MODELING OF NANOPARTICLE AND SOOT FORMATION IN A CO-FLOWING DIFFUSION FLAME

G. Mazzotti¹, A. D’Anna², and J. Kent³

¹ Dipartimento di Energetica, Termofluidodinamica Applicata e Condizionamento Ambientale – Università di Napoli “Federico II”, Napoli, ITALY
² Dipartimento di Ingegneria Chimica – Università di Napoli “Federico II”, Napoli, ITALY
³ School of Aerospace, Mechanical & Mechatronic Engineering, University of Sydney, NSW, AUSTRALIA

Introduction
Combustion-generated aerosols pose significant health and environmental problems. Epidemiological observations consistently find that increased particle concentration is correlated with a variety of detrimental health effects including increased mortality. At the same time, anthropogenic aerosols affect the Earth’s radiation balance directly by backscattering or by absorbing radiation, and indirectly by increasing cloud condensation and thus. A quantitative understanding of particulate formation mechanisms and the ability to accurately model these processes is critical for the goal of zero-emission combustion systems.

In this communication a model of hydrocarbon oxidation and pyrolysis is applied to predict concentration profiles of the particulate (soot and high molecular mass compounds) in a co-flowing diffusion flame of diluted ethylene and air. Predictions are compared with particle volume fraction and sizes measured by classical optical extinction/scattering methods.

Flame Conditions
An atmospheric pressure, axisymmetric, laminar diffusion flame is modelled. The flame is stabilized on a co-flowing burner having a 12 mm diameter uncooled vertical tube for the fuel mixture and a concentric tube (108 mm diam.) for air. The air-annulus is reduced at the burner lip by a ring (i.d. 55 mm) to stabilize the flame. The fuel is a mixture 30.5% (vol) ethylene and 69.5% nitrogen with a total flow rate of 770 cm³/min while the air flow rate is 44,000 cm³/min.

This flame has been studied experimentally by McEnally and Pfefferle [1] and lately, with probe measurements and optical diagnostics by Rolando [2]. Temperature measurements, particulate volume fractions and mean sizes have been obtained for a range of radii at several axial heights.

Modeling
Gas-phase chemistry and aromatic growth
A detailed kinetic mechanism of hydrocarbon oxidation and pyrolysis is used [3-6]. The gas-phase mechanism includes the pyrolysis and oxidation of C1 and C2 species, the formation of benzene and reactions leading to the formation of larger aromatic compounds. The complete detailed reaction mechanism for the initial formation of aromatics consists of 279 reactions and 60 chemical species. Details of the mechanism and rate constants have been reported previously [5,6].
The process of aromatic growth to form higher molecular mass aromatic compounds is modeled by a radical-molecule sequence of reactions involving five-membered ring PAHs. The sequence begins with the H-abstraction from aromatic compounds to produce the corresponding radical. Iteration of this mechanism followed by rearrangement of the carbon framework ultimately leads to the formation of high-molecular-mass compounds. Details on the kinetic mechanism of aromatic growth and on the kinetic constants are reported elsewhere [7].

Collision and subsequent coagulation of the high-molecular-mass compounds is accounted for through the sticking probability, i.e. the probability of coagulation upon collision, which can be related to interactions between molecules, i.e. Van der Waals forces. Particles with sizes around 1-2 nm have a coagulation rate three orders of magnitude lower than the gas kinetic limit; as particle size increases the coagulation rate also increases and even approaches the gas kinetic limit for particles having high polarizability (graphitic-like). The change of the size distribution function of particles due to coagulation has been described by computing the population balance equation described by the Smoluchowsky equation. The size dependent coagulation rate is computed by multiplying the coagulation rate obtained from kinetic theory and the sticking probability evaluated from the interaction potential between particles.

The forming clusters are assumed to be solid particles which add and lose mass by surface reactions after activation of the surface by H atom abstraction. Acetylene is the major species through which mass is added whereas oxygen is the main oxidizing species. A steady-state approximation is adopted for fast reacting intermediates which implies that the number of radical sites is independent of particle size and the rate is determined only by the gas-phase environment [8].

In order to include the aromatic growth mechanism in the diffusion-flame model, the method of moments [9] is used. Three moments of carbon number per mole concentration are modelled; the zeroth moment $M_0$ is mole concentration, the first moment $M_1$ leads to mass concentration and the second moment $M_2$ gives the variance of the particle size distribution function. Mean particle size (C/molecule) is the ratio $M_1/M_0$. An assumed probability density function (pdf) is needed and here a lognormal size distribution function is assumed. The geometric mean and variance of the lognormal pdf is matched to the arithmetic mean and variance obtained from the independent transport equations for $M_0$, $M_1$ and $M_2$. The pdf affects those reactions whose rates are dependent on particle size. A log-normal size distribution function is used in the calculation. Changes in the shape of the size distribution function do not alter model previsions. Computations are performed by an axisymmetric steady-state solver for continuity, axial and radial momentum, species mass fraction, enthalpy and statistical moments.

**Results and Discussion**

Flame structure has been successfully modelled in terms of temperature, stable species and trace compounds. The predicted flame is shortened in the present work because the particulates do not burn out completely. In this paper, we examine the process of aromatic growth and particle inception giving attention to particulate volume fractions and particle sizes.

Figures 1 and 2 report the comparison between modelled and measured volume fractions (right) and particle sizes (left) of the high-molecular-mass compounds as a function of the radial coordinate at two axial locations, namely 30 and 60 mm., i.e. at the beginning of the flame (30 mm) and around its maximum temperature (60 mm). Measured volume fractions and particle diameters are from classical light scattering – extinction techniques [10]. Extinction measurements have been performed both in the ultraviolet and in the
visible range; in this way soot particles as well as their precursors can be measured. Light scattering at one wavelength cannot distinguish between soot and its precursor nanoparticles since it only provides the sixth moment of the size distribution function and the presence of smaller particles is obscured by the larger soot particles. The model results agree quite well with the measured data. At 30mm, the simulation of the particulate volume fraction in the wing region follows reasonably well the experimental data. The agreement is even better at 60mm.

Particle diameter is reproduced at both axial positions to within a factor of two. It should be remembered that the comparison is made between modelled mean size and the measured $6/3$ moment of the size distribution, the latter being weighed by the larger particles.

Fig. 1  Comparison between modelled and measured volume fraction (right) and particle diameter (left) as a function of the radial coordinate at 30mm above the burner exit.

Fig. 2  Comparison between modelled and measured volume fraction (right) and particle diameter (left) as a function of the radial coordinate at 60mm above the burner exit.
At low axial locations (30mm), very small particles with sizes of the order of few nanometer are predicted by the model. These particles, which have a size typical of high-molecular-mass compounds, are formed in the fuel side of the flame and grow up to soot precursor particles in the flame wings. Moving to higher flame heights particles with sizes typical of the primary soot particles (about 20nm) are formed also on the flame centreline. Analysis of the predictions reveals that surface growth is the controlling parameter in the process of soot loading whereas the radical-molecule combination mechanism controls the formation of soot precursors.

Conclusions
A detailed kinetic mechanism is used to simulate the formation of particulate in a co-flowing diffusion flame of ethylene. The model includes hydrocarbon oxidation and pyrolysis, particle inception and coagulation, and finally surface growth and oxidation.

The model predicts with a good level of accuracy the volume fraction of total particulate, in comparison with optical measurements in different flame locations and particularly in the wings of the flame. The model also simulates the mean size of particle diameter in the different regions of the flame showing the formation of nano-sized precursor particles in diffusion flames.

REFERENCES