

MEASUREMENTS AND MODELING OF CARBON AND HYDROCARBON SPECIES EVOLUTION AT SOOT INCEPTION IN PREMIXED FLAMES

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Introduction

The flame environment in which soot inception occurs is very complex from a chemical point of view because of the simultaneous formation of a large number of species. The common problem that combustion scientists has faced in the understanding of soot inception process is the simplification of the ascertained complexity of the large molecular weight (MW) species involved in this process. Indeed, there are not detailed kinetic models and experimental techniques able to follow the formation of specific compounds included in the huge number of aromatic structures and isomers invariably formed in proximity and simultaneously to the first soot particles.

In this work, a detailed description of the molecular growth process which leads to high molecular weight species is reported for a sooting premixed hexane flame. This description was obtained by measuring the axial concentration profiles of main combustion products, light hydrocarbons, polycyclic aromatic hydrocarbons up to 300 u, (PAH) and total particulate (dry soot and soot extract).

A detailed kinetic model combining the different mechanisms of benzene and PAH formation was tested on the experimental data in order to give information on the possible routes through which soot inception occurs. Moreover, a mechanism for the formation of particulate including high molecular weight species and soot was added to the model and compared with the experimental data relative to the particulate concentration and MW distribution measured by Size Exclusion Chromatography (SEC).

Experimental

The experimental system and analytical techniques have been described in detail elsewhere. [1-4]

Briefly, soot extract and dry soot were collected from a premixed laminar hexane/oxygen/nitrogen flame (8.6/32/59.4%; C/O=0.8) stabilized on a McKenna burner. A stainless-steel water-cooled probe was used to sample combustion products along the flame axis. Solid and condensed material (total particulate) collected on the probe wall, on the teflon filter and in an ice-cooled trap placed in the sampling line were extracted with dichloromethane (DCM) to separate the soot extract soluble in DCM, from the solid carbonaceous material (dry soot), insoluble in DCM.

Soot and soot extract were dried, weighed and dissolved in N-methyl-2-pyrrolidinone (NMP) for examination by SEC.

The MW of dry soot and soot extract fractions of the total particulate was evaluated by SEC carried out on a HP1050 High Pressure Liquid Chromatograph equipped with an

UV-visible Diode Array Detector. The analyses were performed on a PL-gel highly cross-linked individual-pore polystyrene/divinyl benzene column 30cm*7.5mm o.d. at a temperature of 80°C and an eluent flow rate of 0.5 ml/min. The solvent used as eluent and to dissolve the samples was N-methyl-2-pyrrolidinone (NMP). Polystyrene standards (Polymer laboratories) in NMP solutions were used for the MW calibration in the 100-100,000 u range.

SEC chromatograms of the particulate fractions showed the presence of four main MW classes of species distributed in the soot extract and in the dry soot in the following way: 200u and 1000u species in the soot extract, 100,000u species both in the soot extract and in the dry soot and species with a MW>100,000u in the dry soot. The exact MW range of the latter species was not evaluated being beyond the linearity range of polystyrene calibration curve.

The experimental MW distributions along the flame have been evaluated from SEC chromatograms detected at a fixed wavelength (350 nm) where soot and soot extract presented quite similar absorption coefficients [5]. The distribution of large MW species was obtained by normalizing the height of corresponding chromatographic peaks (PAH of the 200 u class were excluded) taking into account for the contributions of dry soot and soot extract to the total particulate.

Model

Premixed flame modelling was performed by using the Chemkin software package and a new developed kinetic mechanism and thermodynamic data base [6, 7].

The gas-phase mechanism includes hydrocarbon oxidation and pyrolysis and the formation and molecular growth of aromatic compounds. Propargyl radical combination is the controlling step in benzene formation at flame conditions. The addition of acetylene to C4 radicals is of minor importance becoming prevalent in very fuel-rich or in pure pyrolysis conditions [6, 7].

The molecular growth of aromatic compounds occurs mainly through two routes: the sequential addition of C₂H₂ to aromatic radicals and the combination of resonantly stabilized radicals. The first sequence of reactions (HACA mechanism) has been found to be too slow. It simulates a very low concentration of aromatics, mainly in the post-flame region. The second mechanism, that involving resonantly stabilized radical combinations, shows that aromatics are rapidly formed in the main flame region and they mainly grow up to 2-, 3-ring PAHs such as naphthalene, acenaphthylene and phenanthrene [8].

