Pilot Plants for Industrial Nanoparticle Production by Flame Spray Pyrolysis†

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Abstract

With the rapid advancement of nanotechnology and with nanoparticles beginning to enter into products, the demand for production-level quantities of advanced nanopowders such as multi-component or coated oxides is rising. Such advanced nanoparticles can be effectively made by flame spray pyrolysis (FSP), and research with laboratory reactors yielded a spectrum of new nanomaterials for catalysis, pigments, ceramics, optics, energy and biomaterials, among others. 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 that were realized in industrial-oriented settings. Design considerations for such pilot-scale systems are addressed and guides to production cost estimates are given. Special attention is brought to safe and contained nanoparticle manufacture in order to address the growing awareness of the potential health and environmental effects of nanoparticles.

Keywords: nanoparticles, flame spray pyrolysis, aerosol synthesis, pilot-plant, scale-up

1. Introduction

The past decade has seen intense research on nanoparticle development with special attention paid to gas-phase processes, as these typically produce dry and thermally stable crystalline nanoparticles in one step without the need to handle large liquid volumes, surfactants or precipitation agents (Mädler, 2004). Last but not least, the development of flame synthesis processes for the industrial production of carbon black, fumed silica and pigmented titania in the first half of the last century showed that the production rate of gas-phase processes can be scaled to several tons per hour per reactor, catering, e.g. to a world market of approximately 300,000 tons of fumed silica in 2010 (China Chemical Reporter, 21.11.2010).

The operation principle of classic flame synthesis of silica and titania, the so-called chloride process, relies on the evaporation of metal chlorides prior to their introduction into the flame reactor. This limits the process to synthesis of materials with precursors exhibiting sufficient vapor pressure and thermal stability at moderate temperatures. The development of flame spray pyrolysis (FSP, Bickmore et al., 1996; Mädler et al., 2002) overcame this limitation by directly feeding a liquid precursor-solvent mixture into the flame reactor, atomizing and igniting it. The organic solvent and the precursor thereby provide the combustion enthalpy that drives droplet evaporation, precursor oxidation, cluster formation and growth to product nanoparticles by coagulation and coalescence and/or surface growth in the high-temperature environment (typically > 2000°C) of the spray flame (Mädler, 2004). With FSP technology, almost all periodic table elements can now be transformed into oxide, salt and sometimes even metal nanoparticles, as is apparent from the recent review of Teoh et al. (2010).

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Most material development studies using FSP were realized with laboratory-scale reactors that are now even available commercially (Tethis, 2011) and produce gram quantities of nanoparticles in batch operation. In addition to custom-made solutions addressed in his article, a continuous system to produce nanoparticles by FSP is also available on the market: Hosokawa provides a nanoparticle generator that uses the Flash Creation Method (FCM), a kind of plasma-assisted FSP which is capable of producing ZrO$_2$ nanoparticles at a capacity of 0.97 kg/h (Watanabe et al., 2007) or even several kg per hour depending on the material (Watanabe et al., 2006). Like FSP, the Flash Creation Method can generate not only nanoparticles of single-component oxides but also differently structured nanocomposite particles. Today’s challenge is the translation of these achievements into an industrial production environment through continuously operated pilot plants.

Rather little information is available on FSP process scale-up, design criteria and operational experience for the continuous production of nanoparticles at pilot-plant level. Bickmore et al. (1996) realized the first FSP plant on a pilot scale with a production rate of already up to 100 g/h spinel nanopowder. They reported continuous operation for about twelve hours at a rate of 85 g/h. With an optimized system, it was possible to increase the production rate to 400 g/h of ceria-zirconia nanoparticles (Laine et al., 2000). Mueller et al. (2003) produced silica nanoparticles with a pilot-scale reactor at rates up to 1.1 kg/h. They systematically investigated the effect of the precursor concentration and delivery rate as well as the dispersion gas flow on the product’s primary particle diameter. A similar parameter study was carried out for zirconia at rates up to 600 g/h (Mueller et al., 2004a), whereas temperature and particle diagnostics were employed to understand the growth of zirconia nanoparticles at production rates of 100 and 300 g/h and to develop and validate a simple particle growth model (Mueller et al., 2004b). Heine and Pratsinis (2005) further characterized the spray of this FSP reactor and developed a model accounting for multi-component droplet combustion and zirconia particle growth. Heel et al. (2010) produced cathode materials for solid-oxide fuel cells with an FSP pilot plant at 35 to 400 g/h production rate. They investigated the use of water-based precursor solutions and provided additional enthalpy by a concentric acetylene-oxygen flame. Kilian and Morse (2001) employed an ultrasonic nozzle for atomization of the precursor solution rather than the gas-assisted nozzle used by the other research groups, and manufactured zirconium and aluminum oxide nanoparticles at rates up to 180 g/h.

