CHEMICAL ENGINEERING TRANSACTIONS Volume 17, 2009
Editor Sauro Pierucci
 ISBN 978-88-95608-01-3 ISSN 1974-9791
DOI: 10.3303/CET0917016

Modelling of molecular growth and particle inception in flames

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In order to go deep inside the nature and chemistry of combustion produced particles a kinetic modeling approach is proposed. It is based on the modeling of gas-to-particle transition through sections in which 100 lumped species are used having a C number ranging from 24 to $4X10^8$ and H/C ratio ranging from 0.2 to 1. This approach gives the possibility to numerically follow not only the mass evolution of particles but also their size distribution function and hydrogen content. The model is tested in a premixed flat flame of ethylene/oxygen with C/O=0.8. Comparison of modeled results with experimental data is reasonable both in terms of concentration of species and H/C ratio.

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 and today, is possible to simulate the concentration and size distributions of particles in many combustion systems including laminar premixed and diffusion flames (Smooke et al., 1999; Richter et al, 2005; D'Anna, 2008; D'Anna and Kent, 2008). In recent years the use of new and sophisticated diagnostics has increased our knowledge of particle inception, growth and coagulation. Polycyclic aromatic hydrocarbons (PAHs), which are usually assumed as the main precursors of particles, formed close to the flame front grow in the post-flame regions reaching the molecular masses of the incipient particles, about 1,000 - 10,000u (which correspond to sizes of few nanometers). Thereafter they grow and coagulate determining the size distribution functions of the particles.
These results have stimulated modeling activity. Models of nucleation have been included: PAH of some sizes begin to stick to each other during collision, thus forming PAH dimers. PAH dimers collide with PAH molecules forming PAH 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.

Please cite this article as: Sirignano M., Kent J. and D'Anna A., (2009), Modelling of molecular growth and particle inception in flames, Chemical Engineering Transactions, 17, 93-98 DOI: 10.3303/CET0917016

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. Particle evolution is followed by combining the laws of reacting flows with the population balance for suspended particles.
Today models are able to simulate the concentration and size distributions of particles in many combustion systems including laminar premixed and diffusion flames. 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 repeats a detailed kinetic model of particle formation in premixed flames of ethylene with the aim of predicting concentration profiles of trace pyrolysis products involved in the process of particulate formation, the details of particle size distribution (PSD) functions and the evolution of the H-to-C ratio along the flame.

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 (me.berkeley.edu/gri_mech). 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) (Frenklach and Wang, 1994) and the combination of resonantly stabilized radicals, i.e. the combination of two cyclopentadienyl radicals (Marinov et al., 1996) and the combination of benzyl and propargyl radicals (Colket et al., 1994). 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 (D'Anna, 2008).

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 (D'Anna, 2008).
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 (Moriarty and Frencklach, 2000) leading to the formation of peri-condensed aromatic hydrocarbons (PCAH). However the formation of a five-ring is also possible but it can easily be converted to a PCAH structure.

Table 1. List of reaction for the sectional part with relative rate constant.

Reaction	N°	Rate constant
Ai + H,OH = Ri + H2, H2O	Rx1	8.85E13 exp(-16000,4560/RT)$n_C^{2/3}$H/C
Ai => Ri + H	Rx2	6E14 exp(-113100/RT) n_C H/C
Ri + Rj => Ai+j	Rx3	8E12 $n_C^{1/6}$
Ri + C2H2 => Ai + H	Rx4	3E6 $T^{1.787}$ exp(-3262/RT) $n_C^{0.616}$
Ri + Aj => Ai+j + H	Rx5	2E13 $T^{0.5}$ exp(-4560/RT) $n_C^{1/6}$
Ri + H =>Ai + H2	Rx6	8.85E13 n_C H/C
Ai + H => Ai + H + H2	Rx7	6E14 exp(-30000/RT) n_C H/C
Ai + OH => Ai + HCO	Rx8	3E12 $T^{0.5}$ exp(-10600/RT) $n_C^{0.623}$
Ri + O2 => Ai + 2CO	Rx9	4.3E11 $T^{0.5}$ exp(-8000/RT) $n_C^{2/3}$
Ai + Aj => Ai+j	Rx10	2E13 $T^{0.5}$ $n_C^{1/6}$ γ

Aromatic molecule addition to aromatic radicals (Rx5) leads to the formation of σ-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) (Neoh et al., 1985) and O2 (Rx9) (Xu et al., 2003) 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 (D'Alessio et al., 2005; Israelachvili, 1991): 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 (D'Anna, 2008) 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 $4X10^8$ 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

The kinetic scheme is tested by modeling a premixed laminar flat flame of ethylene and oxygen studied experimentally by Ciajolo et al (1998).

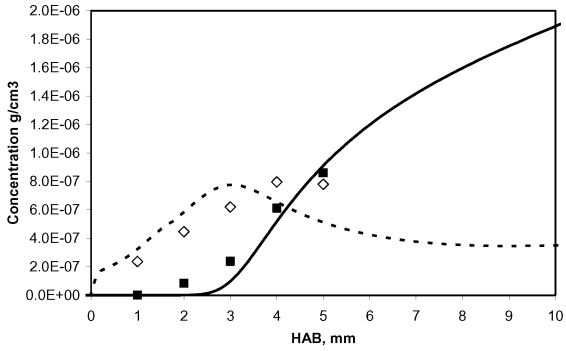

Fig.:1 Soot (■) and CHS (◊) concentration profiles compared with modelled concentration of species which weigh more (__) and less than 10000amu (- -).

