Modelling of Particulate Formation in Rich Premixed Flames

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INTRODUCTION

Particulate matter, even at the low concentrations allowed by modern technologies, has a strong impact on human health. The toxicological mechanisms are still unclear, but there are strong indications that particle size is more important than particle mass in determining health effects [1,2].

A significant amount of anthropogenic particles are emitted from engines and stationary combustion sources in form of nanoparticles. Consequently, there is great scientific and practical interest in the study of their formation and their evolution in the environment.

Many investigations have been focused on the study of the formation and oxidation of soot particles (typical sizes larger than 20 nm) whereas less effort has been concentrated on carbonaceous nanoparticles with smaller sizes down to 2 nm.

From the perspective of numerical simulation, significant efforts have been made to assess fuel-rich combustion processes by means of complex kinetic models. Detailed reaction networks describing the formation and depletion of PAH have been developed and comparisons of model predictions with experimental data measured in experimental systems such as premixed flames have shown encouraging results [3-6]. Following the work of Frenklach and Wang, several authors have extended reaction mechanisms to soot formation by modelling the profiles of soot volume fraction but very few attempts have been made to calculate size distribution of soot particles and aromatic molecules [5].

The purpose of this paper is to present a reaction pathway which, as an extension to the previous PAH formation model [3,4], predicts the size distribution of the aromatic structures formed in flames including nano-sized organic carbon particles and soot.

The computed size distribution functions are compared with those obtained by atomic force measurements performed in a slightly-sooting ethylene/air flame at atmospheric pressure [7].

KINETIC MODELING

Nucleation and growth of particles in combustion systems is the result of a gas-to-particle process which requires detailed modelling of the gas-phase processes and of the reactions involving high molecular mass nano-sized particles. The gas-phase oxidation and pyrolysis of hydrocarbons have been largely studied as well as the formation of benzene and reactions leading to the formation of larger aromatic compounds [3,4].

A few studies have been devoted to the analysis of particle nucleation and growth. Aromatics of increasing size are formed by reactions of acetylene with aromatic rings or by the reactions of reasonantly stabilized radicals (cyclopentadienyl, benzyl and propargyl radicals). They mainly grow up to 2-, 4-ring PAHs such as naphthalene, acenaphthylene, phenanthrene and pyrene which constitute the most abundant gas-phase aromatic compounds detected in flames [8]. Once formed, polycyclic aromatic hydrocarbons can also react with each other increasing the molecular size of the aromatic species. However, the interaction energy between neutral PAHs with 2-, 4-rings is too low to allow dimer formation at flame temperature. The dimer is stable under flame conditions, if the interaction energy is larger than the internal energy of the two molecules, ie. 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 1500 K [5]. However, the concentration of pyrene in the flame is usually one order of magnitude lower than that of naphthalene andacenaphthylene and hence too low to account for the rapid growth of aromatics to high molecular mass structure (the bimolecular process depends on the square of the concentration of pyrene). Other reactions involving 2-, 4-ring PAHs or PAH radicals could be considered. Experimental evidence of the association of aromatics has been found using optical techniques and mass spectrometry [8,9]. The experimental characterization of the high molecular mass aromatic compounds detected in flames has shown that these species behave like polymeric structures made of 2-, 3-ring aromatic compounds connected by aliphatic bonding [9]. Reactions between neutral PAH’s and PAH radicals could be responsible for the initial growth of aromatics. The sequence starts with the H atom abstraction from aromatic compounds (Ai) to produce the corresponding PAH radical (Ais)

\[ \text{Ai} + \text{H} \leftrightarrow \text{Ais} + \text{H}_2 \]  (1)

and continues furnishing higher aromatics through a radical-molecule reaction

\[ \text{Ai} + \text{Ais} \Rightarrow \text{Ais} \]  (2).

