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MODELING OF OXIDATION-DRIVEN SOOT AGGREGATE FRAGMENTATION IN A LAMINAR COFLOW DIFFUSION FLAME

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In this study, three different oxidation-driven soot aggregate fragmentation models with 1:1, 2:1, and 10:1 fragmentation patterns are developed and implemented into a laminar coflow ethylenelair diffusion flame, together with a pyrene-based soot model and a sectional aerosol dynamics model. It is found that the average degree of particle aggregation (n_p) in the soot oxidation region is not correctly predicted if oxidation-driven aggregate fragmentation is neglected; whereas the incorporation of aggregate fragmentation significantly improves the n_p prediction in the soot oxidation region. Similar results are obtained using the 1:1 and 2:1 fragmentation patterns. However, as the pattern ratio increases to 10:1, appreciable difference in the predicted n_p is observed. As the pattern ratio becomes larger, the fragmentation effect diminishes and the predicted n_p approaches that of the original model neglecting fragmentation.

Keywords: Fragmentation pattern; Laminar coflow diffusion flame; Oxidation-driven soot aggregate fragmentation; Soot modeling

1. INTRODUCTION

Combustion-generated soot particles have attracted much research interest for both scientific and practical reasons. Soot particles emitted to the atmosphere have adverse health and environmental effects (Vedal, 1997). Soot particles participate in flame radiative heat transfer. Their formation, thus, affects the heat transfer efficiency of boilers and furnaces, and the propagation of fires. Recently, the interest in soot research has expanded from the global properties of soot, such as soot volume fraction, to detailed properties of soot, such as soot particle nanostructure and size distribution (Iyer et al., 2007; Megaridis & Dobbins, 1988, 1989; Puri et al., 1993; Yazicioglu et al., 2001; Zhang et al., 2009a, 2009b; Zhao et al., 2003). This is not surprising because knowledge of soot particle nanostructure and size

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distribution is particularly helpful for (a) better evaluating the health effects and the optical properties of soot particles, (b) finding ways to eliminate unburned carbon, and (c) better understanding the individual roles of different soot formation processes. Various experimental investigations have been conducted to reveal the nanostructure of soot particles. Experimental observations (Megaridis & Dobbins, 1989; Puri et al., 1993; Yazicioglu et al., 2001) suggest that flame-generated soot particles are fractal-like aggregates, and each soot aggregate is composed of a certain number of small (nano-sized) and nearly spherical primary soot particles.

The development of modeling capabilities of soot aggregate formation is an indispensable part of our overall effort to gain a fundamental understanding of various processes leading to soot aggregate formation. Much progress has been achieved in the development of soot formation models (Appel et al., 2000; Frenklach & Wang, 1994; Smooke et al., 1999) and soot aerosol dynamics models (Appel et al., 2000; Frenklach & Wang, 1994; Park et al., 2005; Smooke et al., 1999; Zhao et al., 2003). Investigation of soot aggregate formation using fundamental soot formation models and detailed aerosol dynamics models offers insights into the complex soot aggregate formation phenomenon. In previous studies (Zhang et al., 2009a, 2009b), soot aggregate formation in the laminar nonsmoking ethylene/air coflow diffusion flame of Santoro et al. (1983) was studied with a pyrene-based soot model (Appel et al., 2000; Frenklach & Wang, 1994), a detailed sectional aerosol dynamics model (Park et al., 2005), and a detailed radiation model (Liu et al., 2004). The structure of the flame (flow field, temperature field, OH mole fraction field, C_2H_2 mole fraction field, and soot volume fraction field) was reasonably well reproduced. Along the annular soot pathline exhibiting the maximum soot volume fraction, the average diameter and the number density of primary soot particles were also reasonably predicted. It is, however, very challenging to reproduce the average degree of soot particle aggregation as indicated by the average number of primary particles per aggregate n_p . To effectively do so, it seems necessary to consider nonunitary soot coagulation efficiency induced by various particle-particle interactions and fluid-particle interactions, which affect soot particle aggregation. It was shown that in the soot surface growth region, n_p was overpredicted by a factor of 8 if unitary soot coagulation efficiency was assumed (Zhang et al., 2009a); however, n_p was well reproduced if a constant 20% soot coagulation efficiency was assumed (Zhang et al., 2009b). Admittedly, the 20% constant soot coagulation efficiency was a simplification of the reality, as the soot coagulation efficiency is likely dependent on factors such as flame local condition including temperature, fluid viscosity, and fluid shear rate, as well as soot properties including soot size, structure, and material property. Nevertheless, in the lack of fundamental understanding of soot coagulation behavior at the present stage, a simple adjustment of soot coagulation efficiency provided good agreement with a wide range of measured flame data and particle structure data (Zhang et al., 2009b).

