Large eddy simulations of nanoparticle synthesis from flame spray pyrolysis

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Abstract

Large eddy simulations of the nanoparticle synthesis from flame spray pyrolysis are presented. A standard reactor is investigated, with ethanol/hexamethyldisiloxane (HMDSO) mixture as spray/precursor composition and oxygen as dispersion gas for the production of silica nanoparticles. Spray evaporation, ignition and stabilisation of the flame are achieved by a premixed methane/oxygen pilot flame. The gas, spray and nanoparticle phases are modelled with Eulerian, Lagrangian and Eulerian approaches, respectively. A modified tabulated chemistry model, adapted from the premixed flamelet generated manifold approach (PFGM) with artificial flame thickening (ATF) is proposed, tested and applied for the system. The control variables are the element mass fractions of hydrogen and carbon together with a joint progress variable. The population balance equation of the nanoparticles is modelled in terms of number, volume and surface area concentration, its subfilter distribution is modelled with a delta function. The combustion of HMDSO and formation of silica particle monomers is described by a two-step global mechanism. The nucleation source term is tabulated as a function of the control variables. The submodels for spray and combustion are validated separately to compensate for the shortage in detailed experimental data for nanoparticle spray flames. Subsequently, simulation results for the particles are presented and discussed, in particular the polydisperse particle size distributions resulting from turbulence.

Keywords: Flame spray pyrolysis, nanoparticle synthesis, silica, large eddy simulation, premixed flamelet generated manifold

1. Introduction

Flame spray pyrolysis (FSP) for the synthesis of ceramic powders (e.g. SiO₂, TiO₂ or Al₂O₃) permits a simple precursor injection into a hot flame and enables a rapid quenching of the aerosol formation [1]. The synthesis of silica nanoparticles from FSP has been the focus of many experimental and computational studies [1–4], but the promising large eddy simulation (LES) approach has never been attempted for such systems before.

1.1. Nanoparticles from flame spray pyrolysis

In self sustaining FSP processes, a liquid precursor is solved in an organic liquid fuel. This mixture is fed into a hot environment, which is provided by a secondary heat source. Oxygen or
air are used as dispersion and sheath gas for the stabilisation of the spray flame [1]. Common precursors for the gas-phase synthesis of silica include Silanes, cyclic and linear siloxanes and tetraethyl orthosilicate (TEOS), depending on the required properties [1, 5].

Solvents like ethanol, methanol or isopropanol are used, which also affect the particle properties. Mädler et al. [1] investigated the influence of the fuel and oxidizer composition and indicated the importance of the evaporation rate and total energy content of the precursor on the powder characteristics. Studies by Engel et al. [3] and Kilian et al. [4] investigated a modified version of the aforementioned spray burner, using a HMDSO/ethanol mixture, O₂ as dispersion and sheath gas and a near stoichiometric CH₄/O₂ mixture for the pilot flame. Laser-sheet based Mie scatter imaging, 2D-chemiluminescence imaging and coherent anti-Stokes Raman spectroscopy were applied to obtain the spatial distributions of OH⁺, CH⁺ and SiO⁺ radicals, the combustion and nucleation zones, as well as the temperature. In this work, HMDSO has been chosen as chlorine-free silica precursor, for which we expect more in situ data from future reactor experiments.

The FSP process can be divided into three main zones [6]: the spray is atomised in the shear layer between the liquid and surrounding environment and evaporated due to the heat of the pilot flame in zone A (Fig. 1). The turbulent flow enhances the mixing of the fuel/precursor vapor with the oxidizer and generates a flammable mixture that is burned in zone B, ignited by the pilot flame. The precursor is decomposed into intermediate species, which react and form SiO₂ molecules that nucleate in zone C. The nuclei coagulate and particles grow, followed by agglomeration and sintering. The modelling of this three zones is described in section 3. These process steps may happen simultaneously at one instant or place inside the flame, as a result of turbulence. As the methods for the experimental analysis of these processes in turbulent flames are limited and costly, deeper insights are likely to become available from detailed simulations by LES or direct numerical simulation (DNS). It should be noted, that the wide range of scales and the complexities of turbulence, aerosol dynamics and chemical kinetics are such that complete simulations with detailed models are not feasible for years. Any simulation must therefor apply a suitable set of simplifying assumptions and models and should be validated against suitable experiments.

