Modeling of Chemical Composition and Internal Structure of Combustion Formed Particles in Diffusion Flames

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1. Abstract

A new developed model is used to gain insights on chemical composition and internal structure of nano-sized particles formed in diffusion flames. Model allows simulating total amount of particulate matter produced in flames, its H/C ratio and morphological details. These enhancements result of great interest to better understand the pathways controlling the molecule-to-particle transition in flames. In particular, diffusion flames allow the evolution of gas phase and particle inception and growth in pyrolytic and oxidative condition to be followed. The two different combustion environments lead to quite different nascent particles in terms of chemical composition and internal structure. In pyrolytic region, aromatic molecule dimerization is the controlling mechanism leading to particles inception resulting in well ordered particle nuclei. Radical-molecule mechanism is the controlling growth mechanism in high temperature oxidation region. Dehydrogenation and surface addition reactions affect the final structure of the emitted soot particles as well.

2. Introduction

In last years, developments in combustion have led to cleaner technologies and to the possibility to strongly reduce pollutant emissions. In particular the impact of the large soot aggregates with dimension of few micrometers has been faced with discrete success. However, nano-sized particles are still produced in combustion device. Their effect on human health is relevant. Moreover they might influence the global warming increasing the scattering of the solar radiation in the atmosphere, but also increasing the amount of troposphere IR radiation [1-5]. Although new diagnostic tools have allowed gaining insights on the soot formation and growth, molecule-to particle transition process is still not completely understood. This process affects not only nascent particle but also the final structure of the soot. Several parameters such as temperature, fuel nature, fluid dynamic of combustion device can strongly influence the inception process and the final particulate emission. The knowledge of the effect of each parameter is helpful not only to prevent particulate emissions but also to control particle formation. In this sense, the production of nanoparticles with specific features has gained relevant importance in last years; their employment in several fields as drug-delivery or advanced coating is increasing [6].

Lab-scale combustion devices allow studying particle inception and growth processes, focusing the attention on the chemical kinetic pathways. In diffusion flames, the simultaneous presence of a pyrolytic and oxidative region promotes different mechanisms for particle nucleation. The resulting soot particles are strongly affected by these pathways. In this sense, opposed-flow configuration offers the possibility to study a one dimensional diffusion flame. A kinetic model based on the discrete sectional method will be used to predict the formation of particles in an opposed flow diffusion flame of ethylene. The model has been already tested in premixed configuration in different richness condition, burning different fuels [7-9].

model in the present developed version furnishes, along with the total mass of particles and its size distribution function, their chemical composition in terms of H/C ratio and information on their formation pathways and final soot structure.

3. Kinetic Model

Hydrocarbon oxidation and pyrolysis is modeled with a detailed kinetic mechanism built onto the GRI mechanism for C1 and C2 species [10]. In aliphatic fuel flames acetylene and methane are the most abundant, gaseous, unburned hydrocarbons and benzene is the first product of the molecular growth process. Benzene formation is considered to occur by the addition of n-C4 radicals to C2H2 and the self-combination of propargyl radicals [11]. The sequential addition of C2H2 to phenyl radical (HACA mechanism) [12-15] and the combination of resonantly stabilized radicals, are the pathways considered for the growth of aromatic cycles up to pyrene [11,15]. Starting from pyrene, all of the compounds with larger molecular masses are considered as lumped species.

As the molecular mass of the aromatic compounds increases a wide number of compounds are formed. Although it is almost impossible to follow each of these species, some classifications are possible. Two broad classes of aromatic molecules can be considered: aromatics in which only \( \pi \)-bonds among C atoms exist, named pericondensed aromatic hydrocarbons (PCAH) and aromatics having both \( \sigma \)- and \( \pi \)-bonds between C atoms consisting of incompletely-condensed oligomers of PCAH. Formation of PCAH is modeled by the H-Abstraction-Acetylene Addition mechanism [12-15].