It is even more challenging for a soot aerosol dynamics model to effectively reproduce n_p after soot particles are transported into the oxidation region because oxidation-driven soot aggregate fragmentation, a potential mechanism affecting n_p , is worth consideration. It has been reported from experimental studies that oxidation could cause breakage of the aggregate chain connecting primary particles, resulting in a decrease in the degree of particle aggregation n_p . Neoh et al. (1984)

observed that soot aggregates could break apart after entering oxidation region due to the strong soot surface regression caused by external oxidation. Under certain conditions, primary soot particles, which are the building blocks of soot aggregates, may also break due to the internal burning caused by the diffusion of O_2 inside primary soot particles. Recently, Xu et al. (2003) reported that soot aggregate fragmentation occurred in the oxidation region in their experimental study of a laminar ethylene/air diffusion flames at atmospheric pressure. Primary particle fragmentation, however, was reported as not significant. In another study, Harris and Maricq (2002) found that the addition of soot aggregate fragmentation to the Schmoluchowski aerosol coagulation model significantly improved the prediction of the signature size distribution observed for light-duty diesel exhaust particulate matter.

Although soot aggregate oxidation-driven fragmentation has been reported to occur, it has not been adequately treated in the modeling of soot formation in flames. The impact of oxidation-driven fragmentation on soot aggregate formation in a laminar coflow diffusion flame has not been reported previously in the literature to our best knowledge and thus remains to be investigated.

2. PROBLEM IDENTIFICATION

In the previous study (Zhang et al., 2009b) neglecting aggregate oxidation-driven fragmentation (referred to as Model 0 hereafter), n_p distribution along the annular soot pathline exhibiting the maximum soot volume fraction agrees well with the measurements of Iyer et al. (2007), as is shown in Figure 1. In Figure 1, z denotes the axial height above the burner. Two points should be noted regarding the measurements of Iyer et al. shown in Figure 1. First, the measured n_p at $z = 1.0$ cm, which is unphysical according to Iyer et al. (2007), is not shown. Second, as noted by Iyer et al. (2007), their n_p measurements were taken mainly in the soot surface growth

Figure 1 Calculated distribution of the average number of primary soot particles per soot aggregate n_p along the annular pathline exhibiting the maximum soot volume fraction using Model 0 without aggregate fragmentation. Also shown are the experimental measurements of Iyer et al. (2007) and Puri et al. (1993).

