Soot Modelling in Benzene and Hexane Diffusion Flames

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Abstract
A detailed kinetic mechanism of aromatic growth, particulate formation and oxidation is presented and is tested in non-premixed laminar flames of benzene and hexane at atmospheric pressure. Model development has been recently updated to account for new experimental data on the formation and oxidation of high molecular mass compounds and incipient particles. Multi-Sectional approach has been adopted. In this version the model accounts for the gas-to-particle transition, the formation of first incipient particles, the evolution of the soot structure and finally the oxidation process.
The newly developed model predicts the structure of the flame both for aromatic and aliphatic fuel. Also the model is able to predict the zone of formation of soot particles with a good agreement with experimental data [1] without any condition-dependent adjustments to the kinetic scheme. A wide range of particle sizes is covered from nanoparticles formed on the fuel side of the flames to larger soot particles and particle aggregates formed in the flame wings. Model gives also information on the predicted trend of the H/C ratio and morphology of the particles for the two different fuels for which no experimental data are available.

Introduction
Recent advances in the experimental techniques for soot analysis have led to a deeper knowledge of the soot structure and to a better evaluation of the mechanisms of soot formation starting from the gas phase. The knowledge of the chemical composition, morphology and rate of formation of the soot precursor has increased the capability to correctly predict the effect of the combustion parameters on soot formation [2-3]. The sectional approach allows to treat all the aromatic compounds with molecular mass higher than the largest aromatic compounds in the gas-phase as lumped species. Last version considers a discretization of the lumped species made on both carbon and hydrogen atoms. Moreover each lumped species is defined as single molecules, clusters of molecules, or aggregates of particles. This approach enabled us to follow the chemical evolution and the internal structure of particles formed in premixed flames [4-6] and recently, in laminar coflowing diffusion flames of methane and ethylene [7].
The model is here used to model coflowing flames of benzene and hexane in order to test its capability to predict the particle formation in different combustion
environments such as those produced by hydrocarbons with different structures. For these flames, experimental data of temperature, and laser induced emission are available in the literature [1].

**Soot Model**

A multi-sectional method is coupled with the detailed mechanism of oxidation and pyrolysis of the hydrocarbons, recently published [7]. Starting from pyrene, all of the compounds with larger molecular masses are considered as lumped species. The lumped species are defined by the number of carbon atoms, the number of hydrogen atoms and the state of aggregation: single molecules, clusters of molecules i.e. individual particles, and aggregates of particles.

The simplest compound that can be obtained from gas-phase kinetics is a larger aromatic molecule which undergoes only chemical reactions. In this case the physical state is still similar to a large molecule and the associated lumped species is called “Molecule”. When molecules undergo a physical stacking, i.e. they interact by van der Waals forces, the compound so formed does not belong to the class of molecules anymore and the lumped species associated is called “Cluster”. Coagulation process has been considered so far as a coalescent one since the compound formed, the cluster, has been defined as a unique entity. If the cluster arises to a solid state character, the possibility to have a coalescent coagulation decreases and the compound formed assumes a chain-like structure, i.e. the well-known final form of the soot aggregates. The compounds that undergo the aggregating coagulation are associated to a lumped species called “Aggregates”.

For all these classes of lumped species, all the reactions have been considered. The molecular mass of all lumped species can grow indefinitely adding acetylene, an aromatic compound from gas phase, or another lumped species. Since the species can explore the different H/C ratio, a dehydrogenation process has to be taken into account. The dehydrogenation is mandatory to predict the H/C ratio of the particles and thus their capability to give radicals and to chemically grow. The molecular growth process competes with molecule oxidation by hydroxyl radical and O2 molecule. OH radical is used to oxidize the stable molecule, whereas O2 molecule oxidizes the radicals.

Fragmentation of particles can occur if the oxidizing species is able to penetrate the particles and remove C atoms from a weak point causing the break-up of the particles and large aggregates into smaller particles and aggregates. These processes can be referred to as oxidation-induced fragmentation and can be seen as particular events of oxidation and it is very important in correctly determining the burn-out rate of particles.

Coagulation is considered irreversible at this stage and its reaction rate is modeled by considering coagulation efficiency with respect to the collision frequency, following D’Alessio et al. [8]. This evaluation of the global coagulation efficiency has been followed by the evaluation of the coalescent and aggregating contributes. The coalescence-agglomeration ratio does not drastically affect the final
concentration of the particles but it does determine the size of the primary particles which constitutes particle agglomerates. Details of all the processes presented here have been reported in a previous work [4-7].

