DETAILED MODELING OF SOOT PARTICLE NUCLEATION AND GROWTH

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Detailed modeling of soot particle nucleation and growth in laminar premixed hydrocarbon flames is presented. The model begins with fuel pyrolysis, followed by the formation of polycyclic aromatic hydrocarbons, their planar growth and coagulation into spherical particles, and finally, surface growth and oxidation of the particles. The computational results are in quantitative agreement with experimental results from several laminar premixed hydrocarbon flames. A detailed analysis of soot particle inception and surface growth processes is presented. Surface growth was described in terms of elementary chemical reactions of surface active sites. The density of these sites was found to depend on the chemical environment. The model predicts the classical picture of soot particle inception and the classical description of soot particle structure.

Introduction

In their 1965 review article on the formation of carbon from gases, Palmer and Cullis wrote: "A major break-through in understanding carbon formation will have been achieved when it becomes possible in at least one case to account for the entire course of nucleation and growth of carbon on the basis of a fundamental knowledge of reaction rates and mechanisms." In this article, we present a detailed simulation of soot particle formation, beginning with fuel pyrolysis, formation of polycyclic aromatic hydrocarbons (PAHs), PAH planar growth and coagulation into spherical particles, and finally, the surface growth and oxidation of the particles. Some initial results of this modeling work have been reported by us previously. Those results, however, were computed at conditions corresponding to shock-tube experiments, for which measurements of soot particle properties are not readily available. Here, we report detailed modeling of soot particle nucleation and growth in hydrocarbon flames. For this purpose, we chose to model soot particle formation and growth in several laminar premixed flames: (a) the low-pressure acetylene-oxygen flames of Bockhorn et al. and Westmoreland et al., and an atmospheric ethylene-air flame of Harris et al. The formation and growth of aromatics followed the basic reaction scheme of Frenklach and co-workers. The formation reactions of the first aromatic ring

\[ n\text{-C}_4\text{H}_6 + \text{C}_2\text{H}_2 \rightarrow \text{phenyl} \]  

\[ n\text{-C}_4\text{H}_5 + \text{C}_2\text{H}_2 \rightarrow \text{benzene} + \text{H}_2 \]
were assigned the rate coefficients of Westmoreland et al.1,11 Other key reactions in PAH growth,

\[\text{arylH} + \text{H} \rightarrow \text{aryl} \cdot + \text{H}_2\] (3)
\[\text{aryl} \cdot + \text{H} \rightarrow \text{arylH}\] (4)
\[\text{aryl} \cdot + \text{C}_2\text{H}_2 \rightarrow \text{aryl-C}_2\text{H} + \text{H}\] (5)
\[\text{aryl} \cdot + \text{O}_2 \rightarrow \text{products}\] (6)

for both parts I and II of the model, were assigned the rate coefficients determined for similar reactions of phenyl, i.e., those of Kiefer et al.,14 Rao and Skinner,15 Fahr and Stein16 and Lin and Lin,17 respectively.

The Sandia burner code18 was used for the flame modeling simulating PAH formation and growth up to coronene. The computed profiles of H, H_2, C_2H_2, O_2, OH, H_2O and of a prescribed-size PAH, A_l, were then used as an input for the particle nucleation and growth simulation. Accomplished with an in-house kinetic code, several simultaneously occurring processes were modeled using a method of moments.19,20 The first part of this model, nucleation, describes the planar growth of PAHs via the H-abstraction/C_2H_2-addition reaction sequence12,13 using the technique of chemical lumping.2,19 This method provides a mathematically rigorous description of the growth process to an infinite size PAH, which can be schematically represented as

\[A_l \rightarrow A_{l+1} \rightarrow A_{l+2} \rightarrow \ldots \rightarrow A_{\infty}\] (7)

where \(A_l\) represents an aromatic species containing \(l\) fused rings. The PAH species formed in (7) are then allowed to coagulate, that is, all the \(A_i's (i = l, l + 1, \ldots, \infty)\) collide with each other forming dimers; the dimers, in turn, collide with \(A_l\) forming trimers or with other dimers forming tetramers; and so on. The coalescence reactions were treated as irreversible having sticking coefficients of unity. As the focus of this work is on very young, small particles, it was assumed that the coagulation dynamics is in the free-molecular regime. A size-independent enhancement factor of 2.2, based on the results of Harris and Kennedy,21 was used in calculations of collision frequencies.

