Mathematical modelling of soot nanoparticles formation and evolution in turbulent flames

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1. Introduction

Detailed mathematical modeling of turbulent combustion processes results in accurate predictions of concentration profiles of fuel, oxidiser and other intermediate products (CO, CO$_2$, H$_2$, and H$_2$O) of the combustion processes. Moreover, the most important chemical reaction pathways, leading to the formation of the most common air-pollutants, are already well known. However, soot particles formation and evolution in combustion processes is a very complex and poorly understood phenomenon. Soot particles, containing several thousands of carbon atoms are formed from simple fuel molecules within few microseconds. The high number of hydrocarbon molecules, forming particles of different form and size, involved in this process can not be easily quantified, and as a consequence a statistical description of the system is necessary. This statistical description is based on a Number Density Function (NDF) that defines how the population of soot particles is distributed over a number of particle properties (identifying for instance particle size, morphology or composition).

In this work, this problem is tackled by solving the Population Balance Equation (PBE), which is a continuity statement written in terms of the NDF, by resorting to a moment-based method which employs a quadrature approximation for overcoming the closure problem (Direct Quadrature Method of Moments, or DQMOM). In the computation a pseudo-bivariate NDF was considered, with the number of primary particles per aggregate (or secondary particle) as unique internal coordinate, and then solving an additional transport equation for the total volume fraction of soot. Since soot particles strongly affect the enthalpy balance, because of the radiation effect, there is a two-way coupling between the flow, turbulence and temperature fields in the flame and soot formation and evolution. For this reason the PBE was implemented and solved within a commercial Computational Fluid Dynamics (CFD) code by resorting to User Defined Functions (UDF) and Scalars (UDS), allowing for the simultaneous solutions of the PBE and the continuity and Navier-Stokes equations, along with the enthalpy balance. The paper is organized as follows. Firstly the turbulence-chemistry interaction (or micro-mixing) problem is presented and secondly the particle dynamics description (through the PBE) is discussed. After describing numerical details, operating conditions and test cases, the main results are discussed and eventually some conclusions are drawn.

2. Turbulence-Chemistry interactions

In this work turbulence was closed with the Reynolds-Averaged Navier Stokes (RANS) approach. This method is based on solving the continuity and Navier-Stokes equations in terms of Reynolds-averaged (or Fauvre-averaged in the case of compressible flows) quantities. The unresolved turbulent scales appearing in the Reynolds stress tensor are then closed, in this work, by resorting to the simple $k$-$\varepsilon$ model, that was found to be a suitable tool for predicting temperature and velocity profiles in non-swirling flames [1]. In the case of turbulent reacting flows also the transport equations of the involved reacting scalars must be considered, resulting in the following equation:
\[
\frac{\partial}{\partial t} \left[ \bar{\rho} \hat{\phi}_\alpha \right] + \frac{\partial}{\partial x_i} \left[ \bar{\rho} \bar{U}_i \hat{\phi}_\alpha \right] - \frac{\partial}{\partial x_i} \left[ \bar{\rho} (\Gamma + \Gamma_t) \frac{\partial \hat{\phi}_\alpha}{\partial x_j} \right] = \bar{S}(\phi_\alpha)
\] (1)

where \( \bar{U}_i \) and \( \hat{\phi}_\alpha \) are the Fauvre-averaged gas velocity and concentration of scalar \( \alpha \), \( \Gamma \) and \( \Gamma_t \) are the molecular and turbulent diffusivity, and the last one is the chemical reaction term, which needs to be closed.

A useful method is the so-called presumed Probability Density Function (PDF) approach [2,3] in which the shape of the PDF is assumed a priori and the conditional scalar moments are then modeled. When the system is not adiabatic, the joint composition-enthalpy PDF should be used; however, the problem is usually simplified assuming that enthalpy fluctuations are independent on the enthalpy level, so that heat losses do not affect the turbulent enthalpy fluctuations, and the PDF of the mixture fraction is used to compute the mean values.

