Direct Numerical Simulation of Soot Formation in Turbulent Non-premixed Flames

By Fabrizio Bisetti, Guillaume Blanquart and Heinz Pitsch

1. Motivation and Objective
Soot particles are recognized as an important cause of health and respiratory problems. Over the past decade, several hundreds of studies linked soot particles to increased risk of lung cancer, asthma and chronic bronchitis. Fine soot emissions (with size smaller than 2.5 µm) have been linked to increased risk of heart attack and they have been identified as the greatest contributor to cancer risk, given their ability to reach deep into the lungs. Recognizing the adverse health and environmental effects resulting from particulate matter (PM), the Environmental Protection Agency (EPA) has been placing increasingly more severe regulations on emissions from cars and trucks for the past ten years. It is expected that EPA will soon place stricter regulations on allowed levels of smoke visibility and on the size of soot particles from combustion devices such as aircraft jet engines.

Soot particles are formed and destroyed during rich combustion of hydrocarbon fuels in many combustion devices: internal combustion engines, jet engines, coal power plant burners, and others. The choice of hydrocarbon fuel mixture, oxidizer, and fuel flow rates, mixing patterns, temperatures, and pressure are design parameters that affect in a complex and non-linear fashion the characteristics of soot emitted from combustion devices, including particle size distribution and surface reactivity. While our understanding of soot formation and growth have much improved in recent years, the prediction of soot emissions still remains a complex task. Soot formation involves a sequence of gas phase reactions forming polycyclic aromatic hydrocarbons (PAH) followed by particle inception, particle/particle interactions, soot particle growth and oxidation by heterogeneous reactions with chemical species in the gas phase. The interaction between turbulent transport and molecular diffusion as well as local flow conditions (e.g. chemical species concentrations and temperature) play a key role in controlling soot concentrations. Presently, our capability to predict soot emissions in realistic combustion devices remains insufficient as the existing models often rely on empirical correlations.

The objective of the present work is to perform two-dimensional Direct Numerical Simulations (DNS) of soot formation and dynamics in non-premixed combustion subject to decaying isotropic turbulence. The present two-dimensional simulation will serve to assess the robustness of the soot solution methodology, before a three-dimensional DNS study is undertaken to investigate soot/chemistry/turbulence interactions in a realistic combustor geometry.

2. Modeling approach
2.1. Overview of soot population dynamics
Soot is formed during combustion due to the aggregation of large polycyclic hydrocarbon (PAH) molecules such as pyrene, which form aggregates of a handful of PAHs with
resulting sizes in the range of 1 nm (Bockhorn 1994). The formation process is often described as *nucleation*. As the number density of soot particles increases, collisions among particles become more frequent. Particle collisions might result in single particles (*coagulation*) or aggregates of a number of *primary* particles (*aggregation*). Typical sizes of soot particles/aggregates range from 1 to 100 nm, while the number of primary particles in an aggregate ranges from 10 to 1000. Figure 1 illustrates the nature of a typical soot aggregate, which might contain hundreds of primary particles. A primary particle might range from 1 to 10 nm in size and often displays a spherical shape. It is important to notice that volume being equal, the surface area available for a single particle is much less than that of an aggregate. Soot particles and aggregates populate a reactive environment, and several gaseous species such as molecular hydrogen, molecular oxygen, radicals (OH and H) and acetylene interact with active hydrogen sites on the soot surface resulting in further mass addition. It is generally accepted that a single reaction event typically results in the mass addition of two carbon atoms via the H-abstraction-C\textsubscript{2}H\textsubscript{2}-addition (HACA) mechanism (Wang & Frenklach 1994). Mass addition on the surface (*surface growth*) accounts for a large portion of the total mass addition and is directly proportional to the total soot surface available for HACA reactions. One then understands the importance of predicting with great accuracy the soot surface, thus accounting for both single soot particles as well as for aggregates. An additional mechanism of mass addition is *condensation* of large PAH molecules on the soot surface without reactions taking place. Finally, soot particles can be attacked by hydroxyl radical and oxygen molecules, which oxidize carbon atoms to carbon monoxide and dioxide, thus reducing the soot particles’ mass (Neoh et al. 1981). This process is called *oxidation*. Soot oxidation is largely responsible for abating the soot volume fraction after non-premixed combustion has occurred in a diesel engine.

