

Pilot-scale Nanoparticle Manufacture

K. Wegner*, A. Gröhn* and S. Multer**

*Swiss Federal Institute of Technology, Particle Technology Laboratory
Sonneggstrasse 3, CH-8008 Zürich, Switzerland, wegner@ptl.mavt.ethz.ch

**Hecht Technologie GmbH, Schirmbeckstrasse 17, D-85276 Pfaffenhofen, Germany

ABSTRACT

The rapid advancement of nanotechnology and the development of an increasing number of nanoparticle-based applications demands for production-level quantities of nanopowders such as multi-component or coated oxides. Such advanced nanoparticles can be effectively made by flame spray pyrolysis (FSP) as research with laboratory reactors has shown for a spectrum of new nanomaterials with applications for instance in catalysis, pigments, ceramics, optics, energy and biomaterials. Here, the transfer of FSP nanopowder synthesis from gram-level lab-scale to pilot reactors with up to 10 metric tons annual production rate is investigated by the example of FSP pilot plants.

Keywords: nanoparticles, production, flame synthesis, scale-up, pilot-scale.

1 INTRODUCTION

A plethora of new nanoparticles has been synthesized at the laboratory scale in the past decade of intense research on nanomaterials many of which were realized by gas-phase processes [1]. Here, flame spray pyrolysis (FSP) has been shown a promising method [2, 3] for production of single- or multi-component nanoparticles [4] of almost all periodic table elements [1]. In FSP, organic solutions containing a metal-containing precursor are typically atomized with oxygen or air and ignited to generate a spray flame [3]. Following droplet evaporation and precursor conversion, nanoparticles are formed and grow by coagulation, sintering and/or surface growth [12]. The resulting particle characteristics (e.g. primary particle size, crystallinity and extent of aggregation or hard-agglomeration) strongly depend on the properties of the spray flame and define the performance of the nanoparticle-based products [3].

For example, biomaterials [5], catalysts [6], food fortification [7], battery materials [8], and advanced pigments [9] have been developed using laboratory FSP reactors with typical production rates of about 10 - 20 g/h. Today's challenge is the translation of these achievements into an industrial production environment which poses questions on continuous nanoparticle manufacture, safe handling and packaging [10].

Here, a fully automated pilot plant for nanoparticle manufacture by flame spray pyrolysis is presented that allows continuous production of nanopowders at rates up to 500 g/h. For the example of zirconia the scale-up from the laboratory reactor is investigated with the help of computational modeling [11] and process operation diagrams, relating synthesis parameters with product nanoparticle properties.

Furthermore, handling of the product nanoparticles that are continuously collected with bag-house filters is investigated. Therefore, the dry nanopowder is discharged from the filter to a pneumatic conveying system that transports it to a packaging site. A filling head with a continuous polymer inliner is investigated for contamination-free nanopowder packaging.

Release of nanoparticles into the workspace during production, conveying and packaging is monitored with a condensation particle counter at different locations in the pilot plant in order to assure operator safety and to guide equipment design and operation.

2 EXPERIMENTAL

Figure 1 shows the stirred tank for precursor preparation, the fluid handling and delivery unit and the FSP reactor chamber of the pilot-scale FSP plant that

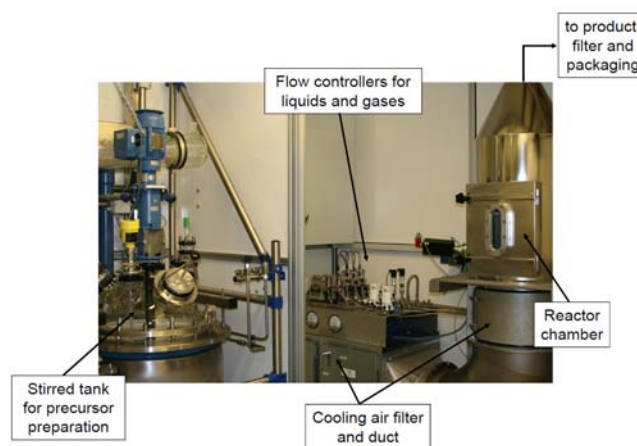


Figure 1: Pilot-scale reactor for continuous production of nanoparticles by flame spray pyrolysis with stirred tank for liquid precursor preparation, supply of combustion and cooling gases and enclosed reactor chamber.

was custom-designed and realized by Wegner Consulting (Zürich, Switzerland, karsten.wegner@gmx.ch) and Friedli AG (Burgdorf, Switzerland, info@friedliag.ch). The multi-product FSP plant is capable of producing up to 1 kg/h of nanoparticles (basis ZrO_2) in continuous mode. A programmable logic controller (PLC, Siemens Simatic S7) allows safe nanopowder manufacture as well as automated start-up and shut-down procedures.

