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Combustion kinetic analysis of flame spray pyrolysis process

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ABSTRACT

The flame spray pyrolysis (FSP) is a well-known process to produce nanoparticles and presents several advantages when compared to others, mainly regarding final product purity and operational flexibility. The correct modeling of the process is fundamental for the applicability of such techniques and, given that the temperature and chemical composition throughout the reactor are essential for the development of the nanoparticles, the correct representation of the chemical reactions is necessary. In this work, the production of zirconia (ZrO_2) nanoparticles via FSP is modeled and the combustion of the precursor-solvent mixture is described through seven sets of different chemical reaction mechanisms to analyse their influence on flame temperature and particle evolution within the process. The reacting turbulent multiphase flow is described by an Eulerian-Lagrangian approach and ZrO_2 nanoparticle growth is estimated by solving the population balance equations from a monodisperse model based on coagulation and sintering. Temperatures and primary particle diameters obtained from simulations are within 9% and 6% accuracies of experimental values, respectively. Although unmatching temperature profiles are found for the different mechanisms considered (mainly in the lower regions of the reactor), a small variation of primary particle diameter is observed when cases are compared.

1. Introduction

Nanoparticles of metal oxides have been the center of intense scientific research and technical development mainly due to the advantageous characteristics such as large surface to volume ratio, chemical stability and catalytic properties, heat and mechanical resistance. Their applications englobe paints, polishing slurries, antimicrobials, drug delivery, chemical catalysis and solar or fuel cell devices [1,2]. Among the different production processes, the flame spray pyrolysis (FSP) features the advantage that numerous metal-organic precursors can be turned into metal oxide nanoparticles during combustion. In particular, in the FSP process, a precursor-solvent combination is dispersed into a droplet spray that combusts in a turbulent spray flame. Gas to particle conversion is conceived as the major mechanism for nanoparticle growth, thus after precursor evaporation and reaction, nucleation occurs due to oversaturation followed by particle growth and coalescence, agglomeration, and sintering. High temperature and velocity gradients within the flame spray allow for rapid quenching and control of particle growth, forming highly crystalline nanoparticles [3,4].

Numerous experimental and numerical studies of the nanoparticle production by FSP have been conducted, mainly focused in describing the effects of operational parameters, such as dispersion gas flow rate [3,5], precursor concentration [5–7], precursor-solvent combinations [8] atomization quality [6,7], nozzle and reactor geometries [9–12]. It was found that increasing the precursor dispersion gas feed ratio results in larger flames with higher particle residence time inside the high-temperature region of the flame, which in turn results in enlargement of the nanoparticle size [5,13–15]. Also, increasing the precursor molar concentration drives the liquid viscosity to higher values, affecting the atomization and flame shape [6].

Numerical investigations of the FSP process capture several aspects of the physical and chemical phenomena in the process occurring at different time and space scales. The turbulent characteristics of the flow are strongly coupled with chemical reactions [6] and thus with nanoparticle formation and growth. The application of Computational Fluid Dynamics (CFD) contributed to the understanding and improvement of the process, mainly due to Population Balance models (PBM) that describe the evolution of nanoparticles within the highly reactive and turbulent flame environment [1,7,16–18]. Torabmostaedi et al. [7] and

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Gröhn et al. [16] made use of bi-dimensional CFD simulations of the flame spray and applied the monodispersed PBM proposed by Kruis et al. [19] to describe the evolution of nanoparticles. These studies consider the Sauter mean diameter (SMD) for the liquid droplets and a single-step mechanism for the combustion by means of the Eddy Dissipation Model, EDM [20]. In previous contributions, a Rosin-Rammler-Sperling-Bennet (RRSB) droplet size distribution has been utilized to represent the entire size range of droplets in the spray [21,22] and the Eddy Dissipation Concept (EDC) model [23] to include a multi-step mechanism for the combustion.

Advanced flame reactor design with in-depth chemical details requires accurate determination of chemical reactions and kinetic parameters. Previous studies of the FSP process [7,16] considered simplified one-step reactions of hydrocarbon-based fuels into CO_2 and H_2O. However, Dryer and Westbrook [24] already pointed out that single-step mechanisms overpredict the total heat of reaction since, at adiabatic flame temperatures, for typical hydrocarbon fuels, substantial amounts of CO and H_2 exist in equilibrium with CO_2 and H_2O. Lacase et al. [25] showed 10% increase of adiabatic flame temperature for lean fuel conditions in a methane jet flowing into air when a single-step mechanism was compared to a detailed mechanism. Similar results were obtained by Brink et al. [26] who used equilibrium calculations for a methane combustor with coaxial fuel and air inlets. To include CO and H_2 species as reaction products in the fuel oxidation, Jones and Lindstedt [27] state a minimum of three global steps reaction or a quasi-global scheme. Reduced mechanisms represent an alternative for global and/or quasi-global mechanisms, that can accurately predict flame temperature and chemical concentration profiles with relatively moderate computational demands [28].

CFD models for prediction of flames use either reduced [28–31] or global mechanisms that can be found in the literature for sprayed [32,33] and non-sprayed systems [26,34–36]. Although the reduced mechanisms decrease the computational costs when compared with detailed mechanisms, they are still complex for industrial or design applications whereas global and quasi-global mechanisms have shown to be suitable for most of the cases. In general, global and quasi-global mechanisms are simple, cheap and readily available [37].