1.2. Numerical studies of flame-made nanoparticles

The evolution of the nanoparticles from the gas phase for cases of practical interest is usually described by the general dynamics equation (GDE) for the continuous distribution function [7]. The GDE incorporates nucleation, growth, coagulation and coalescence as well as convection and diffusion and describes the particle size distribution in space and time. Several methods for the solution of the GDE have been proposed: The most accurate discrete models [8] introduce an additional differential equation (DE) for each discrete size or particle property. Sectional models [9–11] cluster particles of different sizes in classes and introduce additional DE’s for the sections. Combinations of the discrete and sectional models have also been proposed [12]. The method of moments (MOM) and modified MOM models (e.g. QMOM, DQMOM [13–16]) assume that the size distribution can be approximated with a presumed distribution function, i.e. a self-preserving [17] or as log-normal function [18], and solves for the moments of the GDE. Kruis et al. [19] proposed a simple model for the GDE, by introducing transport equations for the number, volume and surface area concentration of the aggregate particles. Coagulation and sintering are described separately in the equations for the number and surface area concentration. The morphology of the particles is considered by replacing the solid sphere diameter with the collision diameter in the coagulation kernel. Sintering is described with an empirical model that correlates the sintering time to the primary particle diameter and temperature. In the present work, the modified Kruis-model with nucleation source term is applied [20, 21]. A detailed overview on models for the GDE is given by Tsantilis [18].

Numerical studies on the evolution of nanoparticles from flame synthesis are mainly limited to Reynolds averaged Navier-Stokes (RANS) simulations. However, in recent years LES studies of TiO₂ synthesis have been carried out by Raman et al. [22] or Fox et al. [23], who applied a QMOM for the solution of the GDE and investigated the influence of the chemical mechanism
on nucleation. Sung et al. [24] extended the model to describe the evolution of the particles with a bivariate number density function. Related work has been published in the sooting flame community, e.g. by Bisetti et al. [25] or Pitsch and Müller [26].

The combination of the LES approach and the monodisperse model was chosen as a path to more accurate and detailed results that consider (at least) the major effects of turbulence, as a step forward from our previous work with RANS [6].

1.3. Particle distributions in turbulent flows

Moving to a turbulent flow problem, one must first discuss what the particle population actually means. Mathematically, a probability density function for the particle properties exists at every point and instant in a turbulent flame. The probability density can be interpreted as the expectation of the particle population within a sampling volume at this point and time, where the sampling volume must be smaller than the smallest scalar scale (Batchelor scale). This Batchelor scale can be orders of magnitudes smaller than the Kolmogorov scale of turbulence when nanoparticles are concerned. We will refer to this population as the local instantaneous population (LIP).

The LIP differs from what one is usually interested in, the local time averaged population, which may be the result of sampling at a point in an experiment. It is possible that a wide local time averaged population results from many local monodispers LIP’s as a result of turbulence; or as a result of a wide LIP resulting from the agglomeration of polydisperse particles. Existing particle diagnostic techniques provide a time averaged local population, which makes it hard to determine the cause for a wide population. We present the first LES of the nanoparticle synthesis from FSP focusing on the effect of turbulence, i.e. many different LIPs are considered in the averaging. Each LIP, in turn, is described by the Kruis-model [19].

2. Setup of the experiments by Kilian et al. [4]

The investigated spray burner (Tethis S.p.A., Fig. 1) was used by many research groups before (e.g. [1–6, 27–29]). The burner consists of a spray nozzle with a concentric annular gap for the dispersion gas, an annular gap for the pilot flame and a sintered matrix for the sheath gas supply. The capillary surmounts the other outlets by 0.5 mm to guarantee a constant spray angle independent of the liquid flow rate [1]. A solution of 5 ml/min ethanol with 0.5 mol/l HMDSO is fed through the capillary, dispersed by an oxygen stream with 51/min. The premixed methane/oxygen pilot with flow rates of 1.5 and 3 l/min is surrounded by oxygen sheath gas of 10 l/min (4). Mädler et al. [1] showed for a cold ethanol spray and a given inner nozzle gap that the median droplet mass diameter depends on the oxidant flow rate. The 3-D numerical

