Modeling of Size Distribution Functions and Chemical Structure of Combustion-Formed Particles

M. Sirignano¹, J. Kent², A. D'Anna¹

1. Dipartimento di Ingegneria Chimica, Università di Napoli “Federico II”, Napoli, Italy
2. School of Aerospace, Mechanical & Mechatronic Engineering, University of Sydney, Sydney, Australia

1. Introduction

The formation of soot in combustion is a complex process involving gas-phase chemical kinetics, heterogeneous reactions on the particle surface and particle dynamics. Modeling of these processes in combustion environments has received great attention in recent years [1-5]. Models, today, are able to approximately simulate the concentration and size distributions of particles in many combustion systems including premixed and diffusion flames [6-13].

In recent years the use of new and sophisticated diagnostics has increased our knowledge of particle inception, growth and coagulation. Polycyclic aromatic hydrocarbons (PAHs), formed close to the flame front and grow in the post-flame regions, reach molecular masses of 1000-3000u typical of incipient particles of few nanometers. Thereafter they grow and coagulate determining the size distribution functions of the particles.

These results have stimulated modeling activity in the area of particle inception. Models hypothesize that PAHs of some sizes begin to stick to each other during collision, thus forming PAH dimmers, trimers and so on. Pyrene was considered the first aromatic species in the PAH series able to form stable dimers at flame temperatures and the dimers were considered as the first soot nuclei. Surface addition mainly by acetylene was responsible for soot loading [2,5].

Models which combine dimerization of PAHs with the formation of ring-ring aromatic species through a purely-chemical mechanism have recently been proposed [8-12]. The growing molecular species acquire the properties of a condensed phase. Surface reactions with gas-phase species, mainly acetylene and PAHs, and coagulation of the particles determine their final concentration and size distribution. Surface growth is based on chemical analogy of gas-phase aromatic chemistry.

In the discrete-sectional method, used here, the ensemble of aromatic compounds with molecular mass higher than the largest aromatic compounds in the gas-phase is divided into classes of different molecular mass and all reactions are treated in the form of gas-phase chemistry using compound properties such as mass, numbers of carbon and hydrogen atoms averaged within each section. The molecular mass distribution of the species is obtained from the calculation and is not hypothesized a priori. Particle evolution is followed by combining the laws of reacting flows with the population balance for suspended particles.

Next generation models need to predict not only particle concentrations and size distribution functions but also their morphology and chemistry in order to better predict particle radiative properties and health effects.

The present paper presents a first approach to follow chemical evolution of the particles formed in premixed flames by simulating both molecular growth and H/C variation of the particles along the flame axis. A previously developed detailed kinetic model of particle formation has been extended to include a double discretization of the particle phase: in addition to the division into sections for the carbon atoms, the scheme also provides different values of H/C for each carbon number. The kinetic mechanism has been tested to simulate a
slightly-sooting premixed flame of ethylene/oxygen for which a large set of experimental data exists.

2. Model development

2.1 Formation of pyrolysis products and cyclization

The gas-phase kinetic mechanism used to model hydrocarbon oxidation and pyrolysis is built on the GRI mechanism for C1 and C2 species [14]. Two reaction pathways are considered for the formation of benzene rings: the addition of n-C4 radicals to C2H2 and the self-combination of propargyl radicals. The formation of naphthalene, the first compound in the PAH series, is modeled through the sequential addition of C2H2 to phenyl radical (HACA mechanism) [5] and the combination of resonantly stabilized radicals, i.e. the combination of two cyclopentadienyl radicals [15] and the combination of benzyl and propargyl radicals [16]. The pathways involving the HACA mechanism and the combination of resonantly-stabilized radicals are also used for the modeling of higher ring PAH. By-products of the molecular growth process are alkyl-substituted PAH and five-membered aromatics such as acenaphthylene. Detailed of the gas-phase mechanism are repeated elsewhere [13].

2.2 Particle inception and growth

As shown in the table 1, the molecular addition sequences begin with the H-loss from an aromatic compound to produce the corresponding radical either through H-abstraction by H and OH (Rx1) or decomposition (Rx2). Aromatic radicals can also react with other aromatic radicals (Rx3) forming biphenyl-like compounds or with H atoms (Rx2-backward) forming stable species [13].

