

DISCRETE MULTI-SECTIONAL APPROACH FOR PARTICLES MODELING IN ETHYLENE/AIR COFLOWING DIFFUSION FLAMES

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Abstract

A new advanced modeling approach has been proposed to give more insights on combustion generated particles. Nowadays particle formation is well predicted in terms of total amount of material. Moreover large efforts in the analysis and prediction of particle size distributions have been spent and results are now quite reliable. However for what concern health an climate effect and the possible appliance of combustion generated nanoparticles in material industry, a detailed comprehension of processes together with a deep knowledge of chemical composition and specific morphology of the particles are needed.

Many detailed computational methods resulted useful tools for the understanding of a single reaction step, whereas a complete analysis of the process still relies to less detailed approaches. Discrete Multi-Sectional approach has been enhanced in last years to take into account the chemical composition and morphology of the particles. However its applicability relies up to now in the one-dimensional case.

In this work, the Discrete Multi-Sectional approach has been tested to model an ethylene/air co-flowing diffusion flame. This is a two-dimensional configuration widely experimentally studied in the literature. For predicting particle size distributions, 25 sections, each with different molecular weight, are counted, ranging from 24 carbon atoms, i.e. coronene, to 10^9 carbon atoms, i.e. a large aggregate. Moreover, H/C ratio is discretized into 5 sections ranging from 0 to 1. Different morphologies are considered taking into account two-dimensional or quasi-planar structures, clusters and large aggregates. Coagulation process controls the passages between these three categories and thus the final internal structure of particles. The code has been previously tested in premixed configuration with different fuel structures and equivalence ratios giving satisfying results in terms of prediction of H/C ratio and particle internal structure.

Recent development of the oxidation rates which includes fragmentation model has been used in this work. It resulted fundamental to correctly predict the total burn out rate at the tail of the flame. Moreover fragmentation strongly influences also the size distribution function of the emitted particles.

Introduction

Modeling of particle formation has been challenged in last years by using different approaches [1]. The detail of predictions provided by these models allows to have information on the total amount of particulate matter and on particle size distribution function. This information has been individuated as key parameter to understand particle formation process in flames.

Chemical composition and morphological aspects of the particles are other important aspects of particle modeling. Recently, a multi sectional method for modeling particles has been developed which provides information also on H/C ratio of particulate matter and details on their physical state.

The model has been tested in premixed flame for aliphatic and aromatic fuels [2] giving good agreement with experimental data. Diffusion flames represent a key point for modeling real combustion systems. Moreover, they result quite difficult to be modeled due to the large range of temperatures and species concentration in the flames. These different conditions favor different particle inception and growth mechanisms. Moreover, in diffusion controlled flames it is possible that total or partial oxidation of the particulate occurs. The latter process can modify the size distribution and the morphology of the particles. As a result, particles produced and eventually emitted from the flame can be quite different depending on the region in the flame in which they are produced/oxidized.

In this work, a coflowing flame of ethylene/air has been numerically investigated with an advanced multi sectional model with the aim of predicting the total particulate concentration, its size distribution functions and particle chemistry and morphology. The flame is the same firstly presented by Santoro et al. and successive widely studied by several research groups.

Model description

An advanced multi-sectional method is used for the modelling of aromatic growth and particle inception. It is based on a previously developed kinetic mechanism of particle formation with a single discretization of the particle phase in terms of C atoms with a fixed H/C ratio. A successive discretization has been introduced to take into account variable H/C ratios. The upper and the lower limit of this discretization are fixed by physical constraints. H/C ratio can reach 0 a bottom limit value, e.g. structures containing just C-atoms, on the other hand H/C ratio equal to 1 representing the value of benzene. The present model also distinguishes between different particle structures based on their state of aggregation, i.e. high molecular mass aromatic molecules (Molecules), clusters of molecules (Clusters) and agglomerates of particles (Aggregates) [3-4]. This allows to follow not only the mass of the formed particles, but also their hydrogen content and internal structure. Two coagulation reactions have been taken into account: coalescence and aggregation. Coalescence leads from molecules to cluster and from clusters to larger clusters; aggregation leads from clusters to aggregates or from aggregates to large aggregates

Oxidation-induced fragmentation is also considered. It can be viewed as the inverse of the coagulation process. During oxidation, the carbon extraction from the high-molecular mass structures could affect the internal structure of soot species, depending on the position of the C-atom that is oxidized. For internal C-atoms, oxidation leads to a breaking up of the particle producing smaller fragments. Since the model separately accounts for aggregates and primary particles different fragmentation processes have to be considered. Aggregates can form smaller aggregates or eventually primary particles (clusters) and clusters can explode forming smaller clusters. Fragmentation is considered forming two new entities of equal mass. Oxygen is considered the only species able to not react on the surface and diffuse towards the points of contact of the primary particles.