2.2. Soot integration and coupling to the flow field

Soot dynamics are described in terms of the moments of an underlying bivariate number density function. An integro-differential equation describes the evolution of the soot number density function due to nucleation, particle-particle collisions, surface growth and oxidation (e.g. Friedlander 1977). Introducing a polynomial approximation for the integrands, it is possible to reduce the integro-differential equation to a system of ordinary differential equations for the moments (Frenklach 2002; Mueller et al. 2008a). In this work we use the newly developed Hybrid Method of Moments (HMOM) of Mueller et al. (2008a,b). The HMOM methodology allows to capture the bimodality of the soot population size probability density function, which reflects the presence of small single
particles as well as large aggregates. A validation study of the implementation of the HMOM method was carried out by numerically simulating soot formation in a counterflow diffusion acetylene/air flame at low strain Pels Leusden & Peters (2000). The results are presented in Figures 2 and 3. While the level of agreement among the simulation and the experimental data might seem less than satisfactory at first, one should appreciate that a factor of two among numerical and experimental data is in fact a very successful achievement and it compares well with other works (Mueller et al. 2008a).

2.3. Normal Heptane Oxidation Chemistry & Soot Nucleation

The description of soot formation and its interaction with a flame-like environment is challenging as chemical species in the gas phase play a very important role in enhancing soot nucleation, growth, and oxidation. Soot nucleation in particular is understood to occur from polycyclic aromatic hydrocarbons (PAHs), which are not present in the initial fuel mixture and are formed during the fuel decomposition. In this work, we simplified the treatment of gas phase chemistry by adopting a reduced mechanism for n-heptane oxidation comprising 48 species and 348 reactions (Blanquart 2008). The reduced mechanism does not contain any steady state species and it has been obtain via a reduction procedure (Pepiot-Desjardins & Pitsch 2008) from a detailed mechanism by Blanquart et al. (2008). Additionally, we described soot nucleation as occurring from acetylene molecules (Leung et al. 1991), rather than from PAHs. The nucleation rate \( (\text{kmol/m}^3/\text{s}) \) of soot particles due to the collision of two acetylene molecules is shown in Eq. (2.1)

\[
K_{\text{nucl}} = A e^{-T_a/T} [C_2H_2] \tag{2.1}
\]

where \( A = 10^{-4} \) and \( T_a = 21.1 \times 10^3 \) K and \( [C_2H_2] \) is the acetylene concentration \( (\text{kmol/m}^3) \) as in Leung et al. (1991).

2.4. Soot surface reactions and oxidation

Interaction of gas phase molecules with active hydrogen sites on the soot surface is the primary process responsible for the increase of soot volume fraction at high temperature. It is generally accepted that a single reaction event results in the mass addition of two carbon atoms via the H-abstraction-C_2H_2-addition (HACA) mechanism (Wang & Frenklach 1994). The rate of volume gain for a particle/aggregate of given area \( S \) is shown in
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Eq. (2.2) and Eq. (2.3).

\[
\begin{align*}
    r &= \frac{k_{1f}[\text{H}] + k_{2f}[\text{OH}] + k_{3f}}{k_{1b}[\text{H}_2] + k_{2b}[\text{H}_2\text{O}] + k_{3b}[\text{H}] + k_{4}[\text{C}_2\text{H}_2]} \\
    K_{\text{surf}}(S) &= \delta V_{2C} \times \left\{ k_4[\text{C}_2\text{H}_2] \left( \frac{r}{1 + r} \right) \chi_H S \right\} (m^3 s^{-1})
\end{align*}
\] (2.2) (2.3)

where \( \delta V_{2C} \) indicates the volume associated with two carbon atoms, which are gained after each HACA event. All reaction rates appearing in Eq. (2.2) and Eq. (2.3) are taken as defined in Blanquart & Pitsch (2008). Also, \( \chi_H \) is the total number of H-sites (including both radical and active sites) per unit surface area. In the present study \( \chi_H = 10^{19} \text{ m}^{-2} \) (Mueller et al. 2008a).

