Modelling inception, surface growth and agglomeration of silica particulates in a turbulent reactive jet flow

G. Neuber¹, O. Stein¹, A. Kronenburg¹,², M. J. Cleary²

¹Institute of Combustion Technology, University of Stuttgart, 70174 Stuttgart, Germany
²School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, New South Wales 2006, Australia

Silica particulates are increasingly used in a wide range of applications due to their unique electrical, optical and mechanical properties. They are frequently used for catalysis and as stabilising and binding agents as well as in the biotechnology sector. The production process of high-quality silica materials, however, requires a stringent control of the particle number, size and shape, but a desired high throughput and the resulting turbulent flow field render any computationally assisted design optimization of the production process difficult.

It has been shown that the precursor chemistry leading to particulate formation [1] as well as interparticulate interactions [2] are crucial for the final product properties and the current work presents a modelling strategy for the prediction of particulate size distributions (PSD) for particulate synthesis processes in turbulent reactive environments.

The temporal and spatial evolution of particulate matter within a carrier phase can be described by the population balance equation (PBE). In our method this equation is coupled with an Euler/Lagrange approach for the calculation of the reactive flow and particulate field, where we use a stochastic particle method for the prediction of the joint scalar filtered density function (FDF) of the reactive scalars and the PSD of the silica particulates. To avoid any ambiguity we strictly distinguish between “particulates”, which are the physical nano-particulates that are formed in the flame synthesis process, and “stochastic particles” which are computational elements for solving the FDF equation in a Lagrangian sense.

While traditional stochastic FDF methods require stochastic particle numbers of 20-50 per LES cell, we employ a so-called sparse-Lagrangian approach where far fewer stochastic particles are required (as low as 1 stochastic particle per 27 Eulerian cells [3]), thus the computational effort for the Lagrangian part can be reduced by around three orders of magnitude compared to traditional particle methods. The key ingredient in sparse modelling of the FDF is the use of a mixing model called multiple mapping conditioning (MMC) [3] to emulate the effects of molecular and turbulent diffusion.

Modelling the interaction between chemistry, turbulence and particulates accurately is challenging and the current work demonstrates the capability of a combined PBE-MMC-LES method to successfully model particulate inception, surface growth and agglomeration of fractal-like structures in a turbulent
reacting jet flow. The model is validated by comparison with measured signals of silica particulates obtained by elastic light scattering.

**Numerical Methods**

We apply a hybrid Euler/Lagrange method where an Eulerian scheme is used to solve the turbulent LES-filtered flow field and an additional mixture fraction equation. A stochastic Monte-Carlo method is used for the prediction of the spatial and temporal evolution of the joint scalar filtered density function (FDF) of the reactive scalars and the particulate size distribution of the silica particulates.

We use the nodal form of the sectional approach, where we discretise the size of particulates in volume space by a finite number of sections, such that the PBE gets following form:

\[
\frac{\partial N_k}{\partial t} + \frac{\partial}{\partial x_i} \left( N_k - D_k \frac{\partial N_k}{\partial x_i} \right) = \dot{s}_k .
\]  

(1)

Here, \( N_k \) is the particulate number density of size section \( k \), \( \dot{s}_k \) is the source term which accounts for particulate inception, surface growth and agglomeration and \( u_i \) and \( D_k \) denote the velocity and diffusion coefficient of size section \( k \), respectively. It must be noted that we apply a unity Lewis number assumption on all the transported scalars including the particulate size sections.

The stochastic Monte Carlo particles carry all the information of the scalars (e.g. species mass fractions, temperature, particle size distribution), such that that the transported scalar vector reads \( \Phi_a = (Y_1, ..., Y_m, T, N_1, ..., N_n) \). They represent an instantaneous solution and the averaged chemistry and synthesis source terms and the turbulence-chemistry-particulate interactions are therefore closed. Two stochastic differential equation have to be solved for a representative number of stochastic Monte Carlo particles,

\[
dx_i = A_i dt + b_{ij} d\omega_j \quad \text{and} \quad d\Phi_a = (W_a + S_a) dt .
\]  

(2)

\( (3) \)

The particle movement is given by Eq. (2), where \( A_i \) is the drift and \( b_{ij} \) is the diffusion coefficient [3], in which the index \( i \) is related to the direction in physical space. Here, \( d\omega_j \) is the independent Wiener process with zero mean and \( \sqrt{\Delta t} \) variance which models a random walk that represents the sub-grid fluctuations. Eq. (3) describes the time development of the transported scalars \( \Phi_a \). The term \( W_a \) represents the change of the transported scalars due to chemical reaction, particle inception, surface growth and agglomeration. The term \( S_a \) is the mixing operator which represents the conditional sub-filter scalar dissipation and needs closure. The mixing between the stochastic particles is modelled by the Multiple Mapping Conditioning (MMC) mixing model [3], which mixes pairs of stochastic particles dependent on their distance in both physical and reference space, which is taken to be the LES mixture fraction.
The particle pairs are selected by minimization of the square distance in physical space and a distance in reference space (here the mixture fraction), using

\[ d^2_{p,q} = \sum_{l=1}^{3} \left( \frac{a_{xi}^{p,q}}{r_m/\sqrt{3}} \right)^2 + \left( \frac{d_{l}^{p,q}}{f_m} \right)^2, \]  

where \( r_m \) and \( f_m \) are weighting parameters [3]. Hence, localness is preserved as mixing takes place only when they are close in both spaces.

