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Effect of nozzle geometry and processing parameters on the formation of nanoparticles using FSP

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ABSTRACT

Two numerical models were developed to simulate the sauter mean diameter (SMD) of the droplets during atomization and the growth of particles inside the flame by coagulation and sintering. These models were linked to CFD to simulate flame spray pyrolysis (FSP) process. The effects of reactor geometries and processing parameters on the temperature and velocity profiles, droplet evaporation and particle growth were predicted using the validated computation models. The results show that increasing the oxidant gap size (from 0.1 mm to 0.5 mm) by keeping the dispersion gas pressure drop constant at 1 bar (transonic regime ∼310–315 m/s) across the nozzle tip increased the gas to liquid mass ratio (GLMR) by a factor of 6. This reduced the flame height and lowered the residence time of the particles in the high temperature zone of the flame, thus, decreased the sintering rate and the growth of nanoparticles. The results also showed that decreasing the oxygen content of the dispersion gas helped to decrease the peak temperature of the flame and reduced the particle size. The simulation results can be used for the FSP equipment design and process optimization.

Keywords: FSP; CFD; Nanoparticles; Aerosol; Particle formation; Agglomeration

1. Introduction

One of the most important problems for the extensive usage of nanoparticles in industry is the complexity in producing the particles with high chemical purity and desirable phase and morphology. This challenge is increased in large production when it is necessary to keep the required particle size and low cost. Flame synthesis (Ulrich, 1984; Pratsinis, 1998) was established as a process for making nanoparticles in one step with low cost. Two flame synthesis methods have been developed to produce nanoparticles: (a) vapor-fed flame synthesis (VFS), (Akhtar et al., 1991; Johannessen et al., 2000, 2001; Pratsinis and Spicer, 1998) and (b) flame spray pyrolysis (FSP), (Mädler et al., 2002; Mädler and Pratsinis, 2002; Mueller et al., 2003, 2004a,b; Heine and Pratsinis, 2005; Heine et al., 2006).

In the VFS process, particles are formed from individual atoms or molecules in the gas phase. The formation of particles begins when the precursor gas is going through a chemical reaction. In this method high temperatures are needed to evaporate the precursor and provide the condition for the chemical reaction. In the process, the temperature of the flame varies from 1200 K to 3300 K depends on the type of the oxidizer and the operation conditions. At the early stage, the partic1es are formed by gas-phase nucleation and grow by coagulation (particles collide with each other and stick to form agglomerates) and later they coalesce into larger particles. The shape of the final product is determined by the rates of coalescence and coagulation. If the rate of sintering is faster than that of coagulation, the particles are spherical otherwise irregular agglomerate shape is developed (Kruis et al., 1993).

In FSP (as depicted in Fig. 1), the solution (liquid precursor and fuel) is atomized by using an air-assisted nozzle to form the droplets. The droplets are then evaporated and ignited by using a small pilot flame (i.e. positioned around the nozzle tip) to form solid nanoparticles like VFS after combustion. The FSP became one of the best aerosol synthesis techniques since both organic and inorganic precursors can be used to produce nanoparticles and it has the advantage

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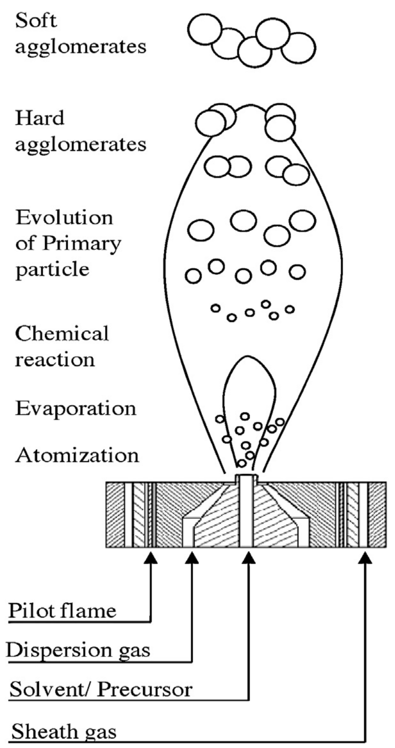

Fig. 1 – Schematic of FSP apparatus.

of dissolving precursor directly in the fuel (Mädler et al., 2002).