![Figure 1: Sketch of the burner with inlet (1) for the fuel/precursor, (2) dispersion gas, (3) pilot and (4) the sheath gas supply with the zones A spray, B turbulent combustion and C particle synthesis.](image)
domain starts 3 mm downstream of the jet-nozzle exit, as primary- and secondary break-up are not considered in the simulations, as shown in Fig. 1 and spans a region of 40 x 40 x 100 mm. A Rosin-Rammler distribution is assumed to describe the droplet diameters, which are used as initial and inlet conditions in the simulations (with a median diameter of ∼8 µm). It is known that the burner is hard to adjust, so that a perfectly straight flame which is not leaning to one side is hard to achieve. As the simulated flame burns perfectly straight, we also provide results 5 mm off the centreline to have additional data for comparison to the experiments.

3. Modelling Approach

The Favre filtered conservation equations for mass and momentum are solved accounting for spray evaporation as outlined below.

\[
\frac{\partial \rho}{\partial t} + \sum \sum \frac{\partial \tilde{u}_j}{\partial x_j} = \Gamma_\rho \tag{1}
\]

\[
\frac{\partial \rho \tilde{u}_i}{\partial t} + \sum \sum \frac{\partial \rho \tilde{u}_j \tilde{u}_i}{\partial x_j} = -\frac{\partial p}{\partial x_i} + \sum \sum \frac{\tau_{ij}}{\partial x_j} + \sum \sum \frac{\tau_{ij}^{sgs}}{\partial x_j} + M_{di} \tag{2}
\]

In Eqs. (1) and (2), \( \tilde{u}_j, \rho, p, \tau_{ij}\) and \( \tau_{ij}^{sgs}\) denote the Favre filtered velocity, the filtered density, pressure and the viscous stress tensor, respectively. An eddy viscosity approach is used to model the residual stresses \( \tau_{ij}^{sgs}\), where the turbulent viscosity \( \mu_t\) is determined with our implementation [30] of Nicoud’s sigma model [31]. The source terms \( \Gamma_\rho \) and \( M_{di} \) account for the exchange of mass and momentum with the spray and are evaluated for each droplet within a LES filter width and are applied to the Euler and Lagrangian phases through two way coupling based on trilinear interpolation.

3.1. Spray submodel - zone A

The spray is described in a Lagrangian framework [32], each physical droplet is represented by one numerical particle \( d \) for which a set of differential equations is solved. Motion and evolution of the droplet mass and temperature (assuming equilibrium conditions [33, 34]) are determined from Eqs. (3-6), where \( x_d, \tilde{u}_d, a_d, m_d \) and \( T_d \) are the position, velocity, acceleration, mass and temperature of the droplets, respectively

\[
\frac{dx_d}{dt} = \tilde{u}_d \tag{3}
\]

\[
\frac{du_d}{dt} = a_d = \frac{f_1}{\tau_d} (\tilde{u}_i - u_d, ) + \left( 1 - \frac{\rho}{\rho_d} \right) g_i \tag{4}
\]

\[
\frac{dm_d}{dt} = \frac{Sh}{3 Sc} \tau_d m_d \ln (1 + B_m) \tag{5}
\]

\[
\frac{dT_d}{dt} = \frac{Nu c_p}{3 Pr c_{pl}} \left( T_g - T_d \right) \ln (1 + B_g) + \frac{m_d L_v}{m_d c_{pl}} \tag{6}
\]

Drag, gravity and buoyancy affect the drop acceleration with \( \tau_d, f_1, \rho_d \) and \( g \), the relaxation time, correction factor for the drop drag coefficient, density and the gravitational acceleration, respectively. The specific heat at constant pressure of the gas \( c_p \) and liquid \( c_{pl} \) and the latent heat of vaporization \( L_v \) are used in Eq. 6 to determine the change of the droplet temperature. The droplet diameter, particle Reynolds number and gas viscosity \( (d_d, Re_d, \mu) \) are used to determine \( \tau_d \) and \( f_1 \).

\[
\tau_d = \rho_d \frac{d_d^2}{18 \mu} \quad \text{and} \quad f_1 = 1 + \frac{3}{20} Re_d^{0.687} \tag{7}
\]
The changes of the droplet mass and temperature are determined with the Schmidt, Prandtl, Sherwood, Nusselt and the Spalding numbers for mass and heat transfer $B_m = (Y^p - Y^F_p)/(1 - Y^F_p)$, $B_h = c_p(T - T_0)/L_v$. Two way coupling of the gas and liquid phase values is achieved by trilinear interpolation.