To model the particulate synthesis we assume fractal-like shapes of the particulates and their form can therefore be described by the power law of agglomerates. The assumption of a fractal-like shape of the particulates seems valid given the transmission electron microscopy (TEM) image of aggregates extracted from the exhaust above the burner, see Fig. 1 (left). We see that the aggregates are built from a large number of primary particles and that neck-formation is not present, thus coalescence processes are negligible. The inception rate of primary particulates is given by the chemical formation rate of the precursor species, which is described by the finite rate chemistry model. The surface growth is modelled as an integral growth and for small particles the growth in size space is based on the free-molecular collision kernel. For larger particles the surface growth is mainly determined by the diffusion of the depositing species towards the particles' surface and a diffusion based model is therefore applied. The harmonic mean of both formulations ensures a correct blending between both approaches. The agglomeration process is described by the Fuchs-Sutugin collision kernel for fractals [4]. The nodal form of the sectional approach conserves mass and primary particle number but introduces a slight broadening of the PSD as outlined in [5].

**Numerical Setup**

The standard stochastic particle classes in OpenFOAM were extended to account for the requirements of an PBE-LES-MMC simulation [6]. The present setup is a turbulent nitrogen jet \((D = 5 \text{ mm}, Re_p = 10 000, T_j = 300 \text{ K})\) laden with 3100 ppm silane \((\text{SiH}_4)\). As depicted in Fig. 1 (right) the cold jet mixes with an established vitiated co-flow using the hot products of a hydrogen-air flame with an equivalence ratio of 0.4 burning at 1447 K with a velocity of \( U_c = 5 \text{ m/s} \). The computational mesh comprises of 1.5 million cells where the jet diameter is resolved with 39 cells. In this study a finite-rate chemistry reaction model is used, containing 67 species and 263 reactions for the precursor chemistry. To minimize numerical diffusion a central difference scheme was used for the filtered velocity conservation equation. All other conservation equations were treated with the total variation diminishing (TVD) scheme. For the sub-grid stresses a sigma-LES-model was used in the simulations. For our PBE-MMC-LES simulations we used about 230 000 stochastic particles for the whole flow domain. The number of particles corresponds to 1 particles per 6.5 LES cells, which lay two orders below common values for dense PDF-LES simulations.
Results and Discussion

Before we assess the capability of our PBE-MMC-LES approach to model particle synthesis the general setup needs to be validated. Therefore we firstly compare results of a reference case without any silane doping of the central jet and therefore no particulate formation in the flow field. In Fig. 2 (left) contour plots of the elastic light scattering ELS signal at a cross section of the jet configuration is shown. In the absence of particulate matter within the carrier phase the ELS signal is a function of species composition and temperature only. For the silane free case predicted and measured signals are normalised with their respective value in the co-flow and the agreement is very good allowing to conclude that our flow field is well predicted.

Fig. 2 (right) compares the measured and predicted ELS signal for the case with 3100 ppm silane doping. Now, the ELS signal is a superposition of a signal as function of composition and temperature as well as signal originating from the particulates as function of particle number and size [7]. The predicted ELS signal is therefore normalised as follows: As for the reference case, the gaseous signal is normalised with the respective value of the coflow. The signal which is emitted by particulate matter is normalised to match the maximum value of the measured counterpart. Then both signals are added. We can see that the agreement is good and the position of the peak value is well matched.
However, for the silane laden case the increase in the predicted ELS signal within the shear layer demonstrates that particulates are formed somewhat too quickly. The experimental data suggests that particulate number and growth are insignificant so far upstream and that larger particulates are predominantly formed at centerline position. For both, the experiment and simulation, the ELS signal starts to decrease at around $z/D = 20$ and this is well predicted by our model, although, the predicted ELS signal is broader than the measured signal and tends to decrease more slowly. We may hypothesize, that the agglomeration process is slightly under-predicted because a unity Lewis number assumption is employed to all discretised size sections which results in an over-prediction of diffusion and a higher particulate number density would result in larger particles at centerline position.

**Summary**

The sparse-Lagrangian PBE-MMC-LES method has successfully been used to simulate silica particulate formation in a turbulent reactive flow. In comparison to conventional stochastic particle methods with more than 20-50 particles per LES cell, the savings in computational cost are substantial. A fairly good match between measured and predicted signals is obtained, but some uncertainties persists, which can mainly be attributed to uncertainties regarding a unity Lewis number assumption. In spite of these discrepancies, the present study symbolises a major step towards the development of validated computational tools for the prediction of nano-particulate flame synthesis. It should be noted that the current study is one of the very few joint computational and experimental studies that address the issue
of nano-particulate synthesis under the influence of turbulence. Compared to other existing studies including particulate synthesis in turbulent reactive systems – such as soot formation - the predictive capability of PBE-MMC-LES is quite good.

References