region of the flame with $z \leq 5.0$ cm. To help assess the performance of Model 0 in predicting n_p in the soot oxidation region when z is larger than 5.0 cm, an earlier set of n_p measurements, covering both the soot surface growth and the soot oxidation regions, taken by Puri et al. (1993) under the same flame condition, was added in Figure 1. We think the two experimental data sets are comparable in this case based on the following considerations: (a) although the n_p level of Iyer et al. is lower than that of Puri et al. (1993), the continuously increasing trend of n_p in soot growth region ($z \leq 5.0$ cm) of these measurements are the same; and (b) the n_p measurements of Iyer et al. fall well within the $\pm 50\%$ uncertainty of n_p measurements of Puri et al., the maximum difference being -43% at $z = 2.0$ cm. The measurements of Puri et al. show that n_p increases with z in the initial soot oxidation region ($5.0 \text{ cm} \leq z \leq 6.0$ cm). This increase of n_p is due to soot coagulation in this region (Puri et al., 1993). However, as soot particles are transported further downstream from $z = 6.0$ cm to $z = 7.0$ cm, n_p starts to decrease. As noted by Puri et al., this decrease of n_p might be an indication of soot aggregate oxidation-driven fragmentation. It is evident from Figure 1 that the predicted n_p by Model 0 monotonically increases with z in the entire soot oxidation region ($z > 5.0$ cm). This continuously increasing trend is not supported by the experimental results of Puri et al. Moreover, the calculated n_p values in the oxidation region seem to be unrealistically high, e.g., n_p is around 500 at $z = 7.5$ cm.

The discrepancy between the predicted and measured n_p profiles in the soot oxidation region shown in Figure 1 suggests that there exists a mechanism in the soot oxidation region that counteracts soot particle aggregation, which is missing in Model 0. As illustrated in Figure 2, if aggregate oxidation-driven fragmentation is implemented (i.e., the external oxidation at the aggregate surface leads to the breakup of the bridge connecting constituting primary particles at a certain weak location), n_p decreases. It seems plausible that this widely reported soot aggregate oxidation-driven fragmentation phenomenon is necessary to be considered in order to possibly reproduce n_p in soot oxidation region.

It was the objective of the present study to develop oxidation-driven soot aggregate fragmentation models and to investigate the effect of soot aggregate

Figure 2 The average degree of particle aggregation n_p decreases if aggregate oxidation-driven fragmentation is implemented.

oxidation fragmentation on the predicted aggregate nanostructure, in particular, the trend of n_p variation in the soot oxidation region discussed previously. In this study, soot aggregate oxidation-driven fragmentation models with three different fragmentation patterns were developed and implemented into the nonsmoking laminar coflow ethylene/air diffusion flame of Santoro et al. (1983). The following portion of the paper comprises of two main parts. The first part (Section 3) reports the development and implementation of soot aggregate oxidation fragmentation models. In the second part (Section 4), the effects of aggregate oxidation fragmentation on aggregate nanostructure are examined.

3. METHODOLOGY

The flame condition, governing equations, soot formation model, soot aerosol dynamics model, radiation model, and the numerical method used in this study are the same as those used in the previous study (Zhang et al., 2009b). Thus, they are presented below only briefly. The only difference is that an additional source term $\frac{\partial N_i^{(A),(P)}}{\partial t} \Big|_{fr}$, which accounts for aggregate oxidation-driven fragmentation, was added into the sectional transport equations for soot aggregates and primary soot particles. Depending on the superscript, quantity $N_i^{(A),(P)}$ is the number of either the i th sectional soot aggregates (with superscript A) or primary soot particles (with superscript P) per unit mass of the mixture. Focus is placed on the development of the aggregate oxidation fragmentation models.