Polycyclic aromatic hydrocarbons may react with each other. The interaction energy between neutral PAHs are due to van der Waals forces. Generally, the formed dimer should be stable under fame conditions, if the interaction energy in the dimer is larger than the internal energy of the two molecules, i.e. larger than the kinetic energy kT of the molecules. Pyrene is the smallest PAH which exhibits sufficiently high interaction energy to form a stable three-dimensional structure at temperatures above 1500K [9]. The concentration of pyrene in flame is usually one order of magnitude lower than that of naphthalene and acenaphthylene [1] and hence too low to account for a rapid growth of aromatics to high molecular mass structure.

The experimental characterization of the high molecular mass aromatic compounds detected in flames shows that these species behave like polymeric structures made of

two-, three-ring aromatic compounds connected by aliphatic bondings. [10] For this reason, the initial growth of aromatics to form high molecular mass aromatic compounds is modeled by reactions of neutral PAHs with PAH radicals. This reaction mechanism is favoured by the presence of a large concentration of five-membered ring PAHs in the PAH inventory. These compounds are exceptional intermediates as they grow rapidly forming resonantly stabilized radical intermediates. The sequence begins with the H-abstraction from aromatic compounds to produce the corresponding PAH radical and continues furnishing higher aromatics through a radical-molecule reaction. PAH radicals can react with other PAH radicals or with H atoms ending the growth sequence. Iteration of this mechanism followed by rearrangement of the carbon framework ultimately leads to the formation of high-molecular-mass compounds [11].

As the molecular mass of the aromatic compounds increases for effect of the radical-neutral PAH reaction sequence, the interaction energy between neutral aromatics due to van der Waals forces increases and becomes even larger than the internal energy of the two species under flame conditions; the molecular mass growth process becoming dominated by neutral molecule interactions [10]. Both reaction pathways are responsible for particle nucleation, i.e., the transition from gas phase species to nascent particles.

A discrete-sectional approach was used for the modelling of the gas-to-particle process. [12] In the discrete sectional technique the ensemble of aromatic compounds was divided into classes of different molecular mass and all reactions were treated in the form of common gas phase chemistry by using the compound properties such as mass, the numbers of carbon and hydrogen atoms averaged within each section. In the sectional method approach, the molecular mass distribution of the species was obtained from the calculation and not hypothesized *a priori*.

A modified version of the gas phase *Interpreter* was used allowing the handling of molecules with molecular masses sufficiently large to follow soot particle inception. In particular 30 classes of neutral PAHs and the corresponding 30 classes of radical compounds were used. Starting from gas-phase PAHs, the size of each class was doubled respect to the previous one. In this way, the largest compound has a molecular mass of 9E9 u which corresponds to diameter of 300 nm based on the assumption of spherical structures and a density of 1.8 g cm⁻³.

Results and Discussion

The main oxidation region of the flame, where fuel and oxygen are consumed and CO and CO₂ are formed, ends at about 2 mm height of the flame, thereafter the molecular growth process starts leading to the formation of pyrolytic species such as acetylene, methane and benzene which axial flame concentration profiles are reported in Fig.1. The agreement between experimental data and modeling results, also reported in Fig.1, appears quite reasonable showing that the maximum formation of benzene occurs just after 2 mm in the flame, i.e. in the pyrolytic region of the flame. In the same region polycyclic aromatic hydrocarbons, high molecular mass aromatics and soot are formed as shown in Fig.2 where their concentration profiles are reported. Modeling results, also reported in Fig.2, fit quite well the rise-decay trend of PAH concentration followed by the rise of soot extract and dry soot concentrations.