Acetylene addition to aromatic radicals (Rx4) is the extension of the HACA mechanism to larger compounds. Due to the high number of sites, where acetylene can be attached, it is possible to hypothesize that each acetylene addition sequence forms a closed aromatic ring [17] leading to the formation of peri-condensed aromatic hydrocarbons (PACH). However the formation of a five-ring is also possible but it can easily be converted to a PACH structure.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ai + H,OH = Ri + H2, H2O</td>
<td>( 8.85 \times 10^{-13} \exp(-16000,4560/RT)n_C^{2/3}H/C )</td>
</tr>
<tr>
<td>Ai =&gt; Ri + H</td>
<td>( 6 \times 10^{14} \exp(-113100/RT)n_C H/C )</td>
</tr>
<tr>
<td>Ri + Rj =&gt; Ai+j</td>
<td>( 8 \times 10^{12}n_C^{1/6} )</td>
</tr>
<tr>
<td>Ri + C2H2 =&gt; Ai + H</td>
<td>( 3 \times 10^{6}T^{1.787} \exp(-3262/RT)n_C^{0.616} )</td>
</tr>
<tr>
<td>Ri + Aj =&gt; Ai+j + H</td>
<td>( 2 \times 10^{13}T^{0.5} \exp(-4560/RT)n_C^{1/6} )</td>
</tr>
<tr>
<td>Ri + H =&gt; Ai + H2</td>
<td>( 8.85 \times 10^{-13}n_C H/C )</td>
</tr>
<tr>
<td>Ai + H =&gt; Ai + H + H2</td>
<td>( 6 \times 10^{14} \exp(-30000/RT)n_C H/C )</td>
</tr>
<tr>
<td>Ai + O2 =&gt; Ai + HCO</td>
<td>( 3 \times 10^{12}T^{0.5} \exp(-10600/RT)n_C^{0.625} )</td>
</tr>
<tr>
<td>Ai + Aj =&gt; Ai+j</td>
<td>( 4.3 \times 10^{11}T^{0.75} \exp(-8000/RT)n_C^{2/3} )</td>
</tr>
</tbody>
</table>

Aromatic molecule addition to aromatic radicals (Rx5) leads to the formation of \(-\) bond linked aromatics here defined oligomers of aromatic compounds (OAC).

OACs have the possibility to lose hydrogen atoms forming pericondensed structures. Two H atom losses are considered: the first is the H abstraction by an H radical (Rx6), the second is the ejection of H2 activated by an H atom (Rx7). The first dehydrogenation channel (Rx6)
consider an abstraction of a H atom by an H radical, that allows to close a more condensed structure. The increase of collision with the mass of particle is considered as well as the effective availability of hydrogen in the particle.

The second dehydrogenation channel (Rx7) is built on the consideration that the radicals formed through the attack of a H atom have such a complex structure that instead of survive in the radical form an aromatic ring is formed. The limiting stage is the rearranging of structure to expel an H atom and form a new stable specie with a lower H/C ratio and consequently higher aromaticity. A dependence on the number of hydrogen present in the structure is considered.

Oxidation by OH radicals (Rx8) [18] and O2 (Rx9) [19] are responsible for mass loss.

Coagulation process is taken into account. PCAHs and OACs grow up until intermolecular interactions (van der Waals-interactions) between molecules become strong enough to form homo-molecular and hetero-molecular clusters of PCAHs and OACs (Rx10). It accounts both for the increase of collisions frequency of particles with the increase of their masses and for the dependence of coagulation efficiency on the temperature. Moreover also the chemistry of particles is considered evaluating the Hamacker constant for the species involved in coagulation [20,21]: from benzenic ring to graphite the values of the Hamacker constant range from 3E–20J to 5E–19J. This new enhancements allow to consider different values of Hamacker for each H/C ratio.

2.3 Computational

A discrete sectional approach is used for the modeling of gas-to-particle transition. To model particulate matter the range of molecular weight of interest is discretized by using lumped species. This approach allows treatment of molecule/particle reactions as in the gas-phase.