3.1. Flame Condition and Modeling Methodology

The flame studied in the present study is the nonsmoking laminar coflow ethylene/air diffusion flame of Santoro et al. (1983), which has been widely studied by many other researchers (Iyer et al., 2007; Liu et al., 2003; Megaridis & Dobbins, 1988, 1989; Puri et al., 1993; Santoro et al., 1987; Yazicioglu et al., 2001). In this flame, the gaseous fuel (ethylene) was delivered upwards through a tube having an inner diameter of 11.1 mm. The oxidizer (air) was delivered through the annulus between the fuel tube and the air tube having an inner diameter of 102 mm. Both the fuel and the oxidizer were delivered at room temperature and atmospheric pressure. The mean velocities of the fuel and air streams were 3.98 cm/s and 8.9 cm/s, respectively. Due to the axisymmetric property of this flame, it was modeled in the two-dimensional axisymmetric cylindrical coordinate system to save CPU time. The fully coupled elliptic conservation equations for mass, momentum, gaseous species mass fractions, sectional soot aggregate and primary particle number densities, and energy were solved. The gas-phase governing equations can be found in Guo et al. (2006), whereas the sectional soot transport equations can be found in Zhang et al. (2009b). The source term in the energy equation due to nongray radiative heat transfer by soot and gaseous species H_2O , CO_2 , and CO was calculated using the discrete-ordinates method in the axisymmetric cylindrical geometry. A statistical narrow-band correlated- k based band model as employed to obtain the absorption coefficients of H_2O , CO_2 , and CO . More details of the radiation model can be found in Liu et al. (2004).

3.2. Sectional Aerosol Dynamics Model and Pyrene-Based Soot Model

The evolution of soot particles under simultaneously occurring soot nucleation, coagulation, surface growth, oxidation, surface condensation, and fragmentation processes is modeled with a sectional aerosol dynamics model (Park et al., 2005), which solves two equations (the number density of soot aggregates and the number density of primary soot particles) per section to simulate the fractal-like soot aggregate structure. In this sectional model, each aggregate was assumed to be comprised of a certain number of equally sized spherical primary particles. All aggregates were assumed to have the same fractal dimension D_f of 1.8 if they were larger than the primary spherule mass, whereas smaller particles were assumed to be dense spheres ($D_f = 3$). The mass range of soot aggregates was divided into a number of discrete sections, each with a prescribed representative mass. The representative mass of all sections formed a geometric series. The sectional spacing factor f_s relates the representative mass of one section with that of the preceding section. According to their mass, soot aggregates are assigned to individual sections. More details of the sectional soot aerosol dynamics model can be found in Park et al. (2005).

Soot nucleation is assumed to occur when two pyrene molecules collide and form a dimer (Appel et al., 2000; Frenklach & Wang, 1994). The coagulation terms are calculated based on the collision kernel of soot aggregates in the entire Knudsen number regime (Park et al. (2005)). As in the previous study (Zhang et al., 2009b), a constant 20% soot coagulation efficiency was implemented in order to effectively reproduce n_p in the soot surface growth region. Soot surface growth and oxidation were modeled by the H-Abstraction/ C_2H_2 -Addition (HACA) reaction scheme listed in Table 3 of Appel et al., (2000). All parameters were kept as original except the parameter α —the fraction of the reactive soot surface. Physically, this parameter takes into account the probability of a gaseous species colliding with the prismatic (edge) planes instead of the unreactive basal planes of particles and the fact that not all of the edge carbon atoms are available for a given reaction. The proposed expression for α by Xu et al. (1997) was used (i.e., $\alpha = 0.004 \exp[10800/T]$). A similar correlation was used by Guo et al. (2006) in the modeling of an ethylene/air diffusion flame. Pyrene-soot surface condensation was implemented that accounted for the growth of soot particles due to the condensation of pyrene molecules on soot surface (Appel et al., 2000). The condensation rate was calculated by the collision theory between pyrene molecules and aggregates (Park et al., 2005). Not all collisions lead to condensation (Kronholm & Howard, 2000). To account for the probability of sticking in each collision, the pyrene-soot condensation efficiency γ was assumed to be 0.5 as in Zhang et al. (2009a). A detailed sensitivity study of the parameter γ on soot formation was provided in Zhang et al. (2009a). It was found that the results were not sensitive to γ if it was larger than 0.5. Soot oxidation is assumed to lead to aggregate fragmentation as discussed previously and also illustrated in Figure 2. Aggregate oxidation-driven fragmentation models are described in Section 3.3.