Zirconium precursor solutions of either zirconium-2-ethylhexanoate (Umicore, Valirex Zr18 D60) in xylenes (Thommen-Furler) or zirconium n-propoxide (70 wt. % in 1-propanol, Aldrich) in ethanol (>99.8 %, Aldrich) were prepared in a 40L glass-lined stirred tank yielding Zr concentrations of 0.5 to 1 mol/L. The precursor was delivered by a centrifugal pump controlled with a mass flow meter to the custom-designed two-phase spray nozzle of the FSP reactor. Oxygen dispersion as well as oxygen and methane pilot flame gases (all PanGas, technical grade) were delivered to the FSP reactor by mass-flow controllers. The FSP reactor consisted of the center spray nozzle with 0.5 mm liquid capillary that was surrounded by the dispersion gas stream and two concentric channels for pilot flame methane (2.5 L/min, inner ring) and oxygen (4.5 L/min, outer ring). The dispersion gas pressure drop was adjusted between 1 and 4 bar by varying the width of the outlet gap. The FSP reactor was centered in a stainless steel chamber through which a co-flow of ambient air was established that has first passed a dual-stage inlet filter.

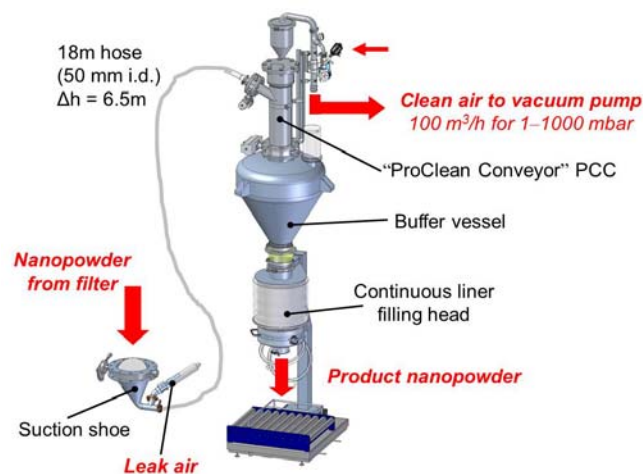


Figure 2: Pneumatic conveying system for the product nanopowders connected downstream the bag-house filter along with low-contamination powder packaging using a continuous liner filling head (Hecht Technologie GmbH, Germany).

The product aerosol formed in the spray flame was ducted through stainless-steel pipes to a continuous bag-house filter equipped with 21 filter bags (needle felt with PTFE membrane, Gore) that were periodically cleaned by

back-pulsing with pressurized air. A sampling port in the aerosol pipe upstream the filter allowed to collect nanoparticle samples for analysis and quality assurance. The cleaned off-gas was metered with a centrifugal fan (up to 1500 m³/h) placed downstream the filter and discharged through a HEPA police filter to the venting system of the building.

Product nanopowders were collected at the bottom of the bag-house filter and could be discharged to a pneumatic conveying system via a butterfly valve. The pneumatic conveying and low-contamination packaging system was realized by Hecht Technologie GmbH (Pfaffenhofen, Germany) and is shown schematically in Figure 2. Nanopowders were conveyed through a 18m long PVC hose (50 mm i.d.) from the suction shoe connected at the bottom of the bag-house filter to a stainless-steel buffer vessel by periodic suction cycles established with a vacuum pump. In each cycle, the ProClean Conveyor (PCC) head is first evacuated, filled with product powder and then pressurized to atmospheric conditions before the powder batch is discharged to the buffer vessel via a butterfly valve.

Product powder collected in the buffer vessel is discharged into a bag formed by closing one side of a continuous PE liner with a clamp (Figure 3). Once the bag is filled, a second clamp is used to close the powder-containing liner and to simultaneously form the bottom of the next bag. This procedure minimizes exposure of workers to the product material and allows low-contamination packaging.

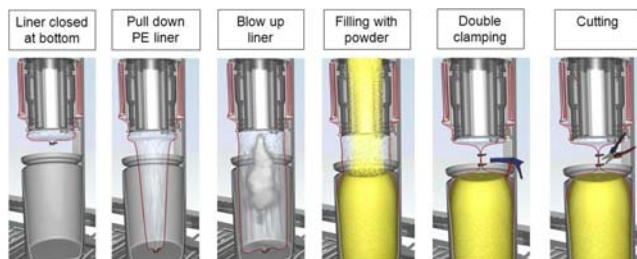


Figure 3: Low-contamination packaging of powders with a continuous liner system (Hecht Technologie GmbH, Germany). The workspace near the clamping location was sampled for determination of the nanoparticle concentration.