Soot oxidation is described as occurring from the attack of O\(_2\) molecules on the active hydrogen sites on the soot surface (Kazakov et al. 1995), as well as from the collision of hydroxyl radicals (OH) on the soot particles/aggregates surface (Neoh et al. 1981). Equations (2.4) and (2.5) describe the rates of volume loss by oxygen and hydroxyl radical oxidation for a particle/aggregate with surface \( S \) and collision diameter \( d_c \).

\[
K_{\text{oxid}, \text{O}_2}(S) = \delta V_{2C} \times \left\{ 2.2 \times 10^{12} e^{-T_a/T[\text{O}_2]} \frac{r}{1 + r} \chi_H S \right\} (m^3 s^{-1})
\] (2.4)

where \( \delta V_{2C} \) indicates the volume associated with two carbon atoms and the activation temperature for oxygen-based oxidation is \( T_o = 3.8 \times 10^3 \text{ K} \) (Kazakov et al. 1995). Also, \( r \) is defined in Eq. (2.2).

\[
K_{\text{oxid}, \text{OH}}(d_c) = \delta V_C \times \left\{ 0.13 \times \frac{8\pi k_B T}{m_{\text{OH}} n_{\text{OH}} d_c^2} \right\} (m^3 s^{-1})
\] (2.5)

where \( k_B \) is Boltzmann’s constant, \( m_{\text{OH}} \) and \( n_{\text{OH}} \) are the mass and number density of OH radicals Neoh et al. (1981). Finally, \( \delta V_C \) is the volume associated with a carbon atom, which is lost at each successful collision among a soot particle/aggregate and an hydroxyl radical. In the present implementation of the HMOM methodology, a third order approximation for the treatment of the change in aggregate surface due to oxidation is used to ensure coherence in the formulation and numerical robustness. The details of the formulation are presented in Appendix A.

2.5. Numerical implementation

The effect of spatial transport can be readily accounted for by including a substantial derivative of the moments. Diffusion as well as thermophoretic effects have been neglected in the present study. The soot dynamics equations can be described

\[
\frac{D}{Dt} \log M_i = \sum_{p=1}^{N} \Omega_i^{(p)}
\] (2.6)

where \( \Omega_i^{(p)} \) indicates a source term for \( \log M_i \) due to an internal evolution process \( p \) of \( N \). In the present study we included nucleation, surface reaction, collisions, and oxidation. Note that moments \( M_i \) vary widely across soot filaments due to the low diffusivity associated with particle phase. For example, particles with a diameter of 10 nm display a Schmidt number of 100. For larger particles with a diameter of 100 nm, the Schmidt number can exceed \( 10^4 \), such that the assumption of negligible molecular diffusion effects appears well justified. Due to the nature of the soot number density as well as because
while $t < t_{\text{max}}$ do
  for $n = 1$ to $N_{\text{sub}}$ do
    advance scalar
    integrate combustion
    advance velocity
    velocity correction
  end for
  integrate soot
  $t = t + \Delta t$
end while

Figure 4. Pseudocode showing the time advancement of soot dynamics in the flow solution procedure.

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$\log M_i^{(n)} \xrightarrow{\text{src}} \log M_i^{(n+1)}$</td>
</tr>
<tr>
<td>2.</td>
<td>$\Delta \log M_i</td>
</tr>
<tr>
<td>3.</td>
<td>$\Delta \log M_i</td>
</tr>
<tr>
<td>4.</td>
<td>$\log M_i^{(n+1)} = \log M_i^{(n)} + \Delta \log M_i</td>
</tr>
</tbody>
</table>

Figure 5. Pseudocode showing the sub-steps in the time advancement of soot dynamics. Step 1 consists in an implicit integration of the sources from time $t$ to time $t + \Delta t$. Step 2 consists in computing a discrete source term from the implicit integration at step 1. In step 3 the change in the moments due to convection using a quick scheme is computed. The final step 4 updates $\log M_i$.

of the chosen moment-based description, the moments $M_i$ can vary up to several orders of magnitude in space, depending on the local soot properties. Hence, it was found necessary to transport the logarithm of the moments $\log M_i$ rather than the moments themselves to improve the robustness of the numerical treatment of the moments’ convective transport. Future plans include a study on the effects of transporting the $\log M_i$ on accuracy and a detailed comparison with the transport of linear quantities. The soot evolution is tied to the local scalar fields through the temperature and species concentrations dependence of the source terms $\Omega_i^{(p)}$. The effect of soot evolution on the local scalar fields (e.g. hydroxyl radical depletion due to oxidation, and acetylene consumption via soot surface growth) is neglected at present. The soot advancement step lies outside of a conventional sub-iteration loop, which handles the variable density treatment of low Mach number convection, diffusion and chemical reactions. The integration procedure is summarized in Figures 4 and 5. At present, a complete, validated and fully functional soot integration framework has been implemented in the structured, low Mach number, variable density code NGA (Desjardins et al. 2008).