Results and discussion

The modeled structure of the investigated flame is reported in Fig.1 (top left). In particular maps of temperature, fuel (ethylene), oxygen and OH radical concentrations are reported. Looking at the maximum temperature and OH radical concentration, it is possible to distinguish the flame front location. It clearly appears that modeling results predict the closure of the flame on the top. Modeling results are in agreement with literature data. It is worth to note that as the flame closes on the top and the OH radical starts to decrease, the oxygen concentration become relevant in the order of 2-4%, whereas the temperature is still in the order of 1500K. These condition strongly favor the oxidation by O₂ and thus also the oxidation-induced fragmentation.

In Fig.1a, acetylene, benzene, naphthalene and pyrene concentrations are also reported. Looking at the values found in literature for this flame the maps show a fair agreement for these species. This means that the main oxidation and pyrolysis processes are matched and the analysis of the particle evolution can be done without making large errors. The shape of acetylene concentration suggests that strong formation occurs just after total consumption of ethylene. Major production of acetylene occurs in the inner part of the flame. In this zone, temperature starts to be considerably high ($X=0.03m$, $R=0$; $T=1500K$) and pyrolysis become more effective. The influence of the diffusion is still to be considered, having generally the effect of smoothing the contours. Benzene shows the same trend of acetylene, remarking the strict link between these two compounds. The concentration map of benzene suggests that the formation of this compound immediately follows the acetylene one. Looking at the first compounds in the PAH series, i.e. naphthalene and pyrene, which formation strongly depends on acetylene and benzene concentrations, they formation appears again shifted toward higher heights in the flame which means also higher residence time according to the analysis the of velocity field.

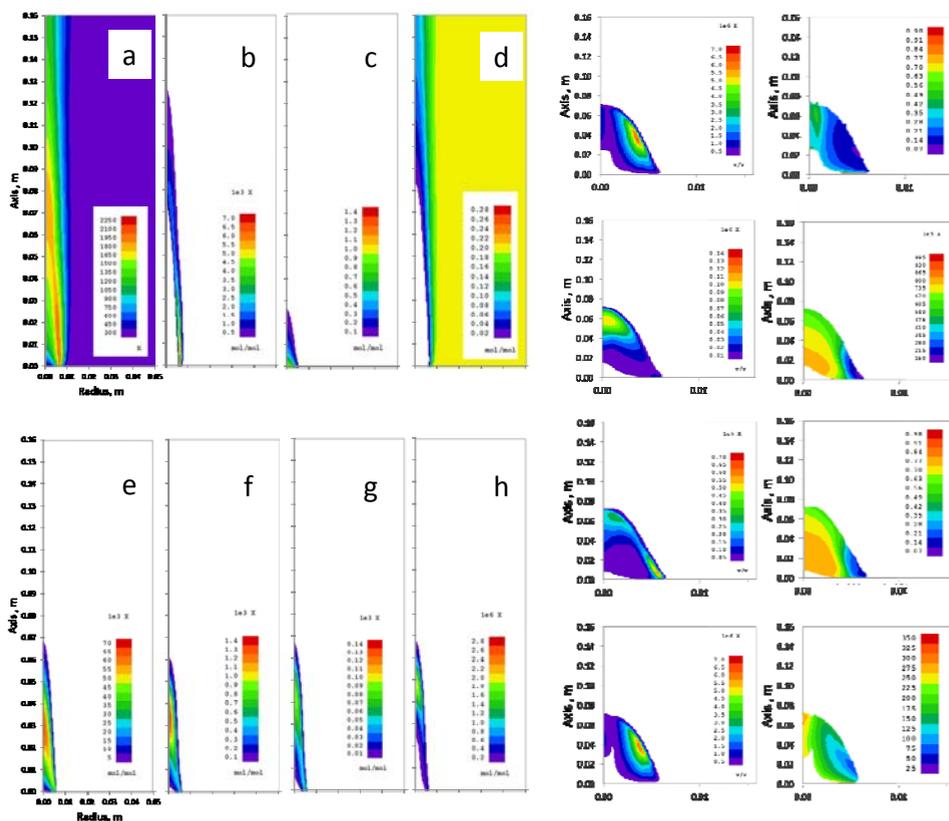


Figure 1. Left column: temperature (a) and molar fraction of different species (b – OH; c – C₂H₄; d – O₂; e – acetylene f – benzene; g – naphthalene; h - pyrene). Right column: Volume fractions of total particulate, Molecules, Clusters and Aggregates (left) and their respective H/C ratios (right).

Finally, the analysis of particle produced in the flame is reported in Fig.1b (right column). Maps of volume fractions of total particulate are reported together with the volume fractions of the different morphologies accounted in the model: Molecules, Clusters and Aggregates. It appears evident that the large part of the total particulate is constituted by aggregates. The volume fraction of the Molecules exhibits a shape similar to the gas-phase PAHs increasing along the streamline and reaching the maximum on the center. Conversely, Clusters volume fraction shows a peculiar shape: after a very fast increase in the first part of the flame their concentration decrease along the streamline; finally in the top of the flame another raise in the volume fraction is observed, just in correspondence of the maximum of PAHs and Molecules concentrations. Aggregates start to increase when cluster concentration decreases suggesting a rapid conversion between these two morphologies due to the coalescence/aggregation ratio change. Their concentration is

strictly confined by the flame front defined by OH, temperature and O₂ concentration. This means that oxidation is quite active on the flame front of the flame. Moreover, for these compounds only a small raise in the concentration is possible to be seen on the top of the flames. The most interesting point is probably due to the raise in particle concentration in the inner part of the flame. In fact this can be due to a different inception mechanism enhanced by the local conditions of temperature.