3.3. Oxidation-Driven Soot Aggregate Fragmentation Models

Fractal-like aggregate fragmentation has long been studied by the aerosol research community. In the sectional representation of the aerosol population

balance equation, the rate of change of the aggregate number density in the i th section due to fragmentation is expressed as (Spicer & Pratsinis, 1996):

$$\frac{\partial N_i^{(A)}}{\partial t} \Big|_{fr} = -S_i N_i^{(A)} + \sum_{j=i}^{SN} \Gamma_{ij} S_j N_j^{(A)} \quad (1)$$

where S_i is the aggregate fragmentation rate, SN denotes the total section number, and Γ_{ij} is the breakage distribution function. The first term in Eq. (1) indicates the loss of the i th section aggregates due to their fragmentation. The summation term indicates the gain of the i th section aggregates due to the fragmentation of aggregates of the i th or larger sections. Γ_{ij} accounts for the gain of the i th section aggregates in each fragmentation of the j th section aggregates and is dependent on the fragmentation pattern discussed subsequently.

Modeling of aggregate fragmentation in general is still a challenging task due to the lack of fundamental understanding of the fragmentation phenomenon. The difficulties are mainly associated with the fragmentation pattern and the fragmentation rate. The fragmentation pattern determines the fragmentation product of an aggregate. A summary of different fragmentation patterns proposed so far was given by Kim and Kramer (2007). Examples include the binary pattern (two fragments with a specific mass ratio; Spicer & Pratsinis, 1996), the normal pattern (a normal distribution of the fragments; Coulaloglou & Tavlarides, 1977; Spicer & Pratsinis, 1996), and the random pattern (random fragments; Kramer & Clark, 1999). Because the exact fragmentation pattern of a soot aggregate is not well known, as a first start, we examined in this study the binary pattern, which is the easiest one to implement and has been commonly used in aggregate fragmentation modeling (Spicer & Pratsinis, 1996). Further theoretical and experimental work is needed to determine the exact fragmentation pattern of soot aggregates, which may be related to the location distribution of the weak bonds connecting primary particles. We examined the binary pattern with three different ratios: 1:1, 2:1, and 10:1. Among them, the 1:1 and 2:1 patterns are the most extensively used ones in the binary pattern category, for instance by Harris and Maricq (2002). The 10:1 pattern, which differs significantly from the 1:1 and 2:1 patterns, was selected to investigate the effect of the pattern ratio on the results. It should be emphasized that these patterns only account for the breakup of aggregate chain (refer also to Figure 2 and related discussion). Primary particle fragmentation caused by particle internal burning, which can lead to an increase of primary particle number, was not considered in this study because particle internal burning was reported to be unimportant in the present flame investigated (Megaridis & Dobbins, 1988).

The second point to be addressed is the aggregate fragmentation rate. In general, the fragmentation rate of an aggregate depends on the structure of the aggregate, the mechanism that causes the fragmentation, and the local condition. Following previous studies (Harris & Maricq, 2002; Tontrup et al., 2000), the fragmentation rate of an aggregate was chosen to be:

$$S_i = A(n_{p,i})^{\frac{1}{D_f}} \quad (2)$$

where A is a coefficient that governs the overall fragmentation rate, $n_{p,i}$ is the number of primary particles in an aggregate of section i , and D_f denotes the aggregate fractal dimension. Eq. (2) reflects the observation that larger aggregates are more likely to fragment than smaller ones because smaller aggregates tend to be more fragmentation resistant than larger ones (Harris & Maricq, 2002; Peng & Williams, 1994). The exponent $1/D_f$ means that the fragmentation rate becomes proportional to the radius of gyration of the aggregate (Harris & Maricq, 2002; Tontrup et al., 2000). Because the present study addressed soot aggregate fragmentation induced by oxidation, the fragmentation rate should be dependent on the soot oxidation rate. This is reasonable because for two aggregates with the same structure but placed under different oxidation conditions, the one that is experiencing stronger oxidation is expected to fragment faster. As a first approximation, the coefficient A was assumed to be a first-order function of the specific soot oxidation rate (i.e., rate of removal of soot mass per unit soot surface area) $r_{ox,s}$,