### 2.6. Initial conditions

The configuration used for this study consists of a two-dimensional slab of fuel surrounded by air. The domain is square and measures 3 cm in size. The boundary conditions are periodic in both the $x$ and $y$ directions. The velocity field is initialized with isotropic turbulence with a prescribed spectrum Passot & Pouquet (1987). A zero mean velocity is imposed. The turbulent velocity fluctuations are set at $u' = 37.25$ cm/s, while the most energetic length scale is $\ell_e = 5.56$ mm, yielding $Re_\lambda \approx 45$.

Figure 6 illustrates the computational arrangement. The fuel slab consists of diluted n-heptane ($15\% C_7H_{16}$ and $85\% N_2$), while air is taken to consist of $21\% O_2$ and $79\% N_2$, all percentages in volume. The stoichiometric mixture fraction is $Z_{st} = 0.148$. At the onset of the simulation, the reactive scalars are mapped from a flamelet solution onto the spatial domain using a prescribed spatial distribution of mixture fraction (Lignell et al. 2007) as in Eq. (2.7)

$$Z(y) = \frac{1}{4} \left[ 1 + \tanh \left( \frac{2}{\delta_Z} (y - y_1) \right) \right] \times \left[ 1 + \tanh \left( \frac{2}{\delta_Z} (y_2 - y) \right) \right]$$

(2.7)

where $y_{1,2}$ are the centers of the two transitions and $\delta_Z$ is the width of the transition.
Figure 6. Schematic of the computational configuration. Line contours denote the initial vorticity field, where thick and thin contours represent counter-clockwise and clockwise vorticity respectively. Also shown are the line contours of mixture fraction.

Table 1. Simulation parameters and relevant length, time and velocity scales.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L$ (mm)</td>
<td>30</td>
</tr>
<tr>
<td>$L_{11}$ (mm)</td>
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</tr>
<tr>
<td>$h_Z$ (mm)</td>
<td>5</td>
</tr>
<tr>
<td>$\delta_Z$ (mm)</td>
<td>2.2</td>
</tr>
<tr>
<td>$u'$ (cm/s)</td>
<td>37.25</td>
</tr>
<tr>
<td>$\tau$ (ms)</td>
<td>13</td>
</tr>
<tr>
<td>$\tau_{flame}$ (ms)</td>
<td>25</td>
</tr>
<tr>
<td>$\chi_{Z, st}$ (1/s)</td>
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</tr>
<tr>
<td>$\Delta x/y$ ($\mu$m)</td>
<td>35.5</td>
</tr>
<tr>
<td>$\Delta t$ ($\mu$s)</td>
<td>10</td>
</tr>
<tr>
<td>$\delta Z$ (mm)</td>
<td>2.2</td>
</tr>
<tr>
<td>Sim time (ms)</td>
<td>15</td>
</tr>
</tbody>
</table>

which determines the initial value of scalar dissipation rate. A very low value of stoichiometric scalar dissipation rate at the onset of the simulation $\chi_{Z, st} = 2D|\nabla Z|^2 = 1.8$ s$^{-1}$ was chosen to avoid excessive straining and flame extinction. Note that the stoichiometric scalar dissipation rate at extinction for a counterflow diffusion flame was found to be approximatively 80 s$^{-1}$. As mentioned above, we used a reduced mechanism describing n-heptane oxidation obtained from the detailed mechanism by Blanquart et al. (2008). This configuration corresponds to a transition width $\delta_Z = 2.2$ mm and a width of the fuel slab $h_Z = 5$ mm, if we let the diffusivity $D$ equal to $1.575 \times 10^{-5}$ m$^2$/s. The flamelet solution was computed with a stoichiometric scalar dissipation rate matching $\chi_{Z, st}$ using the FlameMaster code (Pitsch 1998). Table 1 lists simulation parameters and relevant length, time and velocity scales. The mesh is homogeneous in both directions ($\Delta x = \Delta y = 37.5$ $\mu$m), with an overall mesh resolution comparable to the one employed in a similar study by Lignell et al. (2007). Despite similarities with the work by Lignell et al. (2007), the present computation is unique in that it utilizes realistic n-heptane oxidation and PAH formation chemistry as well as a detailed soot model which is free from tuning constants.
3. Results