Workspace nanoparticle concentrations during zirconia production and packaging were monitored by a condensation particle counter (CPC, TSI, model 3775) equipped with a 1.5m conductive silicone rubber sampling tube. The particle counter can detect particle sizes from 4nm to > 3μm. Concentration measurements were made for up to 10 minutes and compared to the workspace background concentration without nanoparticle manufacture.

3 RESULTS AND DISCUSSION

Figure 4 shows the effect of precursor and dispersion gas feed on the primary particle diameter of zirconia nanoparticles made with the FSP reactor in batch-operation by Mueller et al. [12] along with a pilot plant operation point of this study. Mueller et al. [12] used zirconium n-propoxide in ethanol/n-propanol at concentrations of 0.5 and 1 mol/L as feedstock with dispersion gas flow rates of 25 (triangles) and 50 L/min (circles) at 1 bar pressure drop at the nozzle tip. Here 1 mol/L zirconium 2-ethylhexanoate in xylenes was used. The dispersion gas flow rate was 50 L/min at 3.3 bar pressure drop.

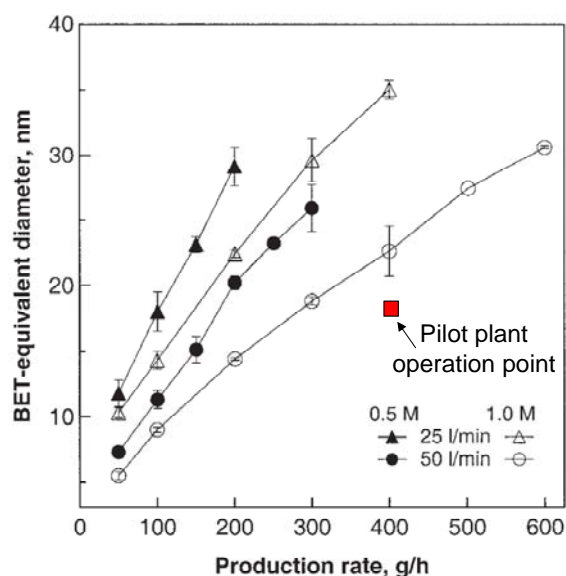


Figure 4: The increase in zirconia primary particle diameter with production rate (data of Mueller et al., 2004 [12]) can be minimized by reducing the residence time of the particles in the flame through optimized precursor atomization (filled square, this work).

In general, increasing the precursor flow increases the primary particle diameter, attributed to increased time for nanoparticle growth in longer and hotter flames. On the other hand, the primary particle diameter is decreased by increasing the dispersion gas flow rate due to faster mixing of reactants and oxidizer as well as higher entrainment of ambient air that cools and dilutes the flame. Both effects lead to shorter and colder flames yielding smaller particles. The increase in primary product particle size during scale-up of the production rate can thus be opposed by simultaneously increasing the dispersion gas flow.

For a given production rate, particles made with the lower molarity precursor are larger since a higher precursor feed corresponding to higher enthalpy flux is required to obtain the same amount of product. Please note that the ZrO_2 particles produced in this study with the

ethylhexanoate precursor and similar conditions as Mueller et al. [12] used (open circles) yielded smaller sized particles of 17.5 nm compared to approx. 22.5 nm. Nanoparticle synthesis with the two precursors and otherwise identical conditions resulted in similar product particle sizes ± 1 nm. Thus, the observed size difference of 5 nm cannot be attributed to the combustion of different precursors. Spray flame diagnostics using Phase-Doppler Anemometry has shown however, that the higher dispersion gas pressure drop used in this study (3.3 vs. 1.0 bar) results in better precursor atomization and faster flames. The observed smaller primary particle diameters can thus be attributed to shorter high temperature residence times of the particles. This shows that precursor atomization with the two-phase nozzle is an important factor in design and scale-up of flame spray pyrolysis reactors.

Figure 5 shows the workspace zirconia nanoparticle concentration during pneumatic conveying and packaging of the product powder. The samples for analysis by condensation particle counter were taken approx. 30 cm from the clamping position below the filling head (see Figures 2, 3). A background concentration of approx. 7800 particles/cm³ was measured during the first 10s shown in Figure 5. No increase in workspace particle concentration was observed when the powder was conveyed from the bag-house filter to the buffer vessel till $t = 85$ s. At $t = 90$ s, the product powder was discharged into the PE bag. A minor increase in particle concentration was observed followed by a decrease while the aerosol is allowed to settle in the bag till $t = 230$ s. The spike at 180s is attributed to a measurement error. The last dosing step shown in Figure 5 includes double-clamping and cutting of the PE liner (see Figure 3). No increase in workspace particle concentration was observed also during this step, indicating that the nanopowders can be safely handled with the conveying and packaging system without increase of the workspace particle concentration above background level.