$$A = Cr_{ox,s} \quad (3)$$

where C is a constant. This expression for A reflects the idea that aggregate fragmentation occurs faster if the soot oxidation rate is higher. The effect of the constant C on the predicted n_p is examined later. Also note that the present aerosol dynamics model assumes point-contact between two primary particles. In reality, two primary particles probably are connected by surface-contact (neck region). If this nonspherical structure of primary particles is considered, there probably exists a delay for fragmentation because fragmentation should occur after the neck region is oxidized to a certain amount. A more rigorous expression for the fragmentation rate requires taking this effect into consideration by using a more advanced aerosol dynamics model that can fully resolve the neck structure of soot aggregates.

Assuming that the sectional spacing factor f_s is between 2 and 3 ($2 \leq f_s \leq 3$), a typical range used in aerosol research, the source terms $\frac{\partial N_i^{(A),(P)}}{\partial t} \big|_{fr}$ due to aggregate oxidation fragmentation for soot aggregates and primary soot particles in each section with the 1:1, 2:1, and 10:1 fragmentation patterns are derived. However, due to the space limit, only the 1:1 pattern governing equations are provided:

1:1 fragmentation pattern

For the last section (section SN):

$$\frac{\partial N_{SN}^{(A)}}{\partial t} \big|_{fr} = (\Gamma_{SN,SN} - 1)S_{SN}N_{SN}^{(A)} \quad (4)$$

$$\frac{\partial N_{SN}^{(P)}}{\partial t} \big|_{fr} = (\Gamma_{SN,SN} - 1)S_{SN}N_{SN}^{(A)}n_{p,SN} \quad (5)$$

For section i with $2 \leq i \leq SN - 1$:

$$\frac{\partial N_i^{(A)}}{\partial t} \big|_{fr} = (\Gamma_{i,i} - 1)S_iN_i^{(A)} + \Gamma_{i,i+1}S_{i+1}N_{i+1}^{(A)} \quad (6)$$

$$\frac{\partial N_i^{(P)}}{\partial t} \Big|_{fr} = (\Gamma_{i,i} - 1) S_i N_i^{(A)} n_{P,i} + \frac{\Gamma_{i,i+1} S_{i+1} N_{i+1}^{(A)} n_{P,i+1}}{f_s} \quad (7)$$

For the first section:

$$\frac{\partial N_1^{(A)}}{\partial t} \Big|_{fr} = \Gamma_{1,2} S_2 N_2^{(A)} \quad (8)$$

$$\frac{\partial N_1^{(P)}}{\partial t} \Big|_{fr} = \frac{\Gamma_{1,2} S_2 N_2^{(A)} n_{P,2}}{f_s} \quad (9)$$

where

$$\Gamma_{i,i} = \frac{f_s - 2}{f_s - 1} \quad (10)$$

$$\Gamma_{i,i+1} = \frac{f_s}{f_s - 1} \quad (11)$$

The breakage distribution functions $\Gamma_{i,i}$ and $\Gamma_{i,i+1}$ weight the newly formed mass into two adjacent sections such that the number and mass of aggregates are conserved, and that the number and size of primary particles are conserved.

It was found that the 10:1 fragmentation model is more complex to develop and implement than the 2:1 and 1:1 fragmentation models because the 10:1 fragmentation model involves breaking an aggregate into more sections.