Here, the scale-up of nanoparticle synthesis by flame spray pyrolysis is reviewed and the design and operation of FSP pilot systems is discussed using the example of pilot plants with >100 g/h production rate. Guidelines for safe and contained nanoparticle manufacture are proposed and production cost structures estimated.

### 2. Process Flow Diagram

Fig. 1 is an example of an FSP process flow sheet. One or more solid or liquid precursors along with organic solvents are introduced into a stirred tank reactor where dissolution and/or chemical conversion and mixing of the raw materials takes place. A pump meters the precursor solution to the spray nozzle where it is atomized with oxygen dispersion gas. Gases including the oxygen and gaseous fuel for spray ignition and stabilization are typically delivered from cylinders to the FSP reactor using mass flow controllers. Filtered ambient air is used to dilute and quench the hot flame aerosol prior to its introduction into the collection device.

For product nanopowder collection in FSP pilot plants, baghouse filters (Mueller et al., 2003; Akurati et al., 2008) or electrostatic precipitators (Bickmore et al., 1996) have been employed. The accumulated product nanopowders in the bottom cone of the baghouse filter are periodically discharged through a butterfly valve or shutter to the product silo below the filter. From here, they can be pneumatically conveyed to a packaging station or directly filled into containers. The process off-gas consisting mainly of air, water and CO$_2$ flows through a second particle collector to remove nanoparticles that might have escaped the primary one. In the process with baghouse filter (Fig. 2), this is typically a high-efficiency particulate air filter (HEPA), while Bickmore et al. (1996) installed a wet scrubber downstream of their electrostatic precipitator. The air flow through the entire system is usually established and controlled by a centrifugal fan which creates a slightly negative pressure in the unit. Unless further off-gas treatment such as DeNOx in the case of nitrate precursor combustion is required, the exhaust fumes are vented to the environment.

### 2.1 Precursor selection and preparation

The selection and preparation of precursor solutions is among the most challenging tasks in the
flame spray synthesis of nanoparticles, especially if multi-component materials are produced, since the following criteria must be considered: homogeneity of product nanopowders, production costs, CO₂ formation and carbon balance, as well as precursor handling.

A homogeneous product powder consisting of fine nanoparticles requires particle formation via gas-to-particle conversion in which the precursor species evaporate from the spray droplet, react and subsequently nucleate to cluster embryos of the product material. In the case of insufficient precursor volatility, undesired precipitation inside the spray droplet can occur resulting in several-hundred-nanometer large hollow or dense particle impurities in the nanopowder by droplet-to-particle conversion (Kodas and Hampden-Smith, 1999).

Process economics suggest the use of low-cost raw materials such as nitrates, chlorides, or carbonates dissolved in simple organic solvents such as ethanol or acetic acid as feed to the FSP reactor. Such solutions, however, are prone to form inhomogeneous product powders, as has been observed both with lab- (Jossen et al., 2005b; Strobel and Pratsinis, 2011) and pilot-scale FSP systems (Hinklin et al., 2004; Jossen et al., 2005a). Reaction of simple metal salt precursors with carboxylic acids prior to their introduction into the flame was shown to significantly increase the nanopowder homogeneity for nitrates (Chiarello et al., 2007; Strobel and Pratsinis, 2011) and carbonates (Jossen et al., 2005a; Kim et al., 2008, 2009), and might be a good trade-off between product powder quality, raw materials costs and complexity of precursor preparation.

Due to their volatility, organometallic compounds are typically well suited for flame spray synthesis, but high market prices and difficulties in handling the often moisture-sensitive species do not make them appear an attractive FSP feedstock. However, like in the synthesis of metal carboxylates, integrating the formation of organometallic precursors into the FSP plant might reduce production costs. For instance, Bickmore et al. (1996, 1998) used aluminum, magnesium or titanium oxides and hydroxides along with ethanolamines as starting materials that were converted into organometallic compounds. Pokhrel et al. (2010) formed tungsten alkoxides by reacting tungsten chlorides with benzyl alcohol under Cl release and used the precursor for the synthesis of WO₃ nanoparticles by FSP.