When an aromatic compound, or its radical add to the radical site instead of acetylene, incompletely-condensed oligomers of aromatics are formed. The formation of an incompletely-condensed aromatic can occur either by H atom substitutions by a pericondensed structure, such as in the formation of bi-phenyl or bi-naphthyl, and by aromatic radical addition to non aromatic double bounds, such as those of pentagons condensed peripherally with hexagons (acenaphthylene type), and those of compounds like phenanthrene. The H/C ratio of the oligomers remains comparable to those of the aromatic molecules involved in the addition reactions and it remains quite unchanged as the molecular weight of the oligomers increases. Due to the less rigid structure of the \( \sigma \)-bond connecting the aromatic molecules, oligomers usually assume a non-planar structure. Both pericondensed and incompletely-condensed aromatics can growth indefinitely forming extremely large molecules. The molecular growth process competes with molecule oxidation by hydroxyl radical and O2 molecules.

Whereas PCAH can only add acetylene or other gaseous hydrocarbons (if an aromatic molecule is added an incompletely-condensed aromatic is formed), an incompletely-condensed aromatic can also undergo dehydrogenation reactions forming pericondensed molecules and they migrate in PCAH class. These reactions were recently introduced [7]. Activation energies were estimated by a sensitivity analysis to reproduce the experimentally observed dehydrogenation process.

The number of C and H atoms furnishes a rough estimation of the molecular structure of aromatics. For a given C atom number, molecules with large H/C ratios are oligomers of small aromatics whereas lower H/C molecules belong to the class of pericondensed aromatics. Molecular growth is schematized similarly to gas phase growth mechanism. Process starts with a formation of a radical, which can be spontaneous or favored by an H or OH radical. Successively addition of acetylene or of another aromatic compound continues the molecular growth process.
Parallel to the molecular growth process, molecules can form clusters of two (dimers) or more units, which constitute the incipient particles. The clustering process is due to van der Waals interaction among large condensed aromatics. Binding energies which form these clusters depend on the dimensions of the aromatic molecules and on the degree of condensation of the aromatic cycles [16-18].

Pericondensed aromatic hydrocarbons have an intrinsic planar structure due to the absence of $\sigma$-bonds. If the molecules arrange in parallel stacks, an ordered particle grows. Structures which contain $\sigma$-bonds tend to assume a non-planar structure. The steric conformation of these molecules hinders $\pi$-electrons of the molecules to reach an interaction distance. This conformation is responsible for lower binding energies which result in less ordered particles. Dehydrogenation of molecules leads to a more pericondensed structure. As the number of condensed cycles increases, binding energies can exceed conformation energies forcing the non-planar structures to assume a more planar shape. As a result, dehydrogenation of particles induces planarity in the molecules included in the particle and increases the level of stacking. Interaction between aromatics belonging to non-planar structures can lead to the formation of multi-stacks connected by $\sigma$-bonds (cross-linking).

When molecules coalesce, they lose their original identity, and they form a particle which can grow indefinitely in mass or number of stacked molecules by other molecule addition and by coalescence of other small particles. It is hypothesized that coalescing molecules completely lose their identity and the formed particle acquires a spherical shape and a solid structure. Coalescence becomes less effective as the number of molecules in the particle increases. For large particles, when the structure is too rigid to modify itself, agglomeration occurs and chain-like structures are formed in which each coagulating entity maintains its original shape.

Another division can be done on the base of reaction pathways which species undergo. Species which grow on by chemical addition and develop planar structure can be considered as molecules. As physical stacking occurs species are no longer considered molecules and clusters are formed. Coalescent coagulation and molecular growth can contribute to the final aspect of clusters. If an aggregating collision occurs a chain-like structure is formed and species can be considered aggregates.

Much more details on the hypothesis beyond the kinetic model and on its feature can be found in recent works [7-9]

4. Modeling results and discussion

An apposed-flow diffusion flame of ethylene has been numerically investigated. The details of chosen experimental conditions the flame front and the soot formation zone are located on the oxidizer side. Particles are hence transported away from the flame toward the fuel side. In this way, soot oxidation is absent and the flame is classified “soot forming” (SF) The oxidizer stream is composed of 22% of oxygen diluted in argon, whereas the fuel stream is composed of 75% of ethylene diluted in argon. The flame appears yellow–orange colored and is slightly sooting. This flame has been already experimentally and numerically investigated by this group [19], but new enhancements in the kinetic model allow gaining much more information on chemical composition and structure of formed particles.