Beginning with the dimers, the forming clusters were assumed to be "solid phase" and allowed to add and lose mass by surface reactions

\[\text{C}_{\text{soot}}^- + \text{H} + \text{H} \rightleftharpoons \text{C}_{\text{soot}}^- + \text{H}_2\] (8)
\[\text{C}_{\text{soot}}^- + \text{H} \rightarrow \text{C}_{\text{soot}}^- + \text{H}\] (9)
\[\text{C}_{\text{soot}}^- + \text{C}_2\text{H}_2 \rightarrow \text{C}_{\text{soot}}^- + \text{H} + \text{H}\] (10)

where \(\text{C}_{\text{soot}}^-\) H represents an arm-chair site on the soot particle surface and \(\text{C}_{\text{soot}}^-\) the corresponding radical. This mechanism is adopted based on the postulate22 that the H-abstraction/C_2H_2-addition (HACA) reaction sequence12 is responsible for high-temperature growth of all forms of carbonaceous materials. Wieschnowsky et al.6 also suggested that the HACA reactions12,13 "offer a key to the understanding of a number of phenomena" observed in their flame study.

Estimation of the rate coefficients of the heterogeneous reactions (8)–(11) was based on analogous gas-phase reactions of one-ring aromatics: benzene and phenyl. In doing so, it was assumed that collision efficiencies on a per-site basis are the same for both gas-phase and gas-solid reactions. Thus, the rate expression for reactions (8)–(11) for the \(i\)th particle was assumed to take the form

\[k_{g,s}C_g\alpha X_{s,s} N_i\] (13)

where \(k_{g,s}\) is the per-site rate coefficient, \(C_g\) is the concentration of the colliding gaseous species \(g\), such as H in reaction (8) or C_2H_2 in reaction (10), \(\alpha\) is the fraction of surface sites available for a given reaction, \(X_{s,s}\) is the number density of surface sites (i.e., number of sites \(s\) per unit area), \(S_i\) is the surface area of the \(i\)th particle, and \(N_i\) is the number density of the \(i\)th particle. \(\alpha\) takes into account the probability for a gaseous species to collide with the prismatic (edge) planes instead of unreactive basal planes of a particle and that not all of the edge carbons are available for a given reaction. It is rather difficult to estimate \(\alpha\) from first principles, and therefore it was left as a free parameter. The values of \(\alpha\) that produced the best agreement between the model predictions and experimental results are presented and discussed in the next sections.

\[X_{\text{C}_{\text{soot}}^- - \text{H}}\, \text{the number density of C}_{\text{soot}}^- - \text{H} \text{ sites, was estimated to be } 2.3 \times 10^{15} \text{ sites/cm}^2, \text{ i.e., one site per } 1.23 \times 3.51 \text{ Å}^2, \text{ where } 1.23 \text{ Å is the half-width of the benzene ring and 3.51 Å is the distance between PAH layers in soot} \text{. The number density of radical C}_{\text{soot}}^- \text{ sites were determined assuming steady state for } X_{\text{C}_{\text{soot}}^-}, \text{ implying that once a site on the particle surface was activated [here, by reaction (8)], it is more likely for this site to react with a major gaseous species (H, H_2, C_2H_2, or O_2 in the present model] before it encounters another particle. The steady state assumption leads to}

\[X_{\text{C}_{\text{soot}}^- - \text{H}} = \frac{k_{g,H}}{k_{g,H} + k[H] + k_{10}[C_2H_2] + k_{11}[O_2]} X_{\text{C}_{\text{soot}}^- - \text{H}}\] (14)
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where, for clarity, the \( k \)'s subscripts refer to per-site rate coefficients \( k_{\text{per-site}} \) of the corresponding reactions, (8) through (11). Note that the \( \alpha \)'s, assumed to be identical for all surface reactions, are cancelled. Equation (14) implies that the number density of radical sites is independent of particle size and determined by the "state" of the gas phase.