3.4. Numerical Method

The governing equations were discretized with the finite volume method. The pressure and velocity coupling was treated using the SIMPLE algorithm (Patankar, 1980) along with a staggered mesh. The diffusive terms were discretized by the second-order central difference scheme, whereas the convective terms were discretized by the power law scheme (Patankar, 1980). The gaseous species and soot equations were solved simultaneously to effectively deal with the stiffness of the system and speedup the convergence process (Liu et al., 1995). The remaining governing equations were solved by the Tri-Diagonal Matrix Algorithm. The thermal and transport properties of gaseous species and the chemical reaction rates are obtained using Sandia's CHEMKIN (Kee et al., 1989) and TRANSPORT (Kee et al., 1986) libraries and the database associated with the selected reaction mechanism (Appel et al., 2000). The flame was modeled in a domain of 15.2 cm (z) $\times$ 4.7 cm (r) with 210 (z) $\times$ 88 (r) control volumes. A nonuniform mesh was used to save computational time while resolving large gradients. Very fine grids were placed in the r -direction and near the burner exit in the z -direction. It has been checked that further refinement of the mesh has negligible effect on the results. To speed up the calculations, the whole computational domain was divided uniformly in the axial direction into 16 subdomains, and each subdomain was assigned to a computing process for the calculation (Zhang et al., 2008; Zhang et al., 2009a). As in Liu et al. (2003), a parabolic profile was assumed for

the inlet fuel velocity and a boundary layer profile was assumed for the air stream velocity. The inlet temperatures for fuel and air were both assumed to be 300 K. Symmetry, free-slip, and zero-gradient conditions were enforced at the centerline, outer radial boundary, and the exit boundary, respectively. In total, 35 sections were used for the sectional model with a sectional spacing factor of 2.35. This sectional distribution gave adequate resolution of particle size and was large enough that the total mass fraction in the largest section was negligible, thus ensuring that the selected range did not clip the largest particles.

4. RESULTS AND DISCUSSION

Figure 3 shows the calculated n_p distributions along the annular pathline exhibiting the maximum soot volume fraction by Model 0 (without aggregate fragmentation) and five different models with aggregate fragmentation. All the models are summarized in Table 1. The five aggregate fragmentation models differ in the fragmentation pattern and the value of the fragmentation constant C in Eq. (3). Models 1, 2, and 3 have the same fragmentation pattern but different C values (i.e., different aggregate fragmentation rates). Models 1, 4, and 5 have the same C value but different fragmentation patterns. Also shown in Figure 3 are the n_p measurements of Puri et al. (1993) and Iyer et al. (2007). It is evident that the value of C has a large effect on n_p . Model 2 ($C=1.0\text{E}+06$) and Model 3 ($C=1.0\text{E}+04$) seemed to overestimate and underestimate aggregate fragmentation, respectively, as manifested by the underprediction and overprediction of n_p , respectively. Model 1 with $C=1.0\text{E}+05$ seemed to give the most reasonable result: unlike the monotonically increasing n_p , predicted by Model 0, which neglected fragmentation, n_p starts to decrease after z reaches approximately 6 cm. This trend of n_p is qualitatively consistent with the measurements of Puri et al. (1993). Quantitatively, the predicted n_p is considered satisfactory as well, considering that the measurement error could be as

Figure 3 Calculated n_p distributions along the annular maximum soot pathline using different models. Model 0 without fragmentation, Models 1~5 with fragmentation. Also shown are the experimental measurements of Iyer et al. (2007) and Puri et al. (1993).

Table 1 Model summary

Model	Fragmentation pattern	C value in Eq. (3)
0	Without aggregate oxidation fragmentation	
1	1:1	1.0E+05
2	1:1	1.0E+06
3	1:1	1.0E+04
4	2:1	1.0E+05
5	10:1	1.0E+05

high as $\pm 50\%$ according to Puri et al. (1993). From Figure 3, it can be found that comparable n_p results were obtained with the 1:1 (Model 1) and the 2:1 (Model 4) fragmentation patterns. The predicted n_p using the 2:1 pattern was only slightly higher than that using the 1:1 pattern. It is interesting to note that Harris and Maricq (2002) also found that the 2:1 and 1:1 patterns gave similar results in their study. Although both fragmentation patterns give similar results, the 1:1 fragmentation pattern (Model 1) is preferred because it is easier to implement. From Figure 3, although the n_p level from Model 5 with the 10:1 pattern agreed fairly well the measurements of Puri et al. (1993), the trend of n_p variation appeared noticeably different in the soot oxidation region especially when $z > 6.0$ cm compared to the measurements of Puri et al. (1993) and Models 1 and 4. The continuously increasing trend of n_p is similar to that of Model 0.