In figure 1 principal combustion by-products are reported. Acetylene is fast produced in the oxidizer side, close to maximum temperature region. Moving toward stagnation plane surface growth takes place and benzene is formed together with gas-phase PAHs. In fuel side and across the stagnation plane, acetylene and PAHs are still present in considerable concentration both due to diffusion transport and to pyrolytic formation.
In figure 2a particulate concentration along the flame axis is reported both as total particulate and, according the division, in molecules, clusters and aggregates. Maximum temperature and stagnation point position has been also reported for clearness. Particles clearly appear on both oxidizer and fuel side. In the oxidizer side, close to maximum temperature region, very fast formation leads to large amount of molecules and clusters and, moving toward stagnation plane, aggregates. This process is mainly due to the high temperature environment, fast radical formation and large presence of species such as acetylene. In the fuel side, the considerable amount of PAH, deriving from fuel pyrolysis, and small aromatics together with the low temperature make physical process to be dominant. As result, in this region, the amount of molecules is very limited and clusters result almost the only species present. However, across the stagnation plane aggregates show a peak of concentration, remarking this as the zone of maximum particulate production.

![Graph showing concentration of acetylene, benzene, and gas phase PAH along the flame axis.](image)

Fig. 1  Concentration of acetylene (---), benzene (- - - ) and gas phase PAH (____) along the flame axis. Stagnation plane and maximum temperature position are also reported.

In figure 2b the H/C ratio of the total particulate and of the three classes is reported. Molecules exhibit a lower H/C ratio in the oxidizer side in correspondence of the high temperature nucleation zone. This result is in accordance with the kinetic mechanism described before: the acetylene addition lead to pericondensed structures and the high temperature favor the dehydrogenation process in the few oligomer-like structure formed. Clusters and, subsequently, aggregates, that are formed starting from molecules, assume the same H/C of these latter.

Moving toward the stagnation plane the decreasing in acetylene addition process make the PAH reactions more relevant and increase the H/C ratio of both molecules and clusters. Looking at the fuel side, clusters with H/C ratio typical of small aromatic are formed, supporting the hypothesis that stacking is the prevalent mechanism in this region. All these particles so formed contribute to the total H/C ratio.
5. Conclusions

An opposed flow flame of ethylene has been numerically investigate with a new sectional kinetic model. This model allow following not only the total mass but also chemical composition and structure of particulate matter. According to from experimental data and modeling activity also recently published [8-9], a division of particular matter into three classes is possible. Molecules, clusters and aggregates can be distinguished. Molecules are species nucleated from a gas phase through pure chemical pathways involving acetylene and small aromatics; clusters are formed through physical process of coalescent coagulation and can undergo other molecular growth mechanism. When coalescence becomes less effective and aggregation coagulation occurs aggregates are formed.

![Fig. 2](image)

**Fig. 2** Concentration (a) and H/C ratio (b) of total particulate matter (___ thin line), molecules (- - -), clusters (___), aggregates (___ heavy line) along the flame axis. Stagnation plane and maximum temperature position are also reported.
According to this division two nucleation mechanism have been distinguished in the investigated diffusion flame. In the oxidative high temperature zone, the large amount of radicals leads to the formation of pericondensed structure. Prevalence of chemical pathway favors the formation of a large amount of molecules, whereas clusters and aggregates appear moving toward stagnation plane. In the fuel side, i.e. the pyrolytic region, the low temperature and the presence of PAHs enhance a physical inception mechanism resulting in the formation of clusters, generally with higher H/C ratio than those formed in the oxidizer side. Both types of nascent particles contribute to the total particulate matter, leading to different structures of soot particles.

6. References

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