3.1. Overview of soot formation

The simulation was computed up to 15 ms, corresponding approximatively to 2.5 turbulence times (based on $u'$ and $L_{11}$). Figures 7 and 8 show the temperature and soot volume fraction at time 15 ms. In both figures, two iso-contour lines (blank or white for clarity only) are drawn at $Z = Z_{st} = 0.148$ and at $Z = 0.21$. The latter iso-counter indicates the approximate location of peak nucleation rate in mixture fraction space. Qualitatively, one recognizes the expected flame wrinkling by the turbulent velocity field. For the most part, the flow has little effect on the gas phase flame chemistry at this low level of scalar dissipation rate. As shown in Figure 8, soot concentrates in sharp, narrow, filament-like regions characterized by steep fronts. Soot is prevalently present on the fuel-side of the flame, with filaments and islands of soot extending well into the fuel slab. In regions of the flame characterized by a strong negative curvature of the stoichiometric contour, non-negligible amounts of soot appear to have penetrated the flame and spread into the air-side of the flame. Note that we define negative curvature when the center of curvature lies in the fuel-side. Conversely, next to regions of positive curvature, soot filaments extend well into the fuel slab. Regions of low curvature show peak levels of soot volume fraction just behind the $Z = 0.21$ iso-contour (rich-side).

Figure 9 shows the temporal evolution of temperature, acetylene mass fraction, hydroxyl radical mass fraction, and soot volume fraction at times 5, 10 and 15 ms. Due to the low levels of scalar dissipation rate imposed on the flame by the turbulent flow field, reactive scalars appear strongly correlated with mixture fraction. This is particularly evident for both temperature and the hydroxyl radical mass fraction, which consistently appears to peak on the lean side of the stoichiometric contour. As it will shown later, the focusing effect is responsible for mildly localizing soot oxidation, directly affecting the soot volume fraction patterns near the flame stoichiometric contours. Figure 9 also highlights the strongly different transport mechanisms for reactive scalars and for soot volume fraction. While the former appear smeared due to molecular diffusion, the latter appears in sharp, thin structures with little effect of diffusion. As we discussed above, soot displays a high Schmidt number in the range of $10^2$ to $10^4$. 
Figure 9. Temperature, acetylene and hydroxyl radical mass fractions, and soot volume fraction at 5, 10 and 15 ms (top to bottom). The two iso-contour lines are drawn at $Z = Z_{st} = 0.148$ and at $Z = 0.21$, the approximate location of peak nucleation rate in mixture fraction space. White colored lines used for clarity only.

Figure 10. Soot number density (particles and aggregates), nucleated soot particle number density, mean primary particle diameter, and mean number of primary particles per aggregate at 5, 10 and 15 ms (top to bottom). The two iso-contour lines are drawn at $Z = Z_{st} = 0.148$ and at $Z = 0.21$, the approximate location of peak nucleation rate in mixture fraction space. White or black used for clarity only.

3.2. Soot distribution and morphology

Figure 10 shows the soot number density (particles and aggregates), nucleated soot particle number density, mean primary particle diameter, and mean number of primary particles per aggregate at 5, 10 and 15 ms during the simulation.
One noticeable feature is that the smallest soot particles described in the model (indicated with \( N_0 \)) populate preferentially the regions behind the \( Z = 0.21 \) iso-contour (rich-side) and they are virtually absent from regions where \( Z < 0.21 \). A second noticeable feature is that soot volume fraction (see rightmost column in Fig. 9) and number density (leftmost column in Fig. 10) appear to be negatively correlated. Regions populated by a large number of particles and aggregates are those with the lowest soot volume fractions. Finally, soot islands which are characterized by large primary particles (high \( d_p \)) are also those with the aggregates having the lowest number of primary particles (low \( N_p \)). The aggregates with the highest numbers of primary particles (high \( N_p \)) are found on the rich side of the flame, deep into the fuel slab. Those aggregates are also the ones with the smallest primary particles (low \( d_p \)). Conversely, the aggregates which lie closer to the stoichiometric contour, or those that have broken through the stoichiometric contour, are characterized by the much larger and fewer primary particles (high \( d_p \) and low \( N_p \)). The aggregates with the largest primary particles are found in regions of high negative flame curvature.