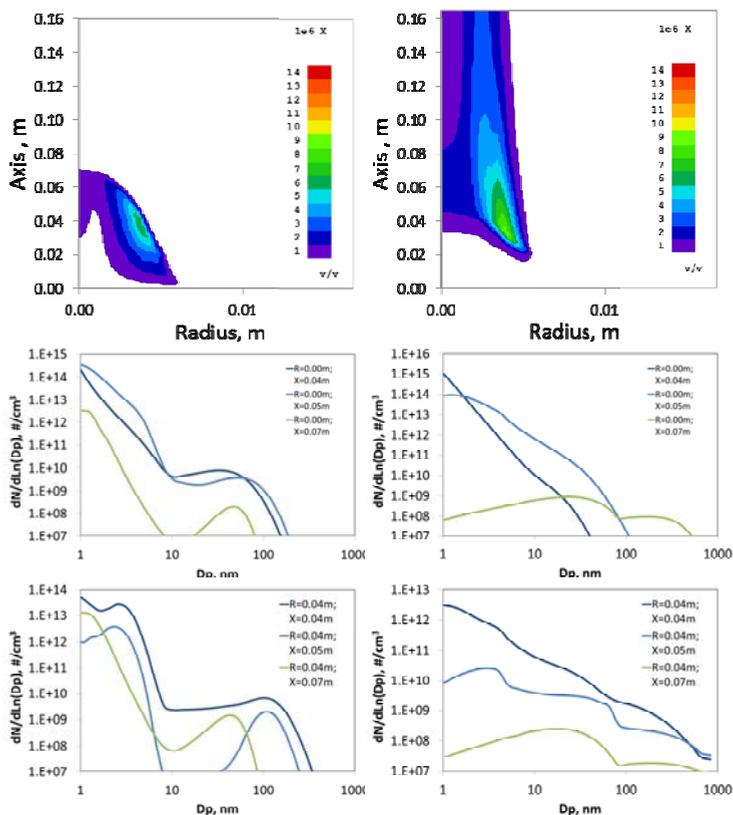


Figure 2. Volume fraction of total particulate and PSD evaluated at different points in the flame. Left column fragmentation is included, right column is neglected.

The picture of particle formation in coflowing flames can be confirmed looking at the H/C ratio of total particulate and three classes of compounds considered. Total particulate exhibit a very low H/C ratio in the zone of maximum production whereas in the top of the flame the H/C approach value quite higher, up to 0.5. Looking at single classes these different processes are even more defined. In fact, Molecules and Clusters exhibit very low values only in the very first part of the flame, where radical concentration and temperature are higher. In the top of the flame, the dehydrogenation process has to be less effective and the both Molecules

and Clusters reach very high value of the H/C ratio. Aggregates follow the same trend probably better evidencing the phenomenon. This behavior is quite similar to that found for opposed flow diffusion flames. In the latter conditions where the residence time is considerable higher the growth process leads to large compounds than in opposed flow flames. In this case oxidation is very effective and particles are totally burnt out. Information about how oxidation affects the particle sizes and concentration can be gained. To test the effect of fragmentation, a test case has been also conducted without this reaction. The results are reported in Fig.2. On the left column the case with fragmentation is reported: map of volume fraction of total particulate is showed together with the particle size distribution (PSD) functions calculated at different axial and radial positions. These positions are representative of the maximum volume fraction in the inner of the flame and of the flame front, i.e. the outer of the flame where oxidation occurs. It is worth to note that in the base case the PSD remains bimodal both in the phase of production and when particles are oxidized. However, when oxidation occurs, particle size distribution becomes orders of magnitude lower in numerical concentration, moving toward smaller diameters. When fragmentation is neglected particles are not totally oxidized. Moreover, the size of the particles remains quite larger and the bimodal shape is totally missed. This demonstrates once again that fragmentation is fundamental in order to get not only the correct volume fraction of particles but also their effective shape and morphology.

Conclusions

In this work, a coflowing flame has been investigated with an advanced multi-sectional method, which allows to predict PSD, H/C ratio and morphological aspect.

Physical interaction and chemical pathway have been found to be separately predominant in dependence on the zones the flame. In the inner part of the flame clustering is more effective, whereas closer to flame front dehydrogenation and acetylene growth are predominant. Oxidation has been also evaluated. Bimodal distribution has been found to be produced both during particle formation and during oxidation, if oxidation-induced fragmentation is considered. Whether oxidation-induced fragmentation is neglected PSD shape is totally missed. This suggests the key role of this process in particle evolution in flames.

References

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