Jossen et al (2005b) reported that the tendency toward the formation of inhomogeneous nanopowders from simple metal salt precursors can be reduced by increasing the combustion enthalpy density and by selecting solvents with boiling points higher than the melting or decomposition point of the precursor. This was also observed by Heel et al. (2010) using mainly water-based nitrate precursor solutions and an acetylene-oxygen supporting flame surrounding the spray. When producing multicomponent materials, precursor selection can affect the product quality, as was reported by Stark et al. (2003) producing ceria-zirconia catalyst supports: the two elements were evenly distributed in the product particles when carboxylic

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**Fig. 1** Flow chart of a plant for nanoparticle synthesis by flame spray pyrolysis with stirred tank for precursor preparation, FSP reactor, baghouse filter for nanoparticle collection and police filter for off-gas cleaning.
(lauric and acetic) acid-derived precursors were used while segregation of a zirconia-like phase was observed using acetic acid, 2-butanol and iso-octane as solvents for cerium-acetatehydrate and zirconium-acetylacetonate.

In view of production costs and CO₂ formation, it is desirable to operate with precursor solutions of high molarity with respect to the total metal concentration. Here, precursors with a low carbon content such as a zirconium-carbonate-derived Zr-propionate with an elemental ratio of Zr:C = 1:6 (Kim et al., 2009) might be more advantageous than zirconium-n-propoxide (Zr:C = 1:12; Mueller et al., 2004a) or zirconium-2-ethylhexanoate (Zr:C = 1:32; Stark et al., 2005).

Further aspects to consider in the design of a precursor-solvent mixture are its soot formation tendency, viscosity and surface tension. Increasing the metal content of the precursor is limited by the increasing viscosity of the solution (Laine et al., 2000) which impedes pumping and spray atomization. In air-assist atomizers, larger liquid viscosity and surface tension result in coarser sprays (Lefebvre, 1989), which in turn affects the temperature and velocity profiles of the flame.

2.2 Reactant feeding

The precursor should be delivered at a low pulsation rate to the FSP reactor since spray flames are sensitive to oscillations in the liquid fuel supply which can affect nanoparticle growth conditions. Lab-scale systems typically use syringe pumps for the low-pulsation delivery of 50 – 100 ml quantities of precursor (Mädler et al., 2002), and some pilot studies have adopted the approach by using large 1l precision syringe pumps (Mueller et al., 2003). A dual pump system (Heel et al., 2010) allows quasi-continuous production by re-filling one syringe while the other is feeding the reactor. Bickmore et al. (1996) delivered the precursor from the precursor tank to the FSP reactor by applying a nitrogen head pressure to the vessel.

Gear pumps have been used for continuous precursor delivery (Killian and Morse, 2001) and provide accurate control over the precursor flow rate by adjusting the drive speed, but they suffer from pulsations. These can be reduced by the design of the gears as in the micro-annular gear pump used by Grass and Stark (2005) for precursor dispensing. A drawback of gear pumps is their susceptibility to particles and the need to thoroughly clean the pump after use. In the FSP pilot plant at ETH Zurich, a centrifugal pump (KSB microchem) designed for the pulsation-free delivery of small liquid volumes was used to feed the flame spray reactor. Unlike gear pumps it is not sensitive to particles in the pumped fluid and is easy to clean. Drawbacks are the need of a mass flow control, sensitivity to downstream pressure changes and no self-priming behavior.

The supply of gases is typically from cylinders with flow rates being controlled by mass flow controllers. Gas consumption is dominated by the dispersion gas, usually oxygen. As a rule of thumb, the production of 1 kg of nanopowder by FSP requires approximately 10l of precursor solution and 5 m³ of oxygen dispersion gas. Dispersion with air appears to be more economic but lowers the oxygen partial pressure in the flame which might result in incomplete combustion, as observed by Mueller et al. (2003) for silica production rates > 100 g/h. Air-operated FSP nozzles exhibit lower flame temperatures than those run with oxygen as the additional nitrogen not taking part in the combustion needs to be heated up, resulting in smaller product particles (Mädler et al., 2002; Mueller et al., 2003).