A possible explanation for the observed distribution of soot number density, volume fraction and primary particles’ size and number lies in the relative competition of particle-particle collision, soot surface growth, and oxidation. Upon nucleation, which in the present simulation occurs rather promptly before turbulence has had time to noticeably wrinkle the flame surface, a large number of tiny soot particles populate a region just behind the \( Z = 0.21 \) iso-contour (rich-side). Large eddies wrinkle the flame, stretching the flame both towards and away from the fuel slab. As a result of local flow convection patterns, soot in regions of negative curvature is convected away from the fuel slab towards surrounding air, while soot in regions of positive curvature is moved into the fuel slab. In general, the differential diffusion of soot and gaseous species, coupled with flame wrinkling and flow convection is such that in regions of negative curvature, soot moves towards the flame, while in regions of positive curvature soot is moved away from the flame. The interplay of differential diffusion and flow convection has been statistically characterized in great detail by Lignell et al. (2007) in a numerical study very similar to the present work. As soot moves towards the flame (in a relative fashion), high temperatures and high surface reaction rates are responsible for strong surface growth, which quickly results in rapid soot volume fraction increase, producing aggregates with larger and fewer primary particles. Thus aggregates appear more sphere-like and more tightly packed. While aggregation and coagulation of particles and aggregates still occur, they are most likely second-order effects. Also, soot oxidation is prevalent in those regions. Conversely, pockets of nucleated particles moving away from the flame do not experience intense surface growth. Aggregates with a large number of small primary particles are formed as particle-particle collisions dominate the soot evolution process for those pockets of soot particles.

3.3. Soot nucleation, surface growth and oxidation

Figure 11 shows the rate of change of soot number density as well as soot volume fraction due to nucleation and surface based processes (growth and oxidation). Several features are worth mentioning. First, as expected, nucleation is very well localized in mixture fraction space and it closely follows the \( Z = 0.21 \) iso-contour. Second, soot volume fraction rates due to surface growth by HACA and oxidation rates are much higher that those due to nucleation by approximately one order of magnitude. Also, surface growth and soot oxidation rates are comparable in magnitude. Noticeably, soot surface growth and oxidation are both highest in a thin region characterized by \( Z_{st} \leq Z \leq 0.21 \). Also, they
are both localized in regions of negatively curved flame fronts, where aggregates characterized by larger and fewer primary particles are also present. Upon close inspection of the soot surface growth and soot oxidation patterns, one finds that, moving along a normal to the flame front (rich to lean) in a location of high (negative) curvature, soot surface growth peaks just before oxidation rate peaks. This arrangement offers an explanation for the mechanism of soot break-through, which seems to occur preferentially at locations of high (negative) curvature in the flame front. Only heavy (i.e. with high mass and volume) soot aggregates, which are formed just behind those cusps, can survive the oxidizing environment as they move (relative to the flame) closer to the flame reaction zone, characterized by a high concentration of hydroxyl radicals. Also, the process outlined above allows to conclude that soot aggregates breaking through the flame are characterized by large and few primary particles as opposed to the aggregates inside the fuel slab, which display large numbers of tiny primary particles.

