Modelling soot particle composition and structure based on detailed PAH chemical mechanism

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1 Introduction

A recently developed comprehensive model for soot formation and growth, named as, the aromatic site - primary particle (ARS-PP) model [1] has been extended in this paper. This model is based on the assumption that a soot particle is formed from planar PAH molecules. The basis for this assumption is the recent experimental findings of Vander Wal et al. [2 and refs. therein], in which stacks of planar PAH molecules were observed in high resolution transmission electron microscopy (HRTEM) images of soot particles from engines. For the growth of PAHs present in soot, a detailed chemical mechanism is used. The ARS-PP model is also able to track the size of primary particles constituting soot (primary particles are the spherical nanostructures forming chain-like aggregate structure of soot). With this detailed model, it is possible to obtain information about the composition (in terms of the number of C and H atoms) and the size distributions of soot particles in combustion devices. This has been shown in [1] for soot particles in a plug flow reactor (PFR). With the current reaction mechanism, the model predicts the C/H ratio of soot particles to lie in between 1 and 2. However, the experiments predict this value in the range of 2 to 8 [3]. This indicates that the present chemical mechanism over-predicts the number of H atoms in mature soot. Furthermore, comparisons between the predicted particle size distributions with the observed ones for soot particles present in a premixed laminar flame and a PFR are shown in [1, 4], and both the studies conclude that the model slightly over-predicts the particle diameter at lower residence times.

The aims of this paper are: (a) to introduce new PAH processes in the chemical mechanism that can dehydrogenate mature soot particles (or PAHs), (b) to study the interaction between PAH molecules to facilitate the formulation of soot nucleation sub-model, and (c) to implement an effective sintering sub-model in the ARS-PP model that can reduce the surface area of soot particles. The effect of these advancements on the model predictions of soot particle composition and size distribution at different heights above the burner in a premixed laminar flame is studied, and some of the results are shown here.

2 ARS-PP model

The ARS-PP model, detailed in [1], is briefly reviewed here along with the modifications suggested in this work. For the description of PAH molecules present in soot, a number of functional sites are

identified, as shown in figure 1, on which the PAH processes present in the chemical mechanism can take place. In this work, a new site, 6-member bay, is introduced in the list of principal site types.



Figure 1. An example PAH molecule showing the principal functional sites.

For a complete description of the 3D aromatic structure of soot particles, along with the information about the site types, other information is also required. For this purpose, a ten-dimensional state space for each soot particle, X_p is defined: $X_P = (C, H, N_{FE}, N_{FE}, N_{ZZ}, N_{AC}, N_{BY5}, N_{BY6}, S_a, N_{PAH})$, where, C and H are the number of carbon and hydrogen atoms respectively, N_x is the number of sites of type x, S_a is the surface area, and N_{PAH} is the number of PAH molecules present in a soot particle. When a PAH process occurs on a soot particle, all the parameters present in the state space are changed according to the fixed rules described in [1]. Given that soot is composed of many PAH molecules, to reduce the computational expense, the structural information about each PAH molecule present in soot particles is neglected in the model. This information is provided by the Kinetic Monte Carlo–Aromatic Site (KMC-ARS) model in terms of correlation and statistics, detailed in [5].

3 KMC-ARS model

The KMC-ARS model considers the growth of a single PAH molecule in a chemical environment, based on the chemical mechanism of the ARS-PP model [5]. The structure of a PAH molecule is tracked after each PAH process. Further information about this model can be obtained from [5]. This model is extended in this work to facilitate the simultaneous growth of multiple PAH molecules together, and to generate PAH ensembles consisting of PAH stacks. The purpose of this extension was to study the interaction between PAH molecules of different sizes and to determine their probability of coagulation after collision (collision efficiency). In [6], the mass spectra of PAH monomers and dimers have been observed for a number of premixed laminar flames. By comparing the experimentally observed PAH mass spectra with the computed spectra (as shown in figure 2), a range of values of PAH collision efficiency is determined. Figure 3(a) shows the variation in collision efficiency with the reduced mass of colliding PAHs. From the KMC simulations with the proposed efficiencies, it was found that for a successful coagulation of the colliding PAHs to take place, a reduced mass, greater than 90, was required. This value agrees very well with the findings of Herdman et al. [6]. In [6], the binding energies of PAHs of different sizes were calculated theoretically, and it was concluded that the colliding PAHs with reduced mass greater than 83 have sufficient binding energies to form stable dimers. Figure 3(b) shows an example computed dimer stack present in a C_2H_4 flame [7]. For a detailed soot nucleation model, in which PAHs bigger than pyrene are also allowed to incept soot, these values of the collision efficiencies will be the foremost requirement. Further details on the method used for the determination of collision efficiency, and the effect of the proposed collision efficiency on model predictions will be given in the full length paper.

4 Soot particle composition

The absence of PAH processes in the chemical mechanism, which can dehydrogenate the PAHs, leads to an under-prediction of the C/H ratio in mature soot particles. To improve the model predictions of



Figure 2. PAH mass spectra for a C_2H_4 - O_2 flame [7] (pressure = 120 mbar, C/O = 1, cold gas velocity = 54 cm/s). PAH monomers and dimers in the computed spectra are represented by gray and black lines, respectively.



Figure 3. (a): Collision efficiencies of the colliding PAHs. (b): Example computed constituents PAHs of a dimer present in a C_2H_4 - O_2 flame [7] (pressure = 120 mbar, C/O = 1, cold gas velocity = 54 cm/s).

soot particle composition, four new PAH processes, listed in table 1, have been included in the PAH reaction mechanism of the ARS-PP model. The possible pathways for process 3 (table 1) and the rates of the elementary reaction involved in the pathways are given in [5]. The rate constants were determined using density functional theory (DFT) with the HCTH/407 and the B3LYP/6-311(d) functionals, and transition state theory. A similar treatment has been done for the other processes. With the inclusion of new proposed processes in the PAH chemical mechanism, the ARS-PP model predicts the C/H ratio of mature soot in the range of 1 to 4, which is an improvement over the previous predictions. The details of the pathways for the proposed processes, and the evolution of the C/H ratio of soot particles with time will be shown in the full length article.

3 Sintering sub-model

The sintering of soot particles is studied using a model that describes the sintering of each pair of neighboring primary particles individually in a soot particle. For this purpose, for each primary particle, a list of neighboring primaries is generated. It is for the first time that such a sintering model, which works "locally" on a soot particle, has been incorporated in a soot model. The driving force for the sintering of two connected primaries is the difference in the surface area of the coagulated primaries and the surface area of a sphere with the same volume as that of the two primaries. The rate of change in surface area of two coagulated primaries is given by:

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$$\frac{dA}{dt} = \frac{1}{\tau} (A - A_s)$$

where A is the surface of the two sintering primaries, A_s is the surface of a sphere with the same volume as that of the two primaries, and τ is the characteristic sintering time. After incorporating this new sintering model in the ARS-PP model, particle size distribution functions (PSDFs) for several premixed laminar C₂H₄ flames were generated and compared to their experimentally observed PSDFs [8] at different heights above the burner. It was observed that at lower heights, the model prediction of the PSDFs improved with the inclusion of this sintering model. Further information about the model, model parameters and the simulation results will be provided in the full length paper.

Table 1: New PAH processes introduced in the PAH chemical mechanism.



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