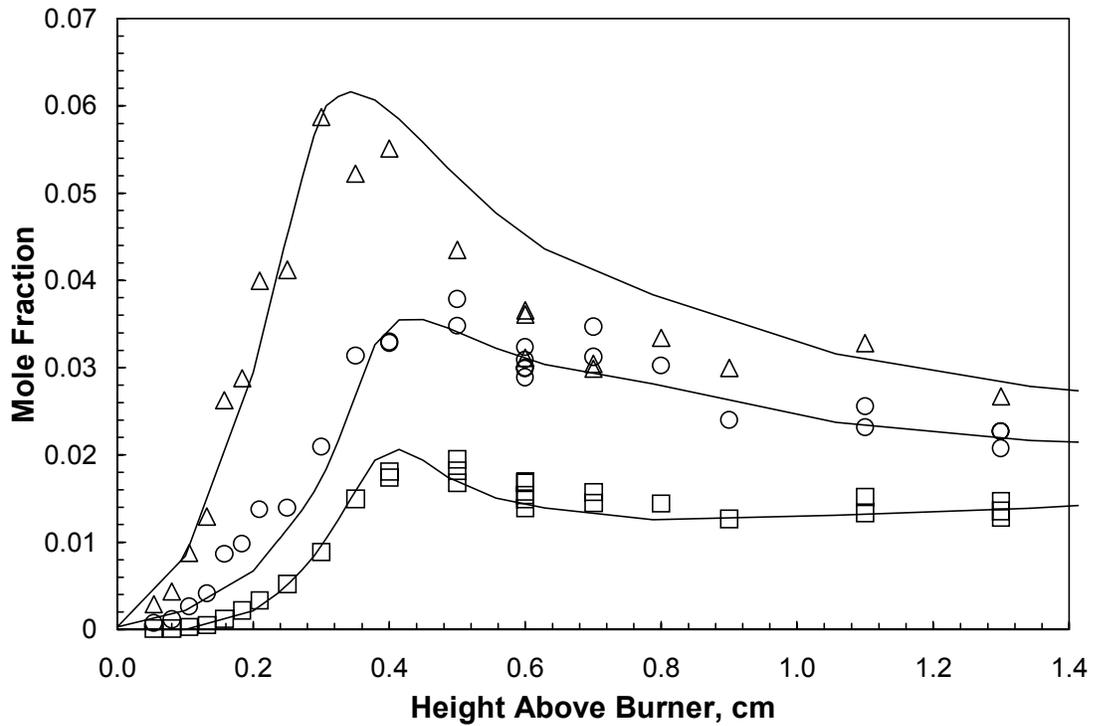


Figure1 Comparison between model predictions and experimental mole fractions of methane, acetylene and benzene.

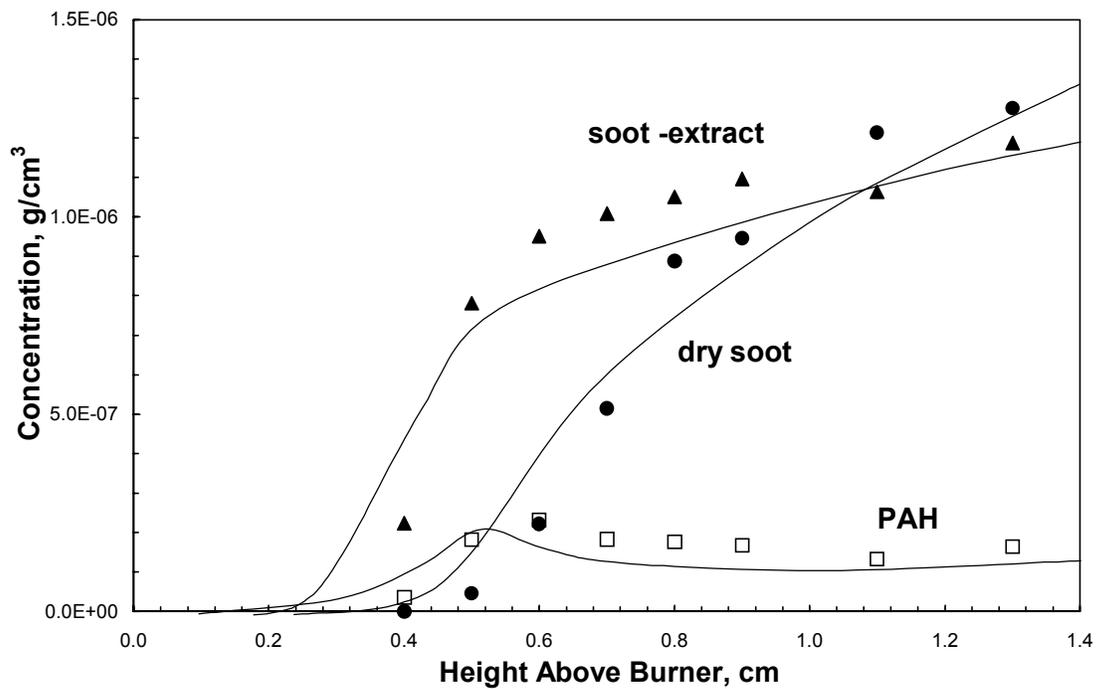


Figure 2 Comparison between model predictions and experimental concentration profiles of PAH, soot-extract and dry soot.