### 3.2. Combustion submodel - zone B

The premixed flamelet generated manifold approach (PFGM) [35, 36] is used, coupled with the artificial thickened flame (ATF) method [37]. Our PFGM/ATF implementation [38] for spray combustion [32] is extended to account for two fuel and one oxidizer species. The composition of the gas mixture is described by the element mass fractions of carbon and hydrogen ($Z_C$ and $Z_H$) according to Eq. (8). The method works for fuels with different C/H ratios.

$$Z_{\alpha} = \sum_{i=1}^{N_{\alpha}} \frac{W_{\alpha,i}}{W_i} Y_i$$

The atomic or molecular weights of element $\alpha$ or molecule $i$ are given by $W_{\alpha}$ and $W_i$, respectively, $Y_i$ is the mass fraction of molecule $i$, and $a_{\alpha,i}$ denotes the number of atoms $\alpha$ in molecule $i$. Assuming unity Lewis number [39], the filtered conservation equation for $Z_{\alpha}$ reads:

$$\frac{\partial \tilde{Z}_{\alpha}}{\partial t} + \frac{\partial \tilde{u}_i \tilde{Z}_{\alpha}}{\partial x_i} = \frac{\partial}{\partial x_i} \left( \rho \frac{\partial \tilde{Z}_{\alpha}}{\partial x_i} \right) + \Gamma_{\alpha}$$

In Eq. (9), $D_e = D + D_t$ is the sum of the molecular and turbulent diffusivity, $D_i$ is calculated from the turbulent viscosity and turbulent Schmidt number $D_t = \mu_t/Sc_t$. A joint progress variable $Y_P = Y_{CO_2} + Y_{CO}$ describes the progress of combustion.

$$\frac{\partial \tilde{Y}_P}{\partial t} + \frac{\partial \tilde{u}_i \tilde{Y}_P}{\partial x_i} =$$

$$\frac{\partial}{\partial x_i} \left( FED + (1 - \Omega) \frac{\mu_t}{Sc_t} \frac{\partial \tilde{Y}_P}{\partial x_i} \right) + \frac{E}{F} \omega_c + \dot{\omega}_E$$

In Eq. (10), $F$, $E$, $\Omega$ and $\dot{\omega}_c$ are the thickening factor, efficiency function, flame sensor and chemical source term [38], respectively. The thermochemical quantities (e.g. $\rho$, $\omega_c$) are determined a priori by solving a set of 1D premixed flames with Cantera [40] - by varying the initial composition of the flamelets as functions of $Z_H$ and $Z_C$ in equidistant steps. The resulting quantities are interpolated from physical space to element mass fraction and progress variable space and stored in the 3D look-up table as functions of $Z_C$, $Z_H$, and the normalised progress variable $Y_{PN}$.

### 3.3. Population balance submodel - zone C

The GDE for aerosols [7] is described with the monodisperse model [19, 20], which describes the evolution of the number concentration, size and morphology of the particles through coagulation and coalescence. A narrow size distribution for the silica primary particles is assumed, as found by Boldridge [41] for aggregates, as a result of sintering at high temperatures. It may be expected that the particle size distribution attains the self preserving size distribution by coagulation [42], implied by the monodisperse model. Gröhn et al. [43] justified the application of the monodisperse model with the aforementioned assumptions in their RANS simulations for the SiO$_2$ synthesis from a turbulent methane/oxygen diffusion flame with a HMDSO precursor [43] and in the FSP process of ZrO$_2$ [28].