The rate constant of the reactions (1) depends on the number of H atoms available for the abstraction reaction and hence on the size of the aromatic compounds. Rate constants have been deduced by scaling the reaction rate of benzene with the number of H atoms which are increasing with the size of the aromatic

\[ k_1 = 5 \times 10^{13} \times \exp(-16000/RT) \times n_C^{0.8}. \]

Rate constants for the reverse reactions (1) have been deduced by means of equilibrium constants. Thermodynamic data for PAHs are available up to C24 species. The equilibrium constants for larger species have been evaluated through the best-fitting of the data from C6 to C24 species

\[ K_{eq} = 0.3627 \times n_C - 2.3593. \]

Currently, the formation of multiple radicals, of significant importance for larger compounds, has not been taken into account.

The radical-molecule reactions (2) have been assumed irreversible due to the great stability of the intermediate compounds which results in a low reverse rate. The rate constants are computed from gas-kinetic collision theory considering the collision of particles of equal size and using a collision efficiency of 5E-3. It strongly depends on the molecular sizes of the reacting species

\[ k_2 = 5 \times 10^{13} \times 9.3 \times 10^{12} \times T^{0.5} \times n_C^{0.166}. \]

Termination occurs primarily by two mechanisms: the first one is the addition (coupling) of two growing radical intermediates forming a stable species

\[ \text{Ais} + \text{Ais} \Rightarrow \text{Ai} \]  (3)

or with H atoms ending the growth sequence

\[ \text{Ais} + \text{H} \Rightarrow \text{Ai} \]  (4).

The rate of reactions (3) is assumed to be 1E12 cm³ mol⁻¹ s⁻¹, evaluated by analogy with gas-phase recombination reactions. The second mechanism involves the H-atom addition to a radical. The starting value for these reaction rates is taken by analogy with a typical reaction between aromatic radicals and H-atoms (i.e. C₁₀H₇ + H). The rate constant decreases by one order of magnitude as the molecular weight of the structure increases up to the maximum allowable value in the scheme. This hypothesis was possible in light of the greater stability of the aromatic radicals for increasing molecular weights and was checked by evaluating the reverse rate for different molecular sizes of the aromatics from thermodynamic data

\[ k_4 = 1.28 \times 10^{20} \times T^{-2.15} \times \exp(-1890/RT) \times (12 \times n_C)^{-0.6}. \]

Iteration of this mechanism followed by rearrangement of the carbon framework ultimately leads to the formation of high-molecular-mass compounds.
As the molecular mass of the aromatic compounds increases because of the radical-molecule reaction sequence, the interaction energy between aromatic molecules due to van der Waals forces increases and becomes larger than the internal energy of these species under flame conditions. At this point, the molecular mass growth process becomes dominated by neutral molecule interactions

$$A_i + A_j \rightarrow A_{i+j}$$ (5).

A size-dependent coagulation kinetic rate is used to account for particle interactions

$$k_5 = \gamma \times 9.3 \times 10^{12} \times T^{0.5} \times n_C^{0.166}$$

with a collision efficiency

$$\gamma = 4.157 \times 10^{-9} \times n_C^2 + 1.11 \times 10^{-17} \times n_C^4$$

Particles can add or lose mass by surface reactions. Acetylene is the most important gas-phase compound to add mass

$$A_{is} + C_2H_2 \rightarrow A_i$$ (6).

The rate constant for this reaction is based on the activation energy of the acetylene addition to phenyl radicals. A size-dependent collision frequency is considered, based on the experimental data of Lam et al. [10] in premixed flames

$$k_6 = 5.9 \times 10^{11} \times T^{0.5} \times \exp(-10160/RT) \times n_C^{0.267}.$$ 

In the present work, a sectional approach is used to follow the transition from gas-phase species to nascent particles. The sectional method follows the description by Pope and Howard [11]. Particle size distribution is defined by a range of sections, each containing a nominal hydrocarbon species in order of increasing atomic mass. There are two bins for each particle size, one for the stable species and the other for the radical. Twenty six sections ($\times 2$) are used in a geometric series with a carbon number ratio of 2 between sections. The carbon number range is $20 - 6.7 \times 10^8$ which represents a particle size range of $1 - 300$nm. This distribution gives adequate resolution of particle size distribution and ensures that the total mass fraction in the largest section becomes negligible thus ensuring that the selected range does not curtail the scheme.