Substituting Eq. (14) into the rate expression (13) for reaction (10), we obtain the rate of surface growth for the \( i \)th particles due to the acetylene addition,

\[
r_{a,i} = 2 \frac{\alpha_{C_2H_2} k_9[H_2] k_8[H]}{k_{-6}[H_2] + k_9[H] + k_{10}[C_2H_2] + k_{11}[O_2]} S_i N_i,
\]

in mass units of carbon atoms. The factor of 2 in Eq. (15) accounts for the addition of two carbon atoms to the soot particle mass per reactive collision.

The rate of oxidation by \( O_2 \) is computed in a similar manner. The reference gaseous reactions for heterogeneous reactions (8)-(11) were reactions (3)-(6), respectively, with the rate coefficients taken from the sources cited above, at the high-pressure limit wherever appropriate. Oxidation by \( \text{OH} \), reaction (12), was assumed to proceed with the collision efficiency of 0.13, based on the results of Neoh et al.\(^{24}\)

The particle dynamics—the evolution of soot particles undergoing simultaneous nucleation, coagulation and surface reactions described above—was modeled by a method of moments (Method II of Ref. 20). This method does not require the assumption of a particle size distribution function (PSDF). The closure of the differential equations for the PSDF moments is accomplished by interpolation between the moments.\(^{2,25}\) The numerical integration of the moment equations took from 20 to 50 s on an IBM 3090/600S main-frame computer.

**Computational Results**

Figures 1–3 present the results computed using the model discussed above for two of the chosen flames: Flame B—flame No. 1 of Bockhorn and co-workers\(^{5–25}\) C\(_2\)H\(_2\)—19.6% O\(_2\)—Argon, pressure 90 torr; and Flame H—an atmospheric 16.5% C\(_2\)H\(_4\)—17.9% O\(_2\)—Argon, of Harris and co-workers.\(^{7–9}\) Both flames were computed with the same kinetic model, assuming \( A_4 \) (pyrene or acepyrene) to be the \( A_i \) species which initiates the planar growth of PAHs and the formation of particles, parts (II) and (III) of our model, respectively. Changing \( A_i \) affects the rate of particle nucleation. For instance, starting with \( A_6 \) instead of \( A_4 \) decreases the nucleation rate in Flame B by a factor of 26 and in Flame H by a factor of 4.

Particle inception in the two flames, B and H, could not be reproduced using the same value for \( \alpha \), the fraction of surface sites available for a given reaction. The best fit quality was obtained with \( \alpha = 0.1 \) for Flame B and \( \alpha = 0.7 \) for Flame H; these numbers were adopted in our simulations. The significance of the difference in the values of \( \alpha \) will be discussed in the next section.

It can be seen in Figs. 1–3 that the model predictions are in relatively close agreement with ex-

**FIG. 1.** Comparison of model predictions and experimental data for Flame B: (a) particle number density; (b) particle surface area; (c) average particle diameter [circles—experimental results, solid lines—model prediction, dotted lines—model prediction using an experimental-like profile for \( A_4 \)]; (d) specific rate of soot particle oxidation by \( O_2 \) [solid line—model prediction, dashed line—from the expression of Nagle and Strickland-Constable].\(^{34}\)
Fig. 2. Comparison of model predictions and experimental data\textsuperscript{a} for soot volume fraction in Flame B: circles—experimental data from flame No. 1 (C/O = 1.3, T\text{max} = 1980 K, H\textsubscript{2}O additive), triangles—experimental data from flame No. 2 (C/O = 1.26, T\text{max} = 2001 K, H\textsubscript{2}O additive); lines—model predictions, (a)—base case, (b)—computed for flame No. 3 (C/O = 1.3, T\text{max} = 1993 K, CsCl additive) with coagulation coefficient divided by 8, (c)—flame No. 2, (d) computed with α = 0.7 including decomposition of surface radical sites with the rate coefficient\textsuperscript{b} $4.5 \times 10^{14} \exp(-36500/T) \text{s}^{-1}$.