2.3 Reactor

The flame spray pyrolysis reactor consists of an atomizing nozzle for dispersion of the precursor-solvent mixture that typically is surrounded by co-flowing streams of gaseous fuel and oxidant feeding the pilot flame. While most work was done with two-phase atomizers, Killian and Morse (2001) used an ultrasonic nozzle for dispersion of the precursor stream. Ultrasonic atomizing nozzles have the advantage of a relatively narrow distribution of small droplets which might lead to fast and more homogeneous evaporation. Furthermore, the large dispersion gas flow rates required for breaking up the liquid in two-phase atomizers are not needed. As a result, the spray flames are typically laminar and exhibit longer particle residence times than the turbulent flames of a two-phase nozzle spray.

Two-phase nozzles are frequently used in flame spray synthesis since they produce fine sprays, are able to effectively atomize high-viscosity liquids and vigorously mix the oxidizing dispersion gas with the liquid precursor (Lefebvre, 1989). Spray velocities are often > 100 m/s (Heine et al., 2005) and can even reach sonic speed resulting in highly turbulent spray flames with a flame temperature above 2500K (Mueller et al., 2004b). High gas velocities cause significant entrainment of ambient air into the spray flame, diluting and quenching it (Heine and Pratsinis, 2006).

Fig. 2 shows the effect of precursor and disper-
sion gas feed on the primary particle diameter of zirconia nanoparticles made with the FSP pilot plant at ETH Zurich. The precursor solution was prepared by reacting zirconium carbonate with the stoichiometric amount of 2-ethylhexanoic acid for obtaining zirconium 2-ethylhexanoate, and using acetic acid as a solvent to achieve a Zr concentration of 0.5 mol/l. The reaction was carried out in a heated stirred tank at 100°C under reflux. Results for 60 l/min dispersion gas flow (circles) are compared to Mueller et al. (2004a), who used zirconium n-propoxide in ethanol/ n-propanol at concentrations of 0.5 mol/l as feedstock with dispersion gas flow rates of 25 (squares) and 50 l/min (triangles). Fig. 2 shows the BET-equivalent particle diameter, derived from a measurement of the specific surface area and assuming monodisperse spherical particles, for production rates of 50 to 300 g/h.

Increasing the precursor flow increases the primary particle diameter in all experiments, 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 nanoparticles. Please note that the ZrO₂ particles produced in this study with the carbonate precursor and a slightly higher dispersion gas flow rate of 60 l/min are much smaller than those made from the zirconium n-propoxide solution at the same production rate and concentration of 0.5M. A possible explanation is the lower enthalpy content of the precursor mixture employed here that was -5.4 kJ/(g gas) while the precursor of Mueller et al. (2004a) had a specific enthalpy of -8.3 kJ/g at 130 g/h. A lower enthalpy content will lead to lower flame temperatures and therefore smaller nanoparticles.

When keeping the mass flow rates of liquid precursor and dispersion gas constant but increasing the dispersion gas pressure drop of the atomizer from 2 to 7 bar, the specific surface area of FePO₄ nanoparticles increased from 91 to 108 nm, as shown in Fig. 3. The delivery rate of the precursor solution containing stoichiometric ratios of iron nitrate and tributylphosphate dissolved in a 1:1 by volume mixture of 2-ethylhexanoic acid was 20 ml/min, while 40 l/min (STP) of oxygen dispersion gas was used. The increase in pressure at constant mass flow rate was realized by decreasing the area of the dispersion gas gap leading to higher gas velocities which improves atomization. This is in agreement with Lefebvre (1989) who reported smaller droplet Sauter mean diameters for higher pressure drops in air-assist atomizers. Smaller droplets lead to faster evaporation and shorter flames which results in shorter high-temperature residence times for particle growth and smaller product particles.

2.4 Particle collection

For the collection of silica nanoparticles produced at rates up to 1.1 kg/h, Mueller et al. (2003) employed a baghouse filter with four PTFE-coated
Nomex bags and 1.7 m² total filtration area. Particles were removed from the filter medium by periodically (every 30 s) introducing a short reverse pulse of pressurized air into individual filter bags while filtration continued with the remaining three bags. The maximum capacity of the centrifugal fan used by Mueller et al. (Stäfa-Wirz AG, Switzerland, type MKV 012) can be estimated at 1000 m³/h, leading to a filter load of approx. 10 m³/(m² × min). This is extremely high compared to the filtration of commercial fumed silica nanoparticles employing a filter load of approx. 0.8 m³/(m² × min) (Gore, 2011), and might not be suitable for continuous production. Using the same filter, Jossen et al. (2005a) report the installation of a check-valve in the aerosol line from the flame reactor to the filter to avoid disturbance of the flame by backflowing aerosol during back-pulse cleaning while producing up to 350 g/h yttrium-stabilized zirconia. This further indicates an insufficient filter size especially for continuous production.

