other species were 1.0.

Other details of the soot model were the same as those in [16]. The free molecular regime was employed for the calculation of coagulation.

Numerical Scheme: Low Mach number assumption was adopted. The governing equations were discretized using the finite volume method in axisymmetric cylindrical coordinates. The SIMPLE numerical scheme [17] was used to handle the pressure and velocity coupling. The diffusion terms in the conservation equations were discretized by the central difference method and the convective terms were discretized by the upwind difference method. To speed up the convergent process, the governing equations of gas species and soot moments were, respectively, solved in a fully coupled fashion at each control volume [18]. Those of momentum, energy and pressure correction were solved using the tridiagonal matrix algorithm.

The computational domain covered an area 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 in the simulation 2 of [14], in which part of fuel nozzle was included in the calculation to account for its heating effect on fuel and air streams, were used as the inlet velocity and temperature conditions in the present study. Totally 160 (z) × 105 (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. It was checked that the further increase of grid number did not significantly influence the simulation results. The thermal and transport properties were obtained by using the algorithms given in [19] and [20]. Radiation heal transfer was calculated by the method given in [5, 6, 8].

#### **RESULTS AND DISCUSSION**



Fig. 1 Predicted and measured soot (ppm).



Fig. 2 Predicted and measured temperature (K).

Figures 1 and 2, respectively, show the predicted distributions of soot volume fraction and flame temperature. For comparison, the experimental results of Gülder et al. [12] are also shown. It is observed that the simulation captured the general features of soot and temperature in the flame.

The value of the peak soot volume fraction and the distribution of soot obtained by the simulation are close to those from the experiment. However, soot volume fraction in the low centerline region was underpredicted. The visible flame height was slightly overpredicted. The differences between the simulation and experiment results are caused by the chemical kinetics and errors existing in experiment.

The primary feature of temperature distribution was predicted. successfully Both simulation and experiment show that the flame temperature peaks in the annular region of the lower part of the flame, and the maximum temperature contours do not converge to the axis in the upper region of the flame. This is because of the strong radiation heat loss caused by soot, as significant amount soot exists in the upper flame region, as shown in Fig. 1. Although not shown, a sensitivity calculation has shown that if soot is not taken into account in the simulation, the maximum temperature contours converge to the centreline at upper flame region. Therefore, radiation heat loss due to the presence of soot is significant in this kind of flames. The peak flame temperature was underpredicted by about 3.5% (73K). It should be an accepted error.



Fig. 3 Radial profiles of soot volume fraction at different axial heights.

Figure 3 displays the radial distribution of soot volume fraction at four axial heights. It is noted that although the distributions of soot volume fraction and peak values at lower flame heights (z = 2.0 and 2.9 cm) were successfully captured by the simulation, the predicted positions of the peak soot volume fraction are further away from centreline, compared to the measured data. At z = 4.0 cm, the peak soot volume fraction was underpredicted. A sensitivity calculation indicated that the prediction of soot volume fraction strongly depends on the profile of inception species, prvene. Appel et al. [16] suggested that the gas phase reaction scheme used in this paper might underpredict the concentration of pyrene for some flames. This may cause the above discrepancies between the prediction and experiment. However, currently there are not perfect chemical reaction schemes for the simulation of soot formation in diffusion flames.

Therefore, developing or improving the gas phase chemistry will be an important subject in the future for the modelling of soot formation in diffusion flames.



Fig. 4 Radial profiles of temperature at different axial heights.



Fig. 5 Inception and surface growth rates (g cm<sup>-3</sup>s<sup>-1</sup>). (a) Inception; (b) Surface growth.

Figure 4 illustrates the predicted and measured radial temperature distributions at four axial heights. Although the peak flame temperature were slightly underpredicted, the prediction of temperature distribution is much better than that of soot volume fraction. The general profiles and the positions of the peak temperature were successfully captured. The slight difference between prediction and experiment is believed to be caused by the discrepancy in soot prediction, which affects temperature calculation through both thermal (radiation) and chemical (reaction) effects.