When non-equilibrium effects are important, the local equilibrium assumption is no more valid, and it is necessary to take into account the fact that the chemical reactions involved have specific finite-rates. The laminar flamelet model [4,5] considers a turbulent flame as an ensemble of discrete laminar flames, and allows the use of a realistic kinetic scheme to account for the conditions in which, due to the stretching of the flame caused by the turbulent strain, that implies higher gradients, and so higher transport rate, the equilibrium conditions are not reached.

3. Soot particle dynamics

As already reported, the evolution of the population of particles is written in terms of the NDF \( \tilde{n}(N;x,t) \), that depends on the number of primary particles per aggregate \( N \), space \( x \) and time \( t \). The Fauvre-averaged PBE, omitting spatial and temporal dependencies, results in the following equation:

\[
\frac{\partial}{\partial t} \left[ \bar{\rho} \tilde{n}(N) \right] + \frac{\partial}{\partial x_i} \left[ \bar{\rho} \bar{U}_i \tilde{n}(N) \right] - \frac{\partial}{\partial x_i} \left[ \bar{\rho} (\Gamma + \Gamma_t) \frac{\partial \tilde{n}(N)}{\partial x_j} \right] = \bar{\rho} J(x,t)\delta(N-1)
\]

\[
+ \bar{\rho} \frac{1}{2} \int_0^N \int_0^{N^*} \beta(N-N^*,N^*) \tilde{n}(N-N^*)dN^* - \bar{\rho} \int_0^{N^*} \beta(N,N^*) \tilde{n}(N) \tilde{n}(N^*)dN^* .
\] (2)

The left-hand side of the PBE contains all the terms related to accumulation and transport of soot particles in the physical space, whereas the terms on the right-hand side represent respectively, nucleation (or inception) of soot particles, rate of birth and death of new particles due to aggregation, and continuous rate of change of the number of primary particles per aggregate due to surface growth and oxidation. According to this notation \( J \) is the nucleation rate, \( \beta \) is the aggregation kernel, and \( \bar{N} \) is the continuous rate of change of the internal coordinate. Details concerning the derivation of this equation and the physical meaning of each term can be found in our previous work [6] whereas in the next section only a brief description will be reported.

A convenient approach for the solution of the PBE is based on the use of a quadrature approximation of order \( N_d \) for the NDF, as follows:

\[
\tilde{n}(N;x,t) \approx \sum_{a=1}^{N_d} w_a(x,t) \delta \left[ N - N_a(x,t) \right]
\] (3)
where \( w_a(x,t) \) are the weights and \( N_a(x,t) \) are the abscissas or nodes of the quadrature approximation. It is possible to show that, given \( 2N_d \) moments of the NDF one can calculate the \( N_d \) values of the weights and the \( N_d \) values of the abscissas of the quadrature approximation, directly solving transport equations of weights and abscissas themselves [7]. Therefore a quadrature approximation of order two (\( N_d=2 \)) is tracked by solving the transport equations for the two weights and abscissas, resulting in the accurate prediction of the first four moments of the NDF, namely \( m_0 \), \( m_1 \), \( m_2 \), and \( m_3 \).

As already reported, in order to describe completely the population evolution, the transport equation for the total volume fraction of soot \( f_v \) particles is also solved:

\[
\frac{\partial}{\partial t} (\bar{\rho} f_v) + \frac{\partial}{\partial x_i} [\bar{\rho} \bar{U}_i f_v] - \frac{\partial}{\partial x_i} (\bar{\rho}(\Gamma + \Gamma_1) \frac{\partial f_v}{\partial x_i}) = \bar{\rho} \left[ v_0 J + \left( \frac{\partial v_p}{\partial t} \right)_{\text{mol}} m_1 - \left( \frac{\partial v_p}{\partial t} \right)_{\text{ov}} m_1 \right],
\]

where as before the terms related to transport in time and space are reported on the left-hand side, whereas on the right-hand side the terms related to nucleation, surface growth and oxidation are reported. According to this notation \( v_0 \) is the volume of a single nucleus, whereas \( v_p \) is the volume of a single primary particle.

As reported, soot formation in turbulent flames presents the so-called two way coupling, in fact, particle nucleation, aggregation, growth and oxidation are mainly determined by the velocity, turbulence and temperature fields in the flame, that in turns are affected by the presence of the soot particles due to the high radiative effect of particulate matter.