In the LES context, a particle size distribution can be derived from sampling in time at one point over monosized particles which have been exposed to different gas histories due to turbulence. Compared to RANS, the LES enables a more accurate description of the turbulent flow field and hence of the mixing and resulting thermochemical properties [26].
The Favre filtered, closure modelled transport equations for the particle number $\tilde{N}$, surface area $A$ and volume $V$ concentration are outlined below. The assumption of a narrow size distribution is only needed on the sub-filter scales, but not for the resolved scales.

\[
\frac{\partial \tilde{N}}{\partial t} + \frac{\partial \tilde{N}}{\partial x_j} (\tilde{u}_j - D_i \frac{\partial \tilde{N}}{\partial x_i}) = \frac{E}{F} \tilde{p} \tilde{I} - \frac{1}{2} \beta \tilde{p} \tilde{N}^2 
\]  
(11)

\[
\frac{\partial \tilde{A}}{\partial t} + \frac{\partial \tilde{A}}{\partial x_j} (\tilde{u}_j - D_i \frac{\partial \tilde{A}}{\partial x_i}) = \frac{E}{F} \tilde{p} \tilde{I} \tilde{a}_0 - \frac{\tilde{p} (A - A_i)}{\tau} 
\]  
(12)

\[
\frac{\partial \tilde{V}}{\partial t} + \frac{\partial \tilde{V}}{\partial x_j} (\tilde{u}_j - D_i \frac{\partial \tilde{V}}{\partial x_i}) = \frac{E}{F} \tilde{p} \tilde{I} \tilde{v}_0 
\]  
(13)

The particle diffusion is neglected due to their low diffusivity [23, 28, 43], the turbulent diffusivity $D_t$ is calculated as described above. The nucleation source term $I$ describes the birth of particle monomers. It is assumed that particle monomers are represented by silica molecules [44]. A reduced reaction mechanism for the oxidation of HMDSO with 3 species and 2 reactions is solved together with a reduced mechanism for ethanol, originating from Marinovs mechanism [45]. The mechanism was adapted to reproduce the SiO LIF measurements by Feroughi et al. [46] and is outlined below (in CGS units).

\[
C_3H_8Si_2O + OH \rightarrow 2 SiO + 6CH_3 + H 
\]  
(14)

with $6.00 \times 10^{12} \ 0.46 \ 15000$

\[
SiO + H_2O \rightarrow SiO_2 + H_2 
\]  
(15)

with $8.50 \times 10^10 \ 0.5650$

The source term $I$ is tabulated as a function of the control variables $I = f (Zc, ZH, Yp)$, and is artificially thickened to be consistent with $Yp$. In Eqs. (13 and 12), $v_0$ and $a_0$ are the monomer volume and surface, respectively. The coagulation frequency $\beta$ is calculated with Eq. (16), the solid sphere diameter is replaced with the collision diameter $d_c$ to account for the fractal shape of the particles [19].

\[
\beta = 4\pi d_c D \left[ \frac{1}{d_c + \sqrt{2}c} + \frac{\sqrt{2}c}{d_c} \right]^{1/2} 
\]  
(16)

\[
g = \left[ (d_c + L)^3 - (d_c^2 + L^2) \right]^{1/2} / [3Ld_c] - d_c 
\]  
(17)

In Eqs. (16) and (17), $D = (k_b T)/(3\pi \mu d_c)$, $c = \sqrt{8k_b T/(\pi \rho_b)}$, $k_b$, $T$, $\rho_b$ and $L = (8D)/(\pi c)$ are the particle diffusion, particle velocity, Boltzmann constant, gas temperature, bulk density and mean free path of the particles, respectively. The characteristic sintering time $\tau$ for silica and the surface area of the completely fused particles $A_S$ in Eq. (12) are calculated as outlined below [10, 21].

\[
\tau = 6.5 \times 10^{-17} d_p \exp \left( \frac{83000}{T} \left( 1 - \frac{d_{p,\min}}{d_p} \right) \right) 
\]  
(18)

\[
A_S = \left( \frac{V}{Nv_0} \right) \frac{1}{N \tilde{a}_0} 
\]  
(19)

The primary, aggregate and collision diameters ($d_p$, $d_a$ and $d_c$) are obtained from Eqs. (20), with the number of primary particles $n_p = (6V)/(\pi N d_p^3)$ and a constant value of 1.8 for the fractal dimension $d_f$, as proposed by Tsantilis et al. [21].