The objective of the present study is to examine the effect of global and quasi-global combustion mechanisms in a CFD calculation on the prediction quality of the FSP process. The predicted flame temperatures and nanoparticle diameters are compared with experimental data obtained from thermocouple and nitrogen adsorption (BET) measurements, respectively. A Eulerian-Lagrangian model composed of mass, momentum, energy and chemical species conservation was applied to predict the velocity, pressure, temperature, and composition fields of the multi-phase flow in the FSP reactor. The PBM was coupled to the fluid dynamics model to predict the particle growth during the process. In this study, zirconium *n*-propoxide ($C_{12}H_{28}O_4Zr$) is employed as a precursor to produce ZrO_2 nanoparticles.

2. Experimental setup

2.1. Particle synthesis

The laboratory FSP reactor setup utilized for production of zirconia nanoparticles is schematically illustrated in Fig. 1. The liquid precursor-solvent mixture was prepared by mixing zirconium *n*-propoxide (70 wt-% in 1-propanol, Sigma Aldrich) and ethanol (> 99.8, VWT Chemicals) with a total metal concentration of 0.5 M or 1.0 M. Afterwards, the precursor solution was fed from a syringe pump (Legato 210, KDS) with a constant rate of 5 mL/min into the air assisted reactor nozzle. Oxygen (99.95 Vol-%, Westfalen) was supplied at 5 L/min as dispersion gas and the nozzle gap was adjusted to maintain a pressure drop of 150,000 Pa ensuring critical flow conditions and rapid liquid atomization at the nozzle tip. Instant spray ignition was achieved with a premixed pilot

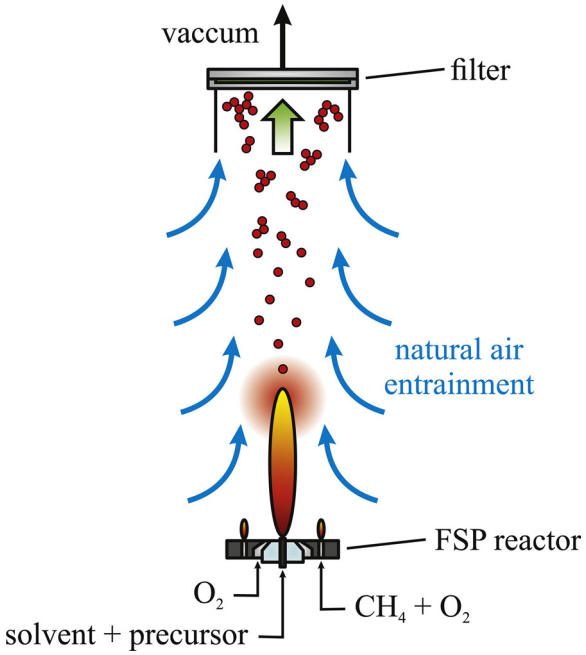

Fig. 1. Schematic representation of FSP reactor used for experimentation.

flame (1.5 and 3.2 L/min of methane and oxygen, respectively) supplied from an annular gap surrounding the liquid spray. All gas flows are reported at 293.15 K and 101,325 Pa and controlled by means of calibrated gas flow controllers (EL-flow, Bronkhorst). Zirconia nanoparticles were formed during evaporation and chemical reaction inside the flame and were collected in the process downstream on glass fiber filters (Pall A/E 25.7 cm in diameter) at 60 cm above the burner (HAB) with the aid of a vacuum pump (Busch SV 1025).

2.2. Spray and flame diagnostics

Droplet sizes in the spray have been measured at 20 mm distance from the nozzle in the line of sight with a laser diffraction spectrometer (Sympatec HELOS-VARIO/KF; HeNe-Laser $\lambda = 632.8$ nm; detection range 0.9–175 µm) under non-burning conditions. The droplet size distributions obtained are fitted to a Rosin-Rammler-distribution function to receive mean droplet diameters (d_d) and spread factors (n_d) which are utilized as relevant droplet parameters for CFD simulation (Table 1). The gas temperature is detected with a thermocouple (OMEGA Engineering, B-type, Pt/30%Rh-Pt/6%Rh, outer diameter 200 µm). The thermocouple is mounted on a 2D traverse unit to allow accurate positioning at horizontal and vertical locations of the burner center plane (varying 1 and 10 mm for radial and axial positioning, respectively). At each position temperature data were recorded and averaged for ~1 s and corrected afterward for radiation and convection losses [38,39]. Assuming a steady state condition with negligible conduction losses through the probe wires and catalytic reactions at the junction surface, a heat balance of the thermocouple probe can be expressed yielding a temperature difference between the real gas temperature (T_g) and recorded temperature of the probe (T_g) as $\Delta T = T_g - T_p = (\varepsilon\sigma T_p^4)/h_c$. Here, the emissivity ($\varepsilon$) of Platinum (0.2 for elevated temperatures), Stefan-Boltzmann's constant (σ) and the convective heat transfer coefficient (h_c) are used, with $h_c = k \cdot Nu_{cyl} / d_p$. For turbulent lateral gas crossflow conditions, the Nusselt number of a cylinder can be expressed by the Reynolds (Re) and Prandtl numbers (Pr) as $Nu_{cyl} = (0.037 \cdot Re^{0.8} Pr)/(1 + 2.443 \cdot Re^{-0.1}(Pr^{0.67} - 1))$ [40]. Intrinsic measurement errors might result from temporal zirconia deposition and layer formation on the thermocouple junction, that is why all temperatures are taken in pure ethanol flame sprays since the