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Analysis of the impact of agglomeration and surface chemistry models on soot formation and oxidation

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Abstract

Models for soot aggregation that account for the influence of soot surface chemistry on mass growth and oxidation are still at the formative stage. Past studies have considered techniques ranging from the method of moments to stochastic approaches and significantly different sensitivities to chemical processes such as mass growth and oxidation have been reported. The method of moments is computationally efficient and can yield encouraging results for laminar flames as well as for turbulent flames when combined with transported probability density function (PDF) methods. However, an assessment of the sensitivity to constituent model assumptions is not trivial and information regarding the soot size distribution is incomplete. In the current work, the ability of a sectional method to reproduce population dynamics data has been evaluated along with the sensitivity of predictions to closure elements associated with soot nucleation, agglomeration, surface growth and oxidation. A detailed chemistry model with 285 chemical species and 1520 reactions was used for the gas phase. It is shown that the approach to the fuel lean sooting limit can be reproduced with reasonable accuracy and that the inclusion of fractal aggregates and surface chemistry effects improve agreement with experimental data.

Keywords: Particle dynamics; Soot; Surface chemistry effects

1. Introduction

The majority of past studies of soot formation under combustion conditions have used models corresponding to the first few moments of the size distribution in order to avoid the task of obtaining the full particle size distribution (PSD) [1,2]. The method does not, however, yield complete information about the entire population distribution. To obtain the full PSD, the population balance equations (PBE) of aggregation should ideally be solved. Such explicit solutions are, however, computationally intractable with the range of particle sizes typically covering 3 orders of magnitude (10^{-9} m to 10^{-6} m). An alternative approach is to use a smaller number of 'representative particle sizes'. A direct consequence of such simplifications is that the Smoluchowski equations for coalescence dynamics will no longer ensure that critical system properties, such as mass, are conserved [3]. Experimental and modelling work on soot formation in ethylene flames using a mass conserving sectional approach [4] has been pursued by Smoke et al. [5,6], while Wen et al. [7]

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used a moving sectional model to study the plug flow reactor configuration of Kronholm and Howard [8]. Morgan et al. [9] simulated soot aggregation in premixed laminar flames using a stochastic method in order to obtain the PSD and an insight into the morphology of soot grains. By comparing the findings of the different studies, it is apparent that significantly different sensitivities to constituent submodels are obtained if more complete models for the aggregate structure of soot particles are used. For example, Patterson and Kraft [10] suggest that geometric effects only lead to a maximum change of 20% in soot mass fraction predictions in laminar premixed flames. By contrast, studies using the method of moments have reported large sensitivities to the fraction of sites (α_s) available for surface reaction (e.g. [11,2]).

The principal uncertainties related to the formation of higher aromatics, associated with soot inception, have been highlighted in several studies (e.g. [12–15]). Significant challenges remain and errors in computed species concentrations exceeding 2 orders of magnitude are not uncommon for 3- or 4-ringed structures (e.g. [11]). More progress has been made for lower PAHs such as naphthalene [11,13,14]. The competitive formation paths during ethylene oxidation include HACA type sequences [11,12], vinylacetylene (C_4H_4) addition to phenyl radical [16,11] and propargyl (C_3H_3) addition to benzyl and methylphenyl radicals [14]. Cyclopentadienyl recombination, leading to naphthalene via the bicyclic C_5H_5–C_5H_4 radical [17,18], has been proposed and questioned [15]. Despite such uncertainties, encouraging progress for indene and naphthalene levels has been reported during ethylene oxidation (e.g. [14]).

In the current work, a fixed sectional approach was developed to study aggregation kinetics and to investigate soot formation dynamics during ethylene combustion in a configuration consisting of a well-stirred reactor (WSR) followed by a plug flow reactor (PFR). Soot nucleation, agglomeration, surface growth and oxidation submodels were included in the calculations. The sensitivity to the different closure elements was explored and comparisons were made with the experimental data obtained by Manzello et al. [19].

2. A sectional approach to soot dynamics

2.1. Aggregation and breakage

A fixed sectional approach was used in the current study with the bins distributed geometrically as

$$m_{i+1} = f_s m_i, \tag{1}$$

where f_s is a geometric spacing factor discussed below. The fixed sectional approach for soot particle dynamics proposed by Kumar and Ramkrishna [20] offers a combination of computational speed and accuracy and was adopted to model agglomeration. Issues associated with numerical diffusion and computational stability are discussed below in the context of chemistry effects. The corresponding PBEs are designed to conserve two moments simultaneously. In the current method, a newly aggregated particle is 'split' and assigned to two adjacent bins such that any two general properties are conserved should the particle size not match any of the representative sizes on the grid. Such a strategy gives the method the potential to reproduce the PSD more accurately and the splitting coefficients need to be calculated only once. Hence, the method is computationally efficient. In the present approach, both the mass and the number of particles are conserved with the particle mass chosen to be the representative size variable. For these criteria, if N_{Bin} number of representative sizes are considered, then the population balance equations for aggregation are given by

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = \sum_{\substack{j,k \\ m_{i-1} \leqslant (m_j + m_k) \leqslant m_{i+1}}}^{k \leqslant j \leqslant i} \left(1 - \frac{\delta_{j,k}}{2}\right) \eta_{i,j,k} \beta_{j,k} n_j n_k - n_i \sum_{k=1}^{N_{\mathrm{Bin}}} \beta_{i,k} n_k, \tag{2}$$

where n_i is the number concentration of size class i at time t, $\beta_{j,k}$ is the rate (in m^3/s) at which particles of size class j attach with class k and $\delta_{j,k}$ is the Kronecker delta. For a particle size class i, the first and second terms on the right-hand side correspond to birth and death due to aggregation. The parameter $\eta_{i,j,k}$ is the fraction of a newly created particle that the size class i will receive when two particles of sizes j and k are combined. Hence, $\eta_{i,j,k}$ effectively assigns the new particle to two adjacent bins and is given by

$$\eta_{i,j,k} = \begin{cases} \frac{m_{i+1} - (m_j + m_k)}{m_{i+1} - m_i}, & m_i \leqslant m_j + m_k \leqslant m_{i+1} \\ \frac{m_{i-1} - (m_j + m_k)}{m_{i-1} - m_i}, & m_{i-1} \leqslant m_j + m_k \leqslant m_i. \end{cases} \tag{3}$$

The rate constants $\beta_{i,j}$ appearing in Eq. (2) take different forms depending on the Knudsen number

$$Kn_i = 2\lambda / d_i, \tag{4}$$

where λ is the particle mean free path and d_i is the particle diameter. If we denote $\beta_{i,j}$ in the free-molecular ($Kn_i \gg 1$), continuum ($Kn_i \ll 1$) and transition ($Kn_i \approx 1$) regimes, as $\beta^{\mathrm{f}}_{i,j}$, $\beta^{\mathrm{c}}_{i,j}$ and $\beta^{\mathrm{t}}_{i,j}$, respectively, then for spherical particles it follows [1,21,22],