experiment for the initial, particle inception part of the flames; however, the computed and experimental results begin to deviate from one another with increasing flame height. One factor identified as a cause of this disagreement is the shape of the PAH profiles. This is demonstrated in Fig. 1, where it is shown that using a narrower (experimental-like\textsuperscript{5}) profile for A\textsubscript{4} improves the agreement between the model and experiment for Flame B. It was also computed that PAH condensation on the particle surface is sufficiently fast to significantly affect the PAH profiles in the post-flame zone.

Whereas particle inception in Flame B could be reproduced with a direct kinetic simulation, using only an imposed experimental temperature profile, particle inception in Flame H could not. All such attempts failed to predict the nucleation rate unless a physically unrealistic assumption $\Lambda_1 = \Lambda_1$ (benzene) was made. This problem was resolved when the experimental concentration profile of H atoms was used in the simulation instead of the computed one. Neither Harris \textit{et al.}\textsuperscript{8} nor the present authors\textsuperscript{10} were able to reproduce exactly the experimental H atom profile in Flame H (see Fig. 7 in Ref. 8). The model is close to the experiment as far as the peak concentration is concerned but greatly underpredicts the initial part of the profile. The discrepancy between the temperature and H atom profiles appeared to slow down the formation and growth of PAHs by several orders of magnitude. Therefore, the experimental profiles of H, OH, H\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}O and benzene, along with that of temperature, were imposed in our simulations of Flame H.

Discussion

Particle Inception:

As expected from the dynamics of Smoluchowski coagulation,\textsuperscript{20,25} the computed rate of nucleation is balanced by the rate of coagulation throughout the particle inception zone. Our model predicts, however, that the nucleation rate decays more slowly with flame height than is usually deduced from experiment. At this time, it is not clear whether this disagreement comes from imprecise knowledge of
the kinetics and thermodynamics of PAH growth,\textsuperscript{10,13} PAH condensation on soot particles, additional unaccounted-for PAH destruction processes, or uncertainties in the determination of experimental nucleation rates. For instance, deconvolution of optical measurements is affected by the assumptions made regarding the particle size distribution function. The latter is usually assumed to be monodisperse or self-preserving whereas the present computations, as well as others,\textsuperscript{7,20,25} indicate that the inception-zone PSDF is much broader than the self-preserving one. The principal difficulties in resolving this problem lie in the limited sensitivity of optical probes and rapid coagulation rates: optical instruments can only see particles larger than a certain undefined size, and withdrawal of a sample by a mechanical probe loses small particles due to their rapid coalescence with large particles. Obviously, this problem affects all particle properties.

Particle inception is primarily determined by PAH coagulation, initiated and controlled by PAH coalescence into dimers. This is demonstrated in Fig. 4, which depicts the average particle mass computed in several numerical tests. We note that excluding all surface processes (cf. curves a and c in Fig. 4), which results in a substantial decrease of the particle mass, does not really change the order of magnitude of the particle size. In other words, the particle size is essentially determined by coagulation. The sensitivity to the coagulation coefficient is demonstrated by curve b in Fig. 4.

Another interesting observation that follows from the results shown in Fig. 4 is that while the average soot particle size is computed to contain $10^3$--$10^5$ carbon atoms, the corresponding average PAH size is only 20 to 50 carbon atoms. This indicates that the crystallites comprising incipient soot particles should be on the order of 7 to 12 Å. For comparison, Thomas\textsuperscript{20} suggested that crystallites in soot are composed of PAHs having 40 or more carbon atoms, and Ebert \textit{et al.}\textsuperscript{23} determined by X-ray diffraction the crystalite size in a mature soot to be 12 to 20 Å. This computational result, that the PAH size is so much smaller than the size of the corresponding soot particles, provides another illustration of the critical role of coagulation in soot formation. It means that molecular reactions alone cannot explain the formation of soot. This is one of the key arguments in refuting\textsuperscript{9} the proposal that soot is formed via spheroidal, polyhedral carbon clusters.