Figure 5 shows the rates of soot inception and surface growth. The surface growth includes all surface processes, i.e. acetylene addition, PAH condensation and particle oxidation. It is observed that at lower flame region, the rate of surface growth is much higher than that of inception, implying that surface growth contributes most to soot formation, based on the total formed soot mass. At upper flame region, surface growth rate becomes negative, because soot oxidation dominates there. Therefore, main soot formation occurs at lower flame region (z < 4.0 cm). These observations are consistent with the current understanding of soot formation mechanism.

Figure 5 further shows that the maximum surface growth rate appears in the annular region around z = 2.0 cm. A further examination of the simulation data has revealed that acetylene addition contributes most to surface growth in this region. In centerline region at z < 4.0 cm, PAH condensation contributes more than acetylene addition. As for oxidation at upper region, radical OH dominates the process, though molecular oxygen also contributes some in the upper centerline region.

Although surface growth contributes most in soot formation, it does not mean that inception is less important. Inception affects particle number density and hence total surface area and surface growth rate. Actually our simulation suggests that the prediction of soot volume fraction is very sensitivity to inception, especially the soot volume fraction in centerline region.



Fig. 6 Formation and destruction rates of benzene from typical reactions.

As mentioned in soot model section, we reduced the scrubbing factor of pyrene to match the measured soot volume fraction in centerline region. A sensitivity calculation suggests that a slight change in the scrubbing factor of pyrene significantly affects the prediction of soot volume fraction in centerline region. By reducing the scrubbing factor of pyrene, we artificially increased the concentration of pyrene and enhanced the inception rate. A reasonable soot volume fraction in centerline region was obtained by setting the scrubbing factor of pyrene as 0.0005. This implies that the used chemical reaction scheme [16] underpredicted the concentration of pyrene in the studied flame. Theoretically the scrubbing factors of

all species should be unity. Therefore, improving the chemistry and thus the prediction of large size PAH, such as pyrene, will be a challenging job in the future.

A pathway analysis based on the simulation of this paper indicates that the formation of pyrene is primarily related to the formation of the first aromatic ring, benzene (A1). Figure 6 shows the rates of major formation and destruction reactions of benzene at z = 2.0 cm. A1  $\Leftrightarrow$  A1- represents the interconversion reactions between benzene and phenyl (A1-), which includes three reactions. It is observed that the formation of benzene is mainly because of the two reactions: C3H3 + C3H3 = > A1and n-C4H5 + C2H2 = A1 + H, with the former being more significant, i.e. the recombination reaction of propargyl (C3H3) dominates the formation of benzene. It has been believed the reaction C3H3 + C3H3 = > A1 is not an elementary one [9, 10]. Unfortunately there is not enough detailed information on this reaction. The current form of this reaction is a global one and the rate calculation was based on experimental observation. Therefore, it may not suit for the calculation of various different flames. It is expected that the future understanding of this reaction will be helpful for the prediction of benzene and soot. The consumption of benzene contributes to the growth of PAH and finally to pyrene.

### CONCLUSIONS

A numerical simulation of soot formation in coflowing laminar ethylene/air diffusion flame has been carried out by detailed chemical kinetics and particle dynamics model. The simulation results were compared with the existing experimental data. It was found that the simulation captured features of soot and temperature obtained by experiment. The maximum value and distribution of soot volume fraction in the studied flame was successfully predicted, although the soot in the lower centerline region was slightly underpredicted. The features of flame temperature were also captured by the Both simulation and experiment simulation. indicated that the maximum flame temperature in the studied flame appears in the lower annual region, suggesting that radiation heat loss due to the presence of soot plays significant role in this kind of flames. The simulation results also indicate that surface growth dominates the total mass of formed soot, and acetylene addition contributes most to surface growth. However, inception significantly

affects the prediction of soot formation through particle number density and surface area.

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