Figure 4 shows the calculated total aggregate number density N_A ($\#/\text{cm}^3$) along the annular pathline exhibiting the maximum soot volume fraction by Model 0 (without aggregate fragmentation) and the five different models with aggregate fragmentation. Also shown are the N_A measurements of Puri et al. (1993). From Figure 4, N_A profiles predicted by the six models show no difference in the lower portion of the flame (i.e., in the soot growth region). All models reproduce N_A reasonably in the soot growth region. N_A profiles predicted by the six models,

Figure 4 Calculated N_A distributions along the annular maximum soot pathline using different models. Model 0 without fragmentation, Models 1~5 with fragmentation. Also shown are the experimental measurements of Puri et al. (1993).

however, differ in the soot oxidation region ($z > 5$ cm). Model 0 and Model 3 both underpredicted N_A in the soot oxidation region because aggregate oxidation fragmentation was underestimated in these models. Model 2 overpredicted N_A in the soot oxidation region due to the excess aggregate oxidation fragmentation imposed in the model. The predicted N_A profiles from Models 1, 4, and 5 all agree fairly well with the experimental data in the soot oxidation region. No appreciable difference in N_A was found for the 1:1 (Model 1) and 2:1 (Model 4) fragmentation patterns. The predicted N_A from Model 5 was slightly lower than that of Model 1.

Although not shown here, Model 1 is found to be able to reasonably well predict the average primary particle diameter and the primary particle number density in both the soot surface growth and the oxidation regions. Furthermore, it has been checked that the average primary particle diameter and the primary particle number density are not sensitive to the implement of the aggregate oxidation-driven fragmentation models. This was not unexpected because primary particle number is conserved in each aggregate fragmentation instance, as discussed in Section 3.3.

5. SUMMARY AND CONCLUSIONS

In this study, three different aggregate oxidation-driven fragmentation models with 1:1, 2:1, and 10:1 fragmentation patterns were developed. The fragmentation models were then implemented into a multidimensional flame code to explore soot aggregate formation and oxidation in the nonsmoking laminar coflow ethylene/air diffusion flame of Santoro et al. (1983), together with a pyrene-based soot model and a detailed sectional aerosol dynamics model.

It was found that the addition of Model 1, which considers aggregate oxidation-driven fragmentation, significantly improved the prediction of the average degree of particle aggregation n_p in the soot oxidation region. On the other hand, Model 0, which neglected aggregate oxidation fragmentation, significantly overpredicted n_p and failed to reproduce its increasing-decreasing trend in the soot oxidation region. Similar results are obtained using the 1:1 (Model 1) and 2:1 (Model 4) fragmentation patterns. However, as the pattern ratio increased to 10:1 (Model 5), an appreciable difference in the predicted n_p was observed. In fact, as the pattern ratio becomes larger, the fragmentation effect diminishes and the predicted n_p approaches that of Model 0. Also, as the pattern ratio increases, the fragmentation model becomes more difficult to implement as it involves breaking an aggregate and assign the fragments to more sections.

Soot aggregate oxidation-driven fragmentation appears to be a very complicated phenomenon. However, because it may significantly affect soot structure that in turn affects soot properties, such as its health effect, environmental effect, and optical property, this phenomenon is worth detailed investigation. In the future, researchers should conduct more detailed theoretical and experimental studies to gain fundamental understanding of soot aggregate fragmentation pattern and rate.

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