We can estimate the effect of the soot on radiative heat transfer by determining an effective absorption coefficient for soot and then take into account the additional radiation term in the enthalpy balance as follows:

\[
S_{h,\text{rad}} = -\sigma a_s \left(T^4 - T_\infty^4\right),
\]

where \( \sigma \) is the Stefan–Boltzmann constant, \( a_s \) is the absorption coefficient of soot and \( T_\infty \) is the radiative environment temperature (set to 300 K).

4. Nucleation, aggregation, surface growth and oxidation kinetics

Particle nucleation, aggregation, surface molecular growth, oxidation and restructuring were taken into account in the model, the rate of each process being evaluated by simplified kinetic expressions available in the literature. For the nucleation rate \( (J) \) two expressions have been evaluated [8,9], that for simplicity will be referred to in what follows as \( J_1 \) and \( J_2 \)

\[
J_1 = \frac{2}{\rho_s C_{\text{min}}} N_A C_{C_2H_2} T^{1.35} \cdot 10^6 \exp \left(-\frac{41000}{RT}\right),
\]

\[
J_2 = N_A \cdot \rho_s^{-1} \cdot T^{1/2} \cdot 6 \cdot 10^6 \exp \left(-\frac{46100}{T}\right) X_{C_2H_2},
\]

where \( N_A \) is the Avogadro’s number, \( \rho_s \) is the soot density, \( C_{C_2H_2} \) and \( X_{C_2H_2} \) are respectively the molar concentration and the molar fraction of acetylene and \( C_{\text{min}} \) is the minimum number of particles in the incipient soot particle.

The rate of appearance and disappearance of particles due to aggregation is quantified by the aggregation kernel \( \beta \) and can be calculated by resorting to the equation that interpolates between the two limiting cases of free molecular (Epstein) and continuum (Stokes-Einstein) regimes [10]. Moreover since soot particles are fractal objects their collision frequency must be written as function of the collision radius of the aggregates involved in the collision event,
(i.e radius of gyration, $R_g$) related to the number of spherules in each aggregate, $N$, by the following relationship:

$$N = k_j \left( \frac{2R_g}{d_p} \right)^{D_f},$$

(8)

where $D_f$ is the fractal dimension, and $k_j$ is the fractal pre-factor based on the aggregate radius of gyration, normalized by the average spherule radius, $r_p = d_p / 2$. The value of $D_f$ has to be assumed or evaluated by some simplified models [11] and in this work a constant value equal to 1.74 as suggested by other authors [12] was considered.

Moreover, in order to correctly model particle evolution we have to take into account that during particle surface growth, primary particles tend to lose their identity, condensing and generating bigger primary particles. This is the so-called obliteration process and cause a decrease in the number of primary particle in the aggregate, whose rate can be calculated as follows [13]

$$\dot{N}_{obl} = \frac{3D_f}{4\pi(3-D_f)} \left( \frac{R_g}{N r_p} \right)^{1-D_f} \left( \frac{r_p}{R_g} - 1 \right) \left( \frac{\partial v_p}{\partial t} \right)_{mol},$$

(9)

where $v_p$ is the volume of the primary particle. The molecular growth rate of a singular primary particle is defined as [9]:

$$\left( \frac{\partial v_p}{\partial t} \right)_{mol} = 6.3e^{-14} \frac{\rho}{\rho_s} T^{0.5} X_{C_H} \exp \left( \frac{-12600}{T} \right).$$

(10)

Also, surface oxidation causes a decrease in the number of primary particles, whose rate is:

$$\dot{N}_{ox} = \left( \frac{\partial v_p}{\partial t} \right)_{ox} v_p,$$

(11)

where the oxidation rate of a particle can be computed by [14]:

$$\left( \frac{\partial v_p}{\partial t} \right)_{ox} = \frac{\rho}{\rho_s} (36\pi)^{\frac{1}{2}} v_p^2 1.085 \cdot 10^{-5} p_o T^{-0.5} \exp \left( \frac{-19778}{T} \right).$$

(12)

5. Numerical details and test cases

The two-dimensional computational grids were prepared using the software GAMBIT under the hypothesis of axial symmetry. The computational domain included only the combustion chamber and the boundary conditions at the inlets were specified through inlet profiles provided with the analyzed experimental data [12].