**Model Prediction in Diffusion Flames**
Model has been tested in coflowing diffusion flames of hexane and benzene. The flames have previously been studied experimentally by Kobayashi et al. [1] by using optical in situ diagnostic to measure the concentrations of the different classes of particles generated in the flames. The Laser Induced Fluorescence (LIF) image of aromatic soot precursors was detected by an intensified camera. The Laser Induced Incandescence (LII) image of soot particles was measured by the same laser diagnostic system but, in order to separate the precursors-LIF image and the soot-LII image, a temporally resolved method was used. More details on the burner and on the experimental procedure can be found in the original paper [1].

**Figure 1.** Modeled temperature (left column), and OH molar fraction (right column), and experimental data for temperature (central column) for benzene (top) and hexane (bottom) flames.

The flames have been modeled as a gaseous flux of hydrocarbon at mild temperature (at 80°C for both fuels). A flux of air was supplied coflowing to the hydrocarbons fluxes, keeping its velocity at the same values as that of the fuels.
Small changes on the coflowing flame velocity do not affect the results. Radiation due soot particles was considered. A fixed coefficient for taking into account this term in the energy equation was used for both flames and it is the same as used in previous works [7].

Figure 1 shows bidimensional maps of temperature and OH for the benzene and the hexane flames as predicted by the model. Experimental temperature data measured by Kobayashi et al. are also reported in the figure as isocontour lines compared to the modeled maps. The general structure of the flames is well captured by the model but the maximum flame temperatures are not. The model is able to predict the “open” tip of the benzene flame and the “closed” tip of the hexane flame and the location of the flame tips in both flames with good approximation. The difference in the flame structure is more evident from the OH-concentration maps. The concentration of OH defines the location of the flames. Clearly the model indicates that the hexane flame has a closed structure in contrast to the open structure of the benzene flames.

![Flame Maps](image)

**Figure 2.** Qualitative comparison of modeled fluorescent particles (soot precursors) and soot particles compared with LIF and LII, respectively, in the hexane flame.

Figure 2 reports LIF and LII measurements compared with the modeled
concentrations of fluorescent species and soot, respectively, for the two flames. We have associated fluorescence to aromatic compounds and soot precursors, i.e. all the species in the model belonging to “molecules” type and the species belonging to “cluster” type having and equivalent diameters smaller than 10 nm. Formation of aromatic compounds and soot precursors is observed in the central part of the flames whereas soot formation occurs in the wings of the flame, in agreement with experimental data. The transition from soot precursors to soot particles was experimentally determined by considering the flame regions in which there were an overlapping between the LIF and LII images. The transition region in the benzene flame was located parallel to the central axis of the flame. For hexane this region is the conical area between LIF and LII images close to the burner.

Figure 3. Modeled H/C ratio of fluorescent compounds (soot precursors) along the flame axis for hexane (dashed line ) and benzene (solid line) diffusion flame.

The modeled sooting region in the hexane flame is wider than that of benzene, in agreement with experimental data. Moreover in the hexane flame the two lateral regions of the soot formation flames merge at the flame tip and soot is completely oxidized in that flame. At locations downstream of the flame tip the concentrations of soot and soot precursors decrease to negligible values in agreement with the absence of LIF and LII signals observed experimentally. Conversely, in the benzene flame the lateral region of soot formation never merges at the flame axis giving the typical “open” tip structure. Soot is not completely oxidized in agreement with experimental results. The concentration of soot in the wings of the benzene flame is much higher than that predicted for the hexane flame. The H/C ratio of the precursors formed in the two flames is reported along the flame axis in figure 3. The model predicts a slight change in the H/C along the flame centerlines. This behavior is in accordance with the experimental evidence of a red-shift in the fluorescence spectra experimentally found which might be associated with an aromatization process of the high-molecular mass compounds in agreement with the hypothesis of annealing of the particles along the flame centerline. However, the low temperature, low total precursor concentration and low radical
concentration in this flame region do not allow a strong dehydrogenation rate resulting in a very low decrease of the H/C along the flame axes.

**Conclusion**

The newly developed model of aromatic growth, particulate formation and oxidation has been used to predict the behaviour of diffusion flames of benzene and hexane for which a set of experimental data exists. The model predicts the different structures of the flames, matching the position and the shape of the flame tips. Good predictions are obtained for fluorescent species and soot comparing modelling results with LIF and LII measurements. The model was able to predict the zone of formation and the transition regions with good approximation in terms of position. Finally the model was used to give information on the H/C ratio of particles in the flames were no experimental data were available. Along the centreline a slight decrease of the H/C ratio is found according with the experimental evidence of a red-shift in the fluorescence spectra along the flame axis.

**References**