\[
d_p = \frac{6V}{A}, \quad d_a = \left( \frac{6V}{\pi N} \right)^{1/3} \quad \text{and} \quad d_c = d_p n_p^{1/3} 
\]  
(20)
4. Testing

The complex global model must be validated, but the experimental investigations of flame spray pyrolysis processes do not provide enough data for it. This is different to the situation in the turbulent flame community around the TNF [47] workshop that provides complete and detailed measurements for one identical setup including the PDF’s of velocity, composition and temperature [48–50]. The present case of flame spray pyrolysis is more complicated than these TNF-flames, which would necessitate even further measurements for model validation and development. Until such are available, we try to achieve a sufficient validation for the individual submodels as outlined below.

We would like to urge the nanoparticle flame synthesis community to work on the creation of one complete experimental dataset to enable a meaningful model validation or falsification.

The presented study was performed with the LES in-house code PsiPhi, which was applied, tested and validated with many LES of non-premixed, premixed and partially premixed flames, for gaseous, solid or liquid fuels [32, 38, 51–54].

A detailed validation of the spray submodel, as used in zone A, requires radial profiles of the droplet distribution, liquid mass or volume flow rate (evaporation rates), velocities and their fluctuations. Masri et al. [55] provided a detailed data set for ethanol spray flames with different equivalence ratios and turbulence levels, by LDV/PDA at different radial positions. The spray modelling in PsiPhi was validated with this dataset for different equivalence ratios and Reynolds numbers [32].

To show the effectiveness of the multi-mixture fraction PFGM model for zone B, it is applied to an artificial 2D test-case, where O₂, H₂ streams and a premixed CH₄/O₂ stream are fed through three inlets with velocities of 5m/s - the geometry and mass fractions are shown together with the velocities in Fig. 2. The investigated test case is independent from the FSP reactor, and is only used for sub-model validation. The results obtained from the PFGM model are compared against the reference data from a direct simulation with finite rate chemistry [56] using Openfoam. The reduced mechanism DRM22 [57] is used in both. Figure 2 shows the satisfactory agreement between the PFGM/ATF combustion model and the finite rate chemistry.

Figure 2: Top: contour plots of the velocity \( u_x \); dimensions and mass fractions. Bottom: profiles of the temperature, axial velocity and mass fractions of CH₄, OH and H₂O at two axial locations (○ finite rate chemistry, - PFGM) for the independent test case.
5. Results

5.1. Spray combustion - zones A and B

As shown in Fig. 3, the spray evaporation and combustion in zones A and B overlap and interact between 5 and 25 mm above the burner. Figure 3a illustrates where the droplets evaporate due to the heat from the pilot flame and the high slip velocities between the droplet and the environment with a maximum mass release at the outer radius of the spray jet. The major amount of the liquid is evaporated upstream of 15 mm, but drops with larger initial mass and droplets in the core of the jet evaporate further downstream into the burnt gases 3a. Spray evaporation was observed to be completely finished at 25 mm height above burner (HAB). The vapor increases the element mass fractions $Z_H$ and $Z_C$ as illustrated for $Z_C$ in Fig. 3b. The progress variable $Y_P$ (Fig. 3c) illustrates the flame front of the spray flame at 5 mm. The intermediate species SiO (Fig. 3d) is mainly predicted between 5 and 20 mm, which is in good agreement with the SiO$^*$ measurements by Kilian et al. [4]. An axial shift of SiO compared to the evaporated particle mass is observed since the evaporated mass is added to the unburnt mixture and subsequently burnt.

![Figure 3: Snapshots of (a) evaporated mass $dm_d$, the Favre filtered (b) element mass fraction $Z_C$, (c) progress variable $Y_P$, (d) mass fraction $Y_{SiO}$, (e) the nucleation source term $I$.](image)

![Figure 4: Axial profiles of the (a) temperature and SiO/SiO$_2$ mass fractions, (b) particle number concentration and (c) particle surface area concentration and volume concentration at the centerline (solid) and at a radius of 5 mm (dashed), obtained from the simulations with (labels with $C_s$) and without slip correction factor.](image)
Figure 4a shows a high mean temperature up to 3000 K in the premixed CH4/O2 pilot. Furthermore, a quick increase of the temperature in the spray flame at 5 mm is observed. The SiO mass fraction and its conversion to SiO2 are shown in Fig. 4a. The decrease of YSiO2 is attributed to the spreading of the jet.