In order to have more insight about the molecular growth mechanism through which soot inception occurs, the molecular weight distributions of all the species larger than PAH have been experimentally evaluated by SEC analysis of total particulate fractions: dry soot and soot extract.

The relative abundance of the 1000 u, 100,000 u and >100,000 u classes along the flame is reported in Fig. 3.

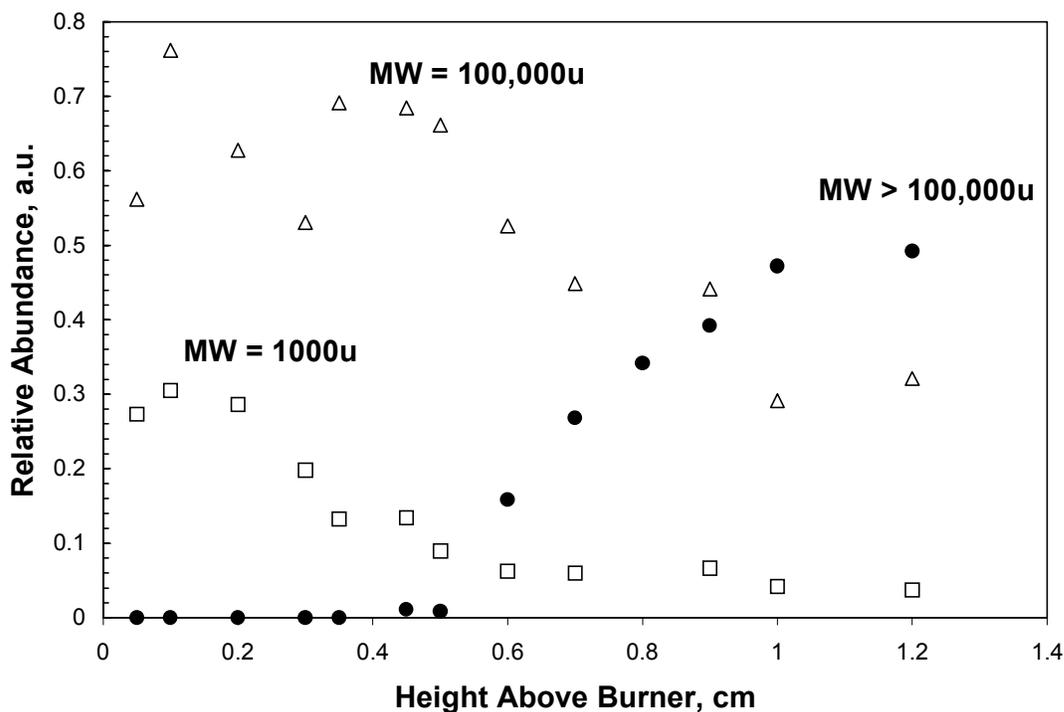


Figure 3 Relative abundance of high molecular mass species along the flame axis.

At the beginning of the pyrolytic region, i.e. after 2 mm in the flame, the 100,000 u class appears predominant with respect to the 1000 u class whereas the largest MW species are completely absent. As the contribution of 1000 u and later on, of 100,000 u classes decreases, species with a MW in excess of 100,000 u are prevalently formed. By assuming a density of 1.8 g/ml and a spherical shape, the size of 1000 u species is of about 1 nm whereas 100,000 u are particles in the 2-6 nm range. By ultrafiltration of dry soot, the >100,000 u class, was found to be mainly constituted of particles with an average diameter of about 20 nm, typical size of elementary particles constituting mature soot particles [13].

The experimental size distribution is reproduced quite well by the modeled size distribution functions in terms of mass concentrations as shown in Fig.4 where modeling results are reported for different flame heights. Subnanometric species, mainly PAH, decrease at the beginning of the pyrolytic flame zone as nanometric particles (2-6 nm) are formed. Downstream of the flame the concentration of nanometric particles

decreases whereas the formation of particles with a diameter $\geq 20\text{nm}$ largely occurs due to the coagulation of 2-6 nm particles.