Large number of studies has been carried out to investigate the effect of FSP parameters on particle purity, phase and morphology. Mädler et al. (2002) investigated the effect of oxidants and mixture compositions on the size of silica primary particles using hexamethyldisiloxane (HMDSO) dissolved in ethanol, iso-octane or methanol. Mädler and Pratsinis (2002) investigated the synthesis of Bi_2O_3 by FSP using the same reactor. Mueller et al. (2003, 2004a,b) studied the high production of silica and zirconia. They developed a simple monodisperse model for the coagulation and sintering of zirconia with 10% accuracy in the prediction of the primary and agglomerate particle size by neglecting the effect of particle polydispersity and droplet evaporation. Heine and Pratsinis (2005) incorporated the effect of droplet evaporation by developing a detailed droplet-particle population balance model.

These studies were focused on particle dynamics based on the experimental input data (such as temperature, velocity, and droplet evaporation). Gröhn et al. (2012) investigated the lab scale production of zirconia numerically. Flame temperature validation was performed for pure solvent in the experiment (effect of precursor in the solution was neglected). This would decrease the peak temperature of the flame since the enthalpy of combustion of the solution would decrease by neglecting the precursor (from 25.4 kJ/ml in ETOH/ZP to 21.4 kJ/ml in pure ETOH, Heine et al., 2006). Recently, Torabmostaedi et al. (2013) numerically studied the effect of process parameters on the spray flame structure and the product particle characteristics at medium scale production rates. The prediction for gas dynamics, initial droplet size and final primary particle size in FSP process was validated against the documented experimental measurements (Mueller et al., 2004a,b; Heine et al., 2006). It was shown that the primary particle diameter can be closely controlled at 15.5 nm in medium production rates by creating a constant residence time for zirconia nanoparticles at high temperature zone through a constant gas to liquid flow ratio (GLFR) at low precursor concentration (0.5 M ZP in ethanol).

In FSP process, the physical and chemical properties of nanoparticles depends on a large number of parameters, such as the burner design, atomization, gas-to-liquid-mass-ratio (GLMR), oxygen content of the dispersion gas, fuel and precursor properties, the concentration of the precursor in the solution, etc. To control the phase, particle size and morphology, it is necessary to optimize all of the relevant experimental parameters.

Since measuring the process parameters experimentally is expensive, time consuming and may not be feasible for some parameters (e.g. the growth and agglomeration of particles during the process), the computational fluid dynamics (CFD) may be an alternative tool for optimizing the FSP process. The ability of CFD to predict the performance of a new design before it is manufactured or implemented makes it an integral part of engineering design and analysis. Using CFD and numerical models, the formation and growth of nanoparticles in FSP can be predicted without the need to produce a prototype of equipment and carry out experimental tests. This study is to investigate the effect of nozzle geometry and processing parameters on the growth of zirconia particles using a commercial code, FLUENT, which will predict the multicomponent droplet evaporation, temperature, velocity and gas density in the flame and the results will be compiled into a software developed in our previous study (Torabmostaedi et al., 2013) based on the model developed by Kruis et al. (1993).

Zirconia is studied here due to its wide applications in industry and the available data for the validation. The aim of this study is to provide information and a better understanding on the effect of nozzle geometry and processing parameters on the gas dynamics, droplet vaporization and ultimately the formation and growth of nanoparticles during flame spray pyrolysis.

2. Modelling procedures

The effect of oxidizer gap size at a constant pressure drop was investigated based on a production rate of 100 g/h of zirconia. Fig. 2 shows the configuration of the nozzle geometry and computational domain which is consistent with the experimental setup of Heine and Pratsinis (2005) and was fully described by Torabmostaedi et al. in the previous study (Torabmostaedi et al., 2013). The nozzle consists of a capillary tube with a diameter of 0.5 mm for feeding the liquid and an annular gap (x, see Fig. 2) for atomizing the liquid droplets. The annular gap size depends on the desired pressure drop on the working mass flow rate and will vary from 0.1 mm to 0.5 mm. There are three more concentric tubes surrounding the atomizing gas inlet. Methane and oxygen were supplied through the first two annuli to form a diffusion flame for the ignition of the main flame. The last annulus is to provide excess oxygen for the main flame close the nozzle exit. The solution of 0.5 mol zirconium n-propoxide 70 wt% in n-propanol diluted in ethanol was injected into a pre-existing methane–oxygen flame. The solvent(s) then evaporates and combusts to form a high temperature flame. In the flame, chemical reactions and particle growth will take place to produce zirconia nanoparticles.

The modelling of gas dynamics, droplet transport, Turbulence, chemical reaction and radiation has been fully described by Torabmostaedi et al. in previous study