As stated earlier, we assumed that PAH coagulation proceeds irreversibly. Yet, the association of small PAHs is expected to be counteracted by the reverse process—cluster decomposition. In fact, Miller \textit{et al.}\textsuperscript{27} suggested that the concentration of PAH dimers should be very low and, therefore, PAH dimerization cannot account for soot particle inception. Their analysis was founded on the presumption that "equilibrium is established at each step." However, one cannot judge the PAH coagulation flux using the equilibrium assumption—these fluxes must be computed kinetically. The equilibrium among individual PAHs and clusters may never be attained, and the mass flux is likely to be driven by an irreversible process following the dimer formation. For example, the binding energy of benzene clusters increases with the number of benzene molecules in the cluster.\textsuperscript{28} It is also possible that a PAH dimer is stabilized by a reaction with an aliphatic, forming a covalently bonded link between the PAH layers. It should be also taken into account that at small sizes, characteristic of PAH molecules produced in (7), the van der Waals enhancement should be larger than the factor of 2.2 assumed in the present study. The collision rate may also be enhanced if a small fraction of PAHs is positively ionized. For instance, the binding energy of the benzene dimer ion\textsuperscript{29} is 71 kJ/mol, as compared to 2–11 kJ/mol of neutral benzene dimers.\textsuperscript{30} In light of all these factors, and considering the present uncertainties in the kinetic and thermodynamic parameters of PAH formation reactions and the lack of data on PAH clusters, the assumption of a PAH sticking coefficient equal to unity is not unreasonable.

\textbf{Surface Processes:}

In their study, Bockhorn and co-workers\textsuperscript{6} observed that the surface growth rate is independent of the surface area of soot particles, contrary to Harris and Weiner,\textsuperscript{31} who postulated that the rate of surface growth is first order in particle surface area. Not only is our model capable of simulating the flames studied by these two research groups,
but it also predicts correctly the experimental trends resulted from seeding the flame with CsCl, employed by Bockhorn and coworkers to suppress coagulation and thereby vary the surface area of incipient soot particles. We have modeled this effect by reducing the coagulation rate coefficient by an arbitrary factor, so that the computed surface area matches the experiment; and this produced the correct trends for other properties as well. Curve b in Fig. 2 depicts the results computed in such a manner for the conditions of flame No. 3 of Wieschowsky et al. As can be seen in this figure, the post-flame slope of curve b is the same as that of curve a, computed for the base case. In other words, our model predicts, in accord with the experimental data, that the slope of the post-flame $df_v/dt$ vs $f_v$ dependence, where $f_v$ is the soot volume fraction, does not change with the change in soot particle surface area. Further analysis of Fig. 2 indicates that the maximum soot volume fraction in case b is overestimated; however, the model prediction for flame No. 2 of Wieschowsky et al. curve c in Fig. 2, is in agreement with experiment. Since the experimental counterparts of computed curves b and c overlap, we conclude, based on several test runs, that the addition of CsCl must retard PAH production.

Our model describes the surface processes in terms of elementary reactions of active sites. The density of active sites is determined, as evident from Eq. (14), by the gas-phase environment—by the competition among reactions (8)–(11). Hence, the dissimilarity in surface growth behavior can be explained by the difference in the dynamics of active sites. For instance, in the limit when term $k_{10}[C_2H_2]$ dominates the denominator of Eq. (14), which is realized at the conditions of low-temperature flames such as Flame H, the surface growth rate

$$r_s = 2\alpha x_{\text{soot}} \cdot k_{\text{ab}}[H] \sum_i S_i N_i$$

(16)

is directly proportional to surface area, $\sum_i S_i N_i$, and the rate of the H-abstraction, $k_{\text{ab}}[H]$. This is illustrated in Fig. 3d: the specific surface growth rate in Flame H is very closely approximated by that of the low-temperature limit, Eq. (16). Analysis of the computational results revealed that the decay in the specific surface growth rate is caused by the decrease in the value of $k_{\text{ab}}[H]$, mainly due to the decrease in the concentration of hydrogen atoms. At the high-temperature conditions of Flame B, the removal of surface radical sites occurs primarily by reactions (9) and (10). We note that while predicting well the experimental observations of Bockhorn and co-workers, our model does not support the interpretation of these results as surface growth rate being independent of soot particle surface area.