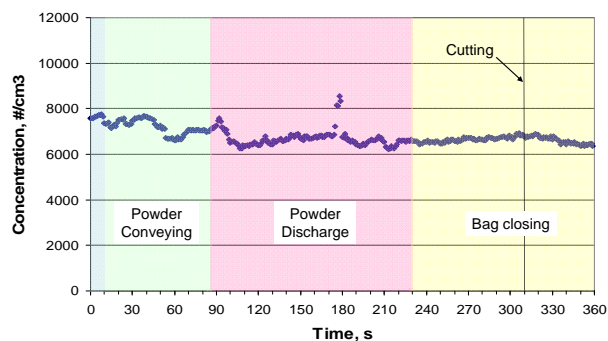


Figure 5: Workspace zirconia nanoparticle concentration during pneumatic conveying and packaging measured with a condensation particle counter. The signal during the first 10s shows the background concentration of approx. 7800 particles/cm³. No increase in workspace particle concentration is observed in the packaging process.

4 CONCLUSIONS

A pilot plant for nanoparticle synthesis by flame spray pyrolysis was realized and successfully performance-tested for production of 400 g/h of zirconia. The automated system was continuously operated for eight hours and yielded product primary particles of 17.5 nm. It was shown that precursor atomization by increasing the dispersion gas pressure drop strongly influences and reduces the product particle size. The increase of the primary particle size with precursor feed can be opposed by simultaneous increase of the dispersion gas flow, yielding guidelines for process scale-up. Pneumatic conveying and packaging of the product powder did not increase the workspace particle concentration indicating that the installed system can be used to safely handle nanopowders.

REFERENCES

- [1] W.Y. Teoh, R. Amal and L. Mädler, "Flame Spray Pyrolysis: An Enabling Technology for Nanoparticles Design and Fabrication", *Nanoscale* 2, 1324, 2010.
- [2] C.R. Bickmore, K.F. Waldner, D.R. Treadwell and R.M. Laine, "Ultrafine Spinel Powders by Flame Spray Pyrolysis of a Magnesium Aluminum Double Alkoxide," *J. Am. Ceram. Soc.* 79, 1419, 1996.
- [3] L. Mädler, H.K. Kammler, R. Mueller and S.E. Pratsinis, "Controlled Synthesis of Nanostructured Particles by Flame Spray Pyrolysis", *J. Aerosol Sci.* 33, 369, 2002.
- [4] R. Strobel and S.E. Pratsinis, "Flame Aerosol Synthesis of Smart Nanostructured Materials", *J. Mater. Chem.* 17, 4743, 2007.
- [5] S. Loher, W.J. Stark, M. Maciejewski, A. Baiker, S.E. Pratsinis, D. Reichardt, F. Maspero, F. Krumeich and D. Günther, "Fluoro-Apatite and Calcium Phosphate Nanoparticles by Flame Synthesis", *Chem. Mater.* 17, 36, 2005.
- [6] B. Schimmoeller, S.E. Pratsinis and A. Baiker, "Flame Aerosol Synthesis of Metal Oxide Catalysts with Unprecedented Structural and Catalytic Properties", *ChemCatChem* 3, 1234, 2011.
- [7] F. Rohner, F.O. Ernst, M. Arnold, M. Hibe, R. Biebing, F. Ehrensperger, S.E. Pratsinis, W. Langhans, R.F. Hurrell and M.B. Zimmermann, "Synthesis, Characterization, and Bioavailability in Rats of Ferric Phosphate Nanoparticles", *J. Nutr.* 137, 614, 2007.
- [8] F.O. Ernst, H.K. Kammler, A. Roessler, S.E. Pratsinis, W.J. Stark, J. Ufheil and P. Novák, "Electrochemically Active Flame-Made Nanosized Spinels: LiMn_2O_4 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiFe_5O_8 ", *Mater. Chem. Phys.*, 101, 372, 2007.
- [9] R. Strobel, H.J. Metz and S.E. Pratsinis, "Brilliant Yellow, Transparent Pure, and SiO_2 -Coated BiVO_4

Nanoparticles Made in Flames", *Chem. Mater.* 20, 6346, 2008.

- [10] K. Wegner, B. Schimmoeller, B. Thiebaut, C. Fernandez and T.N. Rao, "Pilot Plants for Industrial Nanoparticle Production by Flame Spray Pyrolysis", *KONA Powder and Particle* 29, 251, 2011.
- [11] A. Gröhn, S.E. Pratsinis and K. Wegner, "Fluid-Particle Dynamics during Combustion Spray Aerosol Synthesis of ZrO_2 ", *Chem. Eng. J.*, doi 10.1016/j.cej.2012.02.093, 2012.
- [12] R. Mueller, R. Jossen, S.E. Pratsinis, M. Watson and M.K. Akhtar, "Zirconia Nanoparticles made in Spray Flames at High Production Rates", *J. Am. Ceram. Soc.* 87, 197, 2004.