Turbulence was modelled by the RANS approach using the standard $k-\varepsilon$ model, coupled with standard wall functions. The effect of the turbulence model on the final predictions was tested by varying the model constants ($C_{2\varepsilon} = 1.92$ by default). A second-order upwind scheme was employed for spatial discretization, while pressure-velocity coupling was solved with the SIMPLE algorithm.

The laminar multiple-flamelet model and the presumed beta-PDF approach (this latter under hypothesis of instantaneous equilibrium assumption) were tested with two kinetic schemes, found in the literature, each involving 20 species, that we will refer to as $S_1$ and $S_2$. [15]

In order to solve the PBE, DQMOM with two nodes was implemented via user-defined functions within FLUENT 6.1.22. Model predictions then were compared with experiments carried out in the same operating conditions [12] and results are reported in the next section.
6. Results and discussion

Fig. 1 Comparison of axial profiles of simulation results (lines) and experimental data (filled symbols) for (a) soot volume fraction, (b) radius of gyration, (c) total number density of aggregates, (d) total number density of primary particles, (e) mean number of primary particles per aggregate, (f) mean primary particle diameter; Models: blue: flamelets with $S_1$, $J_1$, oxidation & obliteration, std k-$\varepsilon$ with default $C_{2\varepsilon}$; pink: Beta PDF with $S_1$, $J_1$, oxidation & obliteration, std k-$\varepsilon$ with default $C_{2\varepsilon}$; orange: Beta PDF with $S_2$, $J_2$, oxidation & obliteration, std k-$\varepsilon$ with $C_{2\varepsilon}$=1.8; green: Beta PDF with $S_2$, $J_1$, oxidation & obliteration, std k-$\varepsilon$ with default $C_{2\varepsilon}$.

Figure 1 reports the comparison between model predictions and experimental data of the axial profiles of soot volume fraction, radius of gyration of aggregates, total number density of aggregates, total number density of primary particles, mean number of primary particles per
aggregate, and mean primary particle diameter. As it is possible to see, experimental data are compared with model predictions obtained with different turbulence-chemistry interaction models, kinetics schemes ($S_1$ and $S_2$) and nucleation rates ($J_1$ and $J_2$). Moreover, the effect of single parameters, such as the turbulence model (through the turbulent dissipation rate constant $C_2$) and the oxidation rate were separately tested.

The comparison shows that all the model combinations predict fairly well the general behaviour. Soot particles are nucleated in the first section of the flame, where the soot volume fraction increases sharply (see Fig. 1a) whereas in the last sections the soot volume fraction decreases both because of dilution, due to incorporation of fresh air, and because of oxidation. This is also confirmed by the axial profiles of the total aggregate number density and the number density of primary particles (see respectively Figs. 1c and 1d).

The effect of aggregation is clearly visible from Figs. 1b and 1e: as soot particles move along the flame axis their radius of gyration increases as well as the mean number of primary particles per aggregate. Figure 1f shows instead the competition between surface growth and oxidation that directly affects the primary particle diameter.

6. Conclusions

The problem of modelling soot formation in turbulent non-premixed flames was approached exploiting the possibilities of Computational Fluid Dynamics (CFD). The PBE was solved in a commercial CFD code by resorting to DQMOM, which is a novel formulation of the well-known QMOM. DQMOM was applied to the simulation of particle dynamics in a simple ethylene/air jet flame, and the model included all the main processes involved (nucleation, molecular growth, oxidation, aggregation, restructuring) via simplified kinetics expression available in the literature. Simulation results have shown that DQMOM is a suitable tool for the solution of the considered problem and the selected kinetic models allowed to describe the evolution of soot quite accurately. However, since different combination of modelling choices resulted in similar results further speculation to discriminate among possible modelling choices requires more detailed experimental data related to the flame composition, temperature, velocity and turbulence profiles.

References