In the previous version of the scheme [13] each species was characterized by the number of carbon atoms and the H/C ratio. In this paper the scheme contains a double discretization: in addition to the division into 25 sections for the carbon atoms the scheme provides also four different values of the H/C ratio. To better describe all particles produced in combustion in terms of molecular weight and hydrogen content, the carbon atoms range from 24 to 4X108 and the H/C ratio assumes values of 0.2, 0.5, 0.7, 1. Overall the scheme contains 100 lumped species, each considered both in the stable and radical form.

3. Results and Discussion

Kinetic scheme has been developed and tested in premixed flames of ethylene and Benzene. These flame have been already experimentally investigated by Ciajolo et al. [22-24]. In Fig. 1 soot and condensed species concentration profiles for the ethylene flame are reported. Experimental data are compared with modeling results. Model seems able to reproduce experimental data in shape and values. In particular soot inception and final concentration are well matched, whereas for condensed species sight mismatch is still present. In Fig.2 benzene flame is described in terms of soot and condensed species concentration. Modeling result show that the scheme here adopted is able to predict the evolution of particulate matter along the flame. Soot profile is well reproduced both at the inception and at the end of the flame where a plateau is reached. Condensed species show a rapid decrease after soot inception; this behavior is found both experimentally and numerically.

To analyze chemical properties of species produced in flame, a comparison between experimental and numerical evaluation of H-to-C ratio for soot particles has been conducted. In Fig. 3 H-to-C ratio for soot particles is reported. Moreover temperature is also reported, in order to better understand the differences and similarities between the two flame. Model is able to reproduce H-to-C ratio in shape for both flames, whereas a slight mismatching on
Fig. 1 Soot (□) and CHS (△) concentration profiles compared with modeled concentration of species which weight more (___) and less than 10000 amu (- -) for ethylene flame.

Fig. 2 Soot (□) and CHS (△) concentration profiles compared with modeled concentration of species which weight more (___) and less than 10000 amu (- -) for benzene flame.

values is still present. Experimentally soot particles are separated on the base of solubility inorganic solvent, whereas numerically only particles larger than $3 \times 10^5 \text{u}$ are considered soot. This difference in definition could be responsible in part for the mismatching: particles smaller than $3 \times 10^5 \text{u}$ could be insoluble because of their low H-to-C ratio.
By analyzing particles concentration, H-to-C ratio and temperature profile, it comes out that in ethylene flame soot particles evolves toward a higher value of H-to-C ratio and the process seems to occur more gently than in benzene flame. On the opposite benzene, that exhibits a strong soot inception, presents a strong dehydrogenation that leads to more structured soot particles. This different behavior can be in first approximation attributed to the different temperature history in the two flames: ethylene flame has a flame front located at lower height above the burner than benzene whereas this latter reaches higher temperature on the flame front and in post oxidation region.

![Experimental H-to-C ratio for soot particles produced in ethylene (■) and benzene(▲) flame compared with modeled (solid and dashed heavy lines respectively) are reported (right axis). Temperature profile used for modeling in ethylene (solid light line numerical) and benzene (dashed light line) flames are also reported (left axis).](image)

4. Conclusions

New enhancements to a detailed kinetic scheme for modeling particulate matter produced in combustion have been proposed. The sectional scheme now also provides for discretization of hydrogen content in each section. This enhancement allows to a better understanding of the chemical characteristic of products. The comparison with experimental data for a ethylene and benzene flame shows that the model is able to reproduce the concentration profile of soot and CHS. Model has showed also a good reliability in the prediction of H-to-C ratio of soot particles. Trends of soot particles dehydrogenation is matched in both cases whereas there is still some mismatching in values. In ethylene flame aromatization process of soot particles occurs more gently than in benzene flame. Finally soot particle produced in benzene flame are more structured. This behavior is possible to be linked to higher temperature in benzene flame at flame front and in post oxidation zone.

5. References

14. [http://www.me.berkeley.edu/gri_mech/index.html](http://www.me.berkeley.edu/gri_mech/index.html)