Model computations are conducted with the Premix code of the Chemkin software package. A modified version of the gas phase Interpreter allows for the handling of 52 additional species which represent the two bins for each particle size, one for the stable species and the other for the radical.

**FLAME CONDITIONS**

An atmospheric pressure premixed flame of ethylene/air is modelled. The flame is operated at a C/O ratio of 0.77 and a cold gas velocity of 10cm/s. In this conditions the flame is slightly-sooting.
The flame was investigated with probe measurements and optical diagnostics by Minutolo et al. [12]. Temperature, particulate volume fractions and size distribution functions were measured. Spectral UV-visible absorption and laser light scattering measurements allowed the identification of two classes of particles: soot particles, which absorb light in the whole spectral range and nano-organic carbon particles (NOC) which are transparent to the visible radiation. Atomic Force Microscopy was used for the determination of the size distribution functions of the particle number concentration at different heights above the burner outlet [7].

RESULTS AND DISCUSSION

The predictive capability of the kinetic model, extended in the present work, has been successfully tested in rich premixed flames of ethylene and benzene for all the key species involved in the pyrolytic process. Here, we show the predictive capability of the model for the volume fractions of NOC particles (lower than 10 nm) and soot (larger than 10 nm). Figure 1 shows the comparison between model predictions and experimental data for soot and NOC particles. Also reported in the figure is the temperature profile used in the simulation and the predicted concentration profile of PAH up to 200 μm.

The model predicts reasonably well the fast formation of NOC particles just downstream of the flame front followed by a decline in correspondence of soot particle inception but the formation of soot is predicted to be larger. PAH contributes for about 20% to the total organic carbon in good agreement with the results of Ciajolo et al. [8] obtained in similar flame conditions.

Consistent with the number of hydrogen atoms, ratios between radicals and parent species computed in the flame increases with the size of the molecules as shown in Fig.2 where these ratios are reported along the flame axis together with the mole fraction profiles of the sum of radical and parent species. Relative abundance of radicals increases in the main oxidation zone where a larger concentration of H and OH radicals are present and decreases in the post-oxidation region of the flame.

The use of the sectional method allows the molecular mass distribution of the combustion-formed aerosol to be obtained. Figure 3 reports the distribution functions of the particle number concentration computed along the flame axis at 4, 8 and 10 mm compared with the experimental size distribution obtained by D’Alessio et al. [7] by means of AFM measurements.

The model shows three modes of the size distribution functions of particle number concentration. The first one is below 1 nm and corresponds to PAH, the second one at about 2 – 3 nm is due to NOC particles and a third one at 10 – 20 nm is due to soot. The relative abundance of the three modes of the distribution function changes along the flame axis, the mode at 10 – 20 nm being more evident at high flame heights. These results are in reasonable agreement with the experimental data. AFM measurements show a bimodal distribution, this
technique being unable to detected species in the gas-phase or below a mean size of 1nm. It has recently been shown that the adhesion efficiency of particles on mica disks used for AFM measurements decreases by orders of magnitude as the mean particle size decreases below 5nm thus reducing the capability of the technique to measure small particles.

CONCLUSIONS

The formation of nano-sized organic particles and soot particles with diameters up to 200nm have been modelled in a rich premixed flames at atmospheric pressure by using a detailed gas-phase kinetic mechanism of fuel oxidation and pyrolysis coupled with particle inception and coagulation mechanisms. The particle ensemble is divided into classes and particle properties such as the numbers of carbon and hydrogen atoms are averaged within each section. An interesting feature of this method is the ability to represent all particle reactions in the form of gas phase chemistry.

The model has shown three modes in the size distribution functions of particle number concentration in reasonable agreement with experimental data. The first mode is below 1nm and corresponds to PAH, the second one at about 2 – 3nm is due to NOC particles and the third one at 10 – 20nm is due to soot. The model has been able to correctly predict the concentration profiles NOC particles (lower than 10 nm) and soot (larger than 10 nm) along the flame axis in the slightly-sooting ethylene/air flame.

Fig. 3 Comparison between predicted size distribution functions of species number concentration versus equivalent diameter and experimental data obtained by AFM at three flame heights.
REFERENCES