Our latest pilot plant at ETH Zurich is equipped with a baghouse filter of 15 m² filtration area (Mikropul GmbH, Germany) by 21 filter bags (GORE® membrane on aramid needle felt, W.L. Gore & Associates GmbH, Germany). Fig. 4 shows the pressure drop across the filter bags during production of iron phosphate nanoparticles with 20 nm primary particle size. The production rate was 270 g/h at total gas volume flows of 1125 m³/h (circles) and 1500 m³/h (triangles), corresponding to filter loads of 1.25 and 1.67 m³/(m² × min), respectively. About half an hour after production start-up, the pressure drop across the filter reached stable values of 1450 - 1550 Pa at 1125 m³/h flow. Reverse-pulse cleaning was initiated when 1400 Pa were reached. At 1500 m³/h or 1.67 m³/(m² × min) filter load, a stable operation point could not be established, and after half an hour of operation, the suction limit of the centrifugal fan downstream of the filter was reached. As the pressure drop continued to increase, the capacity of the centrifugal blower decreased leading to overheating of the filter since insufficient cooling air was introduced into the unit.

The particle concentration and size in the off-gas duct downstream of the baghouse filter installed at ETH Zurich was determined with a scanning mobility particle sizer (SMPS, TSI DMA model 3081 with CPC model 3775). The measurements were performed during production of the FePO₄ nanoparticles at intervals of 5 min. Scans in the size range of 10 to 365 nm were carried out with 60 s scan time and assuming unit particle density. Fig. 5 shows a representative particle size distribution recorded 40 minutes after production start-up. A total concentration of 72,900 particles per cm³ was measured and lies within the range of 69,800 and 83,600 / cm³ observed for 4 scans during 20 min. of operation. The particle concentration in the workspace was 1100 ± 200 per cm³ observed for 4 scans during 20 min. of operation. Thus, an approximately 70 times higher particle concentration was observed in the off-gas of the filter during stable operation with reverse-pulse cleaning switched on.

The particle size distribution (Fig. 5) shows that most particles have diameters of > 50 nm with the calculated count mean diameter being 129 nm. This indicates agglomerates of the FePO₄ primary particles with 20 nm BET-equivalent particle diameter which must have penetrated through the filter bags.
or the bag seal at the filter head plate which separates the product compartment from the clean gas compartment. Even at full capacity of the centrifugal fan (1,500 m$^3$/h), the mass of particles penetrating through the filter bags is in the range of mg/h at 290 g/h production rate leading to a very high filter efficiency of > 99.9%.

The disadvantage of baghouse filters in FSP plants is their large size required by handling the diluted aerosol at temperatures of maximum 220°C and the need to replace all filter bags for a product change in order to avoid cross-contamination. Fig. 6 shows how the baghouse filter dominates the FSP pilot plant installed at ARCI, Hyderabad, India. It is designed for a nanoparticle production rate of 1-2 kg/h and is equipped with a filter holding 70 bags.
with total area of $\sim 50 \text{ m}^2$. Such a system is oriented toward small-scale production while pilot plants with lower capacities and less filter bags are recommended for research-oriented units.

Wire-in-cylinder electrostatic precipitators were used by Bickmore et al. (1996) for collection of FSP-made spinel nanoparticles from a magnesium-aluminum double alkoxide. At 100 g/h production rate, a collection efficiency of $65 \sim 75\%$ is reported. The remaining particles were removed from the off-gas with a counter-current packed bed water scrubber or a baghouse filter (Sutorik and Baliat, 2002). Since the low bulk density product powders caused filling of electrostatic precipitator tubes and restriction to the gas flow, two precipitator tubes were operated in parallel: one was used for nanoparticle collection while the powder was manually recovered from the other (Sutorik et al., 1998). Due to its simple geometry, the wire-in-cylinder electrostatic precipitator has the advantage of easy cleaning and maintenance between runs with different products. The use of metal and ceramic components enables collector operation at higher a temperature, e.g. 400°C (Bickmore et al., 1998), which in turn reduces the quenching gas requirement.