Figure 5: Snapshots of the Favre filtered (a) particle number $N$, (b) surface area $A$ and (c) volume concentration $V$, (d) primary particle diameter $d_p$, (e) number of primary particles $n_p$, (f) aggregate diameter $d_a$.

5.2. Particle synthesis - zone C

The particle number concentration $N$ as shown in Fig. 4b and 5a, increases first due to the birth of monomer particles, and decreases afterwards as a result of coagulation. The surface area $A$ shown in Fig. 4c and 5b and volume concentration $V$ (Fig. 4c and 5c) rise sharply at 5 – 8 mm due to nucleation (Fig. 3e). Subsequent turbulent mixing with the environment leads to a slow reduction of the mean volume concentration $V$, as illustrated in Fig. 4c. The surface area concentration $A$ decreases quickly because of sintering in the high temperature region, the curve flattens out with decreasing temperature.

Figure 5 illustrates the influence of turbulence downstream of 30 mm, where the particle laden flow is mixed with the environment. The model predicts that the primary particle diameter as illustrated in Fig. 5d starts to grow at 15 – 25 mm, where the number of primary particles (Fig. 5e) is at a maximum and starts to decrease. This indicates the high impact of sintering by a reduction of $A$ at almost constant $V$.

As shown in Fig. 6, a rather good agreement between the particles primary and aggregate diameter is observed for large HAB, which results from the fast sintering of the aggregates to larger primary particles. In contrast to the simulations, Kilian et al. [4] observed larger aggregates predominantly.
5.3. Sample averaged particle size distribution

Figure 6 illustrates size distributions (based on particle numbers) for the particle primary diameter (a), aggregate diameter (b) and collision diameter (c) obtained by the sampling over 256 instants within 0.01 s, which corresponds to 5-10 flow-through times with respect to the mean velocities at the sampling points. The sampling-volume is one filter volume with (0.25mm)$^3$.

The sampled size distribution of the primary diameter on the centerline, as shown in Fig. 6a (dark bars), shows a narrow distribution of small particles up to 40 mm due to nucleation with some first influence of sintering with increasing primary diameter. At this location the aggregate and collision diameters (Fig. 6b and 6c) have a bimodal size distribution, indicating a large number of nucleated particles with small diameters and larger fractal shaped particles with larger diameters. The larger particles result from coagulation without sintering at this point. This bimodal shape is the result of particles which have been exposed to different histories due to turbulence. Further downstream, the distribution of the primary particles diameter is bimodal first, and the peak value is shifted towards larger values due to sintering. (The mean value changes into the same direction.) The peak value of the aggregate diameter and collision diameters are also shifted towards larger values. At 80 mm above the burner, the primary and aggregate particles still grow, and their size distributions converge towards each other. Furthermore, the distribution of the collision diameter highlights the location of nucleation, coagulation and sintering. A local maximum collision diameter is found at 40 mm, where nucleation seems to be finished and sintering gets dominant. Generally, turbulent mixing has increased at downstream locations, leading to a broader size distribution of the primary and aggregate particle diameters.

6. Conclusions

A large eddy simulation of the nanoparticle synthesis from flame spray pyrolysis was presented. The width of the sampled size distribution of the primary, aggregate and collision diameters was shown to be narrow first and increase especially at far downstream locations with
increasing impact of turbulent mixing. In contrast to RANS simulations, the size distribution is the direct result of the time-resolved flow field, without applying further models such as presumed distribution functions.

The proposed approach is helpful in understanding the interaction between the spray evaporation, gas phase combustion and particle synthesis. Furthermore, the simulations with the global approach can be used to optimize a reactor such that the size distribution can become narrower by optimizing the turbulent flow field. However, there is a case for better modelling in the future, and a strong need for more complete, detailed and repeated experimental reference data to enable the development, validation or falsification of existing or future models.

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