### 3.4. The role of soot oxidation

A second numerical simulation neglecting soot oxidation reactions was performed to assess the importance of soot oxidation on soot dynamics. The results are presented in Figure 12. The first most striking feature lies in the peak soot volume fraction. If the effect of soot oxidation is neglected, soot volume fraction peaks at approximatively 2 ppm, while if soot oxidation is included, the maximum soot volume fraction is 0.06 ppm. Thus, soot oxidation accounts for a very large reduction in peak soot volume fraction for the present configuration and at time 15 ms. When soot volume fraction is compared on the same scale, one notices that the extent of soot break through is much inhibited by soot oxidation (compare the first and second columns). The third and fourth columns of Fig. 12 show the evolution of the primary particle diameter. As by design of the soot dynamics model used in the present study, mass loss due to oxidation occurs via
Figure 12. Soot volume fraction and primary particle diameter evolution for two simulations. The results from the base case simulation, including soot oxidation is shown on the first and third column, while a second simulation in which the effect of soot oxidation was neglected is shown on the second and fourth columns. Snapshots taken at 5, 10 and 15 ms (top to bottom). The two iso-contour lines are drawn at $Z = Z_{st} = 0.148$ and at $Z = 0.21$, the approximate location of peak nucleation rate in mixture fraction space.

a progressive shrinking of the primary particles’ mean diameter. Consequently, primary particles in the aggregates near the stoichiometric contour are considerably larger in the absence of oxidation. In the present simulation, primary particles which have not been oxidized are larger than those that have undergone oxidation by approximately a factor of five at 15 ms. However, the primary particle diameter of soot aggregates, which are located deep into the rich side ($Z > 0.21$) of the flame, shows little sensitivity to the treatment of oxidation as soot cannot be oxidized at such distance from the flame front. The comparative study discussed above allows to conclude that oxidation cannot be neglected in the present arrangement.

4. Acknowledgments
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Appendix A
The rate of change of moment $M_{x,y}$ due to oxidation is written as

$$\frac{dM_{x,y}}{dt} = K \sum_i [(V_i + \delta V)^x (S_i + \delta S)^y - V^x S^y] f(V_i, S_i) N_i$$  \hspace{1cm} (4.1)$$

Equation 4.4 must be simplified in order for the summation over all particle volumes and surfaces to be closed. Now define the number of primary particles in a soot aggregate of
volume $V$ and surface $S$ as

$$N_p = \frac{1}{36\pi} V^{-2} S^3 \quad (4.2)$$

It is assumed that during oxidation, the number of primary particles remains constant, while the size of the primary particle is reduced as consequence of the loss of carbon atoms. Such requirement places a constraint on $\delta S$ as a function of $V$, $\delta V$ and $S$ as follows

$$S + \delta S = S \left(1 + \frac{\delta V}{V}\right)^{2/3} \quad (4.3)$$

Once Equation (4.4) is substituted in Eq. (4.4) we obtain

$$\frac{dM_{x,y}}{dt} = K \sum_i \left[ \left(V_i + \delta V\right)^x S^y \left(1 + \frac{\delta V}{V}\right)^{2y/3} - V^x S^y \right] f(V_i, S_i) N_i \quad (4.4)$$

In order for Equation (4.4) to be expressed in terms of moments $M_{x,y}$, the functions on the right side of the summation must be expressed in polynomial form, thus requiring an approximation for $(1 + x)^\alpha$, where $x = \delta V/V$ and $\alpha$ is a non-integer, positive number. Since the volume of mass loss is much smaller than the volume of the soot particle/aggregate $|x| < 1$, a binomial series expansion can be used

$$(1 + x)^\alpha = 1 + \alpha x + \frac{1}{2} \alpha(\alpha - 1)x^2 + \frac{1}{6} \alpha(\alpha - 1)(\alpha - 2)x^3 + \text{h.o.t.} \quad (4.5)$$

In the course of this study it was found that a first order approximation (i.e. $1 + \alpha x$) results in inaccuracies that not only cause gross errors in the conservation of $N_p$, but also in convergence difficulties in the implicit integration process, which at times lead to integration failures and non-physical states of the system. Hence, for the present study, terms up to $x^3$ were kept in the binomial series expansion. The description of the oxidation process is particularly challenging because as the soot particle/aggregate volume $V$ tends towards zero (as consequence of the oxidation process), becoming comparable to the volume loss $\delta V$, the approximation in Eq. (4.5) is less and less accurate, resulting in the above mentioned difficulties in conserving $N_p$. In the present work we inhibit the treatment of oxidation as $\delta V/\langle V\rangle > 10^{-3}$, where $\langle V\rangle$ is the mean soot particle/aggregate volume. Such feature, while not ideal, was found to be necessary to obtain a robust and reliable treatment of oxidation.

REFERENCES