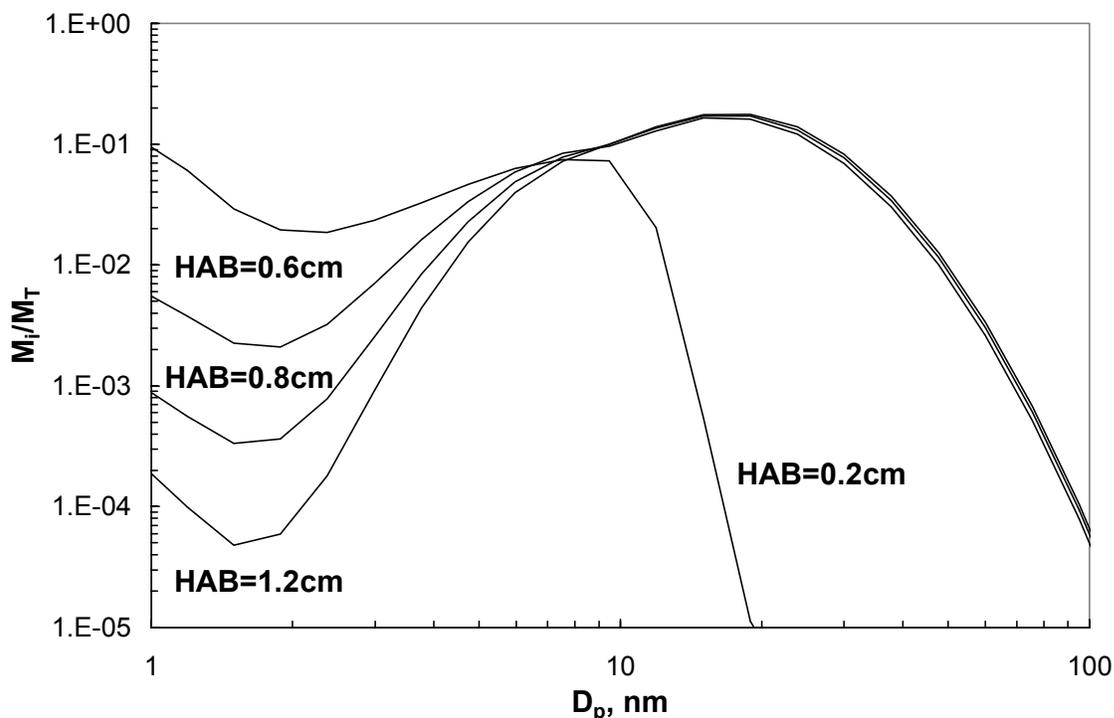


Figure 4 Modeled size distribution functions of particulate, in terms of mass concentrations, at different flame heights.

This implies that growing soot particles collide with each other forming larger particles. Initially, the colliding particles coalesce forming new spherical particles. Later on they could agglomerate into fractal aggregates, i.e., chainlike structures, but this is observable only in strongly-sooting conditions.

Conclusions

High mass species of 1000 u, 100,000 u and $>100,000$ u molecular weight were experimentally evaluated by SEC analysis of the particulate sampled in a premixed sooting hexane flame.

The contribution of 1000 u and 100,000 u aromatic species to the total particulate is predominant in the pyrolytic region of the flame, decreasing along the flame as species with a MW in excess of 100,000 u are formed. In particular 1000 u species, corresponding to subnanometric molecules, decrease at the beginning of the pyrolytic flame zone as nanometric particles (2-6 nm) are formed. Downstream of the flame the concentration of nanometric particles decreases whereas the formation of particles with a diameter $\geq 20\text{nm}$ largely occurs due to the coagulation of 2-6 nm particles.

The model has shown to be able to catch the formation of aromatic species from benzene through PAH up to young soot particles by considering that: i) propargyl radical

combination is the controlling step in benzene formation at flame conditions, ii) PAH formation is controlled by cyclopentadienyl radical combination and the addition of propargyl radicals to benzyl radical, being the HACA mechanism of minor importance, iii) particles with sizes of the order of 2-6 nm are formed through a radical/molecule addition mechanism and finally, iv) the coagulation of 2-6 nm particles is responsible for the formation of 20nm particles which constitute soot primary particles.

References

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