The computed rates of several surface processes for Flames B and H are shown in Fig. 5. Analysis of these results indicates that oxidation by OH and $O_2$ is quite insignificant in the post-flame zone. The surface growth of soot mass is primarily determined by two processes: acetylene addition via the HACA reaction sequence, and PAH condensation on the particle surface. The relative contribution of each of these processes appears to change with experimental conditions. Thus, while the acetylene addition dominates surface growth in Flame H, PAH condensation prevails in Flame B. Analysis of the computational results indicated that the main contribution of the PAH condensation occurs at the early stages of PAH coagulation. Our numerical prediction of PAH participation in surface growth is in accord with the experimentally-based conclusions of Haynes and Wagner and Lam et al. The reliability of our model is further supported by the facts that the computed net surface growth rate is in close agreement with that determined by Harris and Wiener (Fig. 3d) and that the predicted rate of soot oxidation by $O_2$ agrees well with the expression of Nagle and Strickland-Constable (Fig. 1d).

Finally, we address the issue that different values of $\alpha$, the fraction of surface active sites, were required to simulate Flames B and H. Deterioration (or annealing) of the soot particle surface has been advanced to explain the decay in the empirical surface growth rate coefficient with reaction time. We showed above, however, that this decay can be explained by the decrease in the H atom concentration which reduces the density of surface radical sites. Nonetheless, our modeling results indicate that $\alpha$ should be lower at higher temperature. We attempted to simulate the reduction in $\alpha$ by assuming that $C_{\text{soot}}$ sites decompose with the

\[ \text{FIG. 5. Computed rates: (a) PAH condensation; (b) acetylene addition, reaction (10); (c) oxidation by OH, reaction (12); (d) oxidation by } O_2, \text{ reaction (11).} \]
rate coefficient of Braun-Unkhoff et al.\textsuperscript{36} for phenyl fragmentation. This considerably overpredicted the experimental data (cf. curves \textit{a} and \textit{d} in Fig. 2). The decomposition rate coefficient had to be increased by more than an order of magnitude to bring the computed values into agreement with the experimental ones; but then the shape of the \( \frac{df_{\text{C}}}{df} \) vs-\( f_\text{C} \) dependence became very distorted. The latter could be resolved only when the \( C_{\text{soot}} \) decomposition was assumed to be temperature independent, which however does not have any possible physical explanation. Disappearance of \( C_{\text{soot}} \) sites could also not be explained by reactions with CO, CO\textsubscript{2} or H\textsubscript{2}O. Furthermore, all these attempts to simulate Flame B destroyed entirely the agreement for Flame H. This leads us to conclude that the parameter \( \alpha \) represents a steric phenomenon. At high temperatures, soot particle crystallites are more mobile and align themselves in a more orderly fashion, such that the edge planes of neighboring crystallites face each other, thus limiting the access of gaseous species to the reactive carbon sites, and the unreactive basal planes constitute then most of the particle surface.

Conclusions

Our model predicts what is essentially the classical picture of soot particle inception:\textsuperscript{37} formation of PAHs, their coagulation into clusters and cluster coagulation, and surface growth due to chemical and physical processes. The model also predicts the classical structure of soot particles:\textsuperscript{38} a less dense particle core, composed of randomly oriented PAH oligomers, and a more dense concentrically-arranged particle shell. Surface growth processes can be understood in terms of elementary chemical reactions of surface active sites. The number density of these sites is determined by the chemical environment.

Acknowledgments

The computations were performed using the facilities of the Penn State Center for Academic Computing. The work was supported by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant No 88-0072. The US Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation thereon.

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