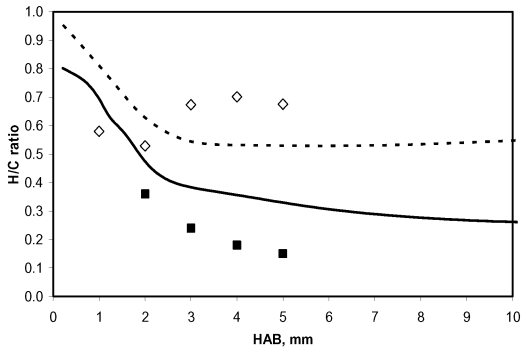

Fig.:2 Experimental H/C ratio of soot (■) and H/C ratio of CHS (◊) compared with modeled profiles of H/C ratio. Species which weigh more (__) and less than 10000amu (- -).

To compare the results of the model with experimental data, soot particles are defined as species with molecular weight higher than 10000amu. All the species with molecular

weight lower than 10000amu are grouped to be compared with DCM-soluble condensed hydrocarbon species (CHS).

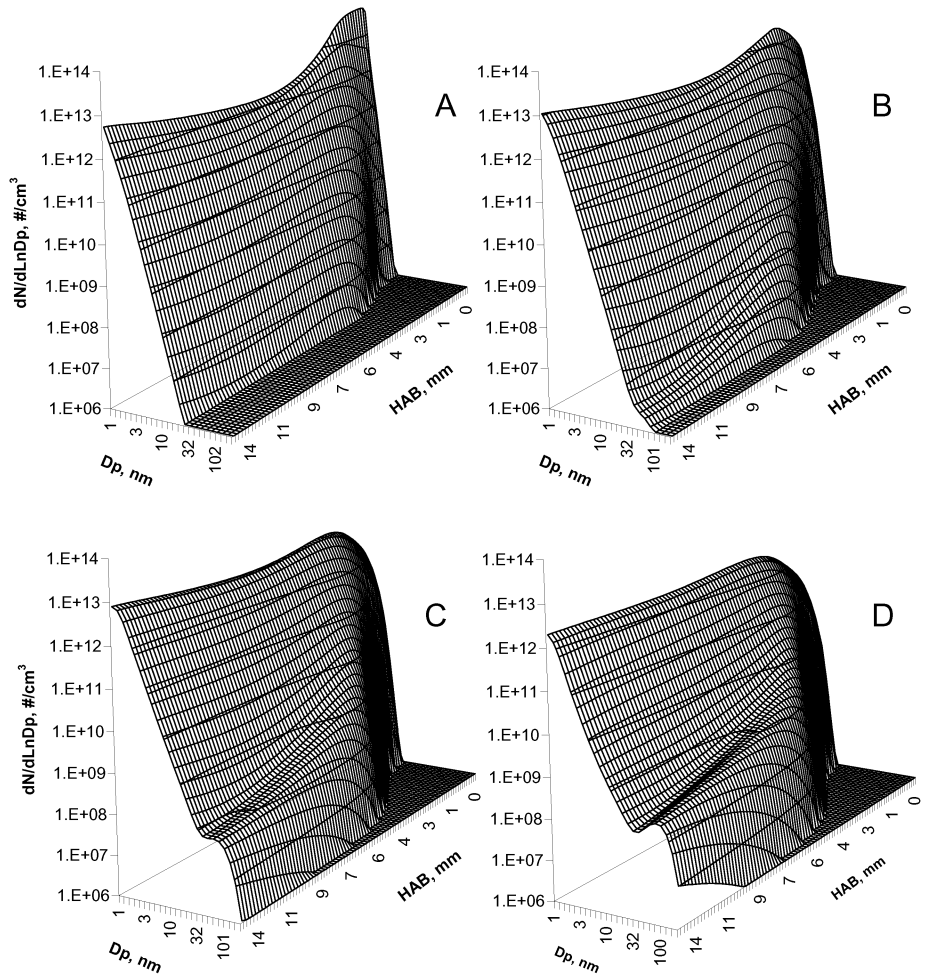

Fig.:3 Modelled Particle Size Distribution Function of different classes of particles. A particles with H/C of 1; B particles with H/C of 0.7; C particles with H/C of 0.5; D particles with H/C of 0.2.

Comparisons with experimental data in Fig.1 shows a good agreement: the model satisfactory simulates both the inception of soot particles and the peak of CHS concentration. Figure 2 shows the comparison of H/C ratio for the two classes of compounds. The model correctly reproduces the tendency of soot particles to decrease their hydrogen content and the H/C ratio of the CHS profile is matched in shape. However there is still some mismatching in the absolute values. From a sensitivity analysis it appears that the inception of particle is linked with the formation of

molecules of molecular weight of 2000-3000amu, which coagulate and dehydrogenate forming soot particles. This consideration are substantially confirmed by the particle size distribution functions (PSDFs) reported in Fig3. The class with high H/C (0.7 or 1) (Fig3A-B) exhibits a unimodal PSDF with a peak at 3nm; the class with H/C equal to 0.5 (Fig3C) shows a bimodal distribution with a first peak around 3nm and a second peak around 20nm and finally the class with the lowest H/C (Fig3D) show a marked bimodal distribution with the first peak lower by an order of magnitude and a second peak at higher values than the other classes. It is possible to associate the high H/C particles with oligomers of aromatic compounds (OACs) and the particles with H/C of 0.5 and lower to the pericondensed aromatic hydrocarbons (PCAHs)

4. Conclusion

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 shows that the model is able to reproduce the concentration profile of soot and CHS. Moreover, it is able to characterize the products in terms of H/C ratio. PSDFs of the different classes modeled allow PCAHs to be distinguished as the main precursors of soot particles. These compounds can be produced directly form acetylene addition to smaller structure or by dehydrogenation of OACs mainly produced by polymerization of small PAHs.

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