2.5 Off-gas and effluents

The typical off-gas of an FSP plant not employing chloride precursors contains the combustion products CO$_2$ and water highly diluted with the process cooling air. As shown in Fig. 5, the particle concentration in the gas stream behind a baghouse filter was up to $10^3 / \text{ cm}^3$. In order to eliminate this particle contamination, the off-gas is passed through a high-efficiency particulate air filter (HEPA) before it is vented to the environment. This filter also acts as a police filter in the case of failure of the primary particle collector. Particle size and concentration measurements downstream of the class H13 HEPA filter (Camfill-FARR, Switzerland) installed in the ETH pilot plant gave a particle concentration of only 35 / cm$^3$, about 30 times less than in the workspace. Particles of size 14 to 280 nm were detected which might have penetrated through the seals or imperfections in the filter media of the HEPA filter. In the event that other combustion by-products are formed, such as NOx from nitrate precursors, appropriate off-gas treatment units (e.g. DeNOx) must be installed in the off-gas duct in agreement with local regulations.

Nanoparticle-contaminated effluents are not generated during the dry nanoparticle production process. However, water is used to clean the aerosol piping and nanopowder collector for a product change or maintenance. Resulting nanoparticle suspensions cannot be discharged to the communal waste-water system since waste-water treatment plants might not be able to fully remove the nanoparticles. Limbach et al. (2008) showed that 6wt% of cerium nanoparticles escaped through a model waste-water treatment plant. The strategy employed in our pilot plants is the collection and thickening of the nanoparticle suspensions in designated settling tanks with the help of

![Fig. 6](image_url) Front view of the FSP pilot plant during installation at ARCI (Hyderabad, India) for production of several kg/h of nanoparticles with the baghouse filter for nanoparticle collection ($\sim 50 \text{ m}^2$ filtration area) at the back in the center, the stirred tank for precursor preparation on the right and the control cabinet for process automation on the left side of the platform.
Swirl flames and evaporation. The resulting slurry is recovered and disposed of as hazardous waste or is treated at high temperature to destroy the ceramic nanoparticles by sintering.

3. Safety Considerations

Three hazards can be associated with the flame spray synthesis of nanoparticles that might not be as pronounced in other chemical production processes: hazards due to the handling of relatively large quantities of organic solvents and metal-organic compounds as feedstock, flame combustion at high temperature and hazards associated with the nanoparticles produced. As the first two hazards are typically well known and addressed by national or international regulations, the main challenge is to avoid the release of nanoparticles into the environment and the workspace. Therefore, the entire processing unit should be fully enclosed with well-defined and secured access and interface points. The placement of the centrifugal fan at the end of the process chain ensures a slightly negative pressure inside the entire unit that minimizes the escape of nanoparticles. The cooling air inlet duct should be equipped with appropriate filters that not only purify the inflowing air but also prevent the release of nanoparticles in the case of a pressure build-up in the unit and generation of an aerosol backflow, as was reported by Jossen et al. (2005a) during reverse-pulse cleaning of the baghouse filter. The FSP reactor itself should be fully enclosed (see Fig. 7) and well sealed since individual nanoparticles are present in and above the flame. Nanoparticles are immobilized again during particle collection, in the form of a filter cake or wall deposit. Fig. 7 shows by example of the FSP pilot plant at Tecnan, Spain, how the distance between the flame reactor and the filter was kept as short as possible to minimize the volume in which individual nanoparticles and small agglomerates are present as well as the amount of particle losses to the walls.

As pilot plants see frequent product changes, cleaning of the unit and change of the filter bags must be realizable in a safe and comfortable manner for the personnel with minimum nanoparticle release to the workspace. It is therefore recommended that the filter bags are changed from the clean gas side on the top of the baghouse filter without the need to access the product compartment as this will result in the release of nanoparticles. Wet-cleaning of the filter and the aerosol ducts before a filter change or maintenance with fixed installations of clean-in-place (CIP) nozzles is highly recommended since this removes the majority of the nanopowder from the system and agglomerates or binds remaining nanoparticles, minimizing dust formation.

A process control system (PLC) monitors all relevant process streams during automated production including nanoparticle concentrations in the off-gas. The process should safely shut down in an automated routine in the case that process parameters are off-limits or a high nanoparticle concentration indicates a leakage in the filter. The process control system should be complemented by continuous workplace exposure measurements using submicron particle counters, as performed by Wang et al. (2011) during pilot-scale production of silicon nanoparticles and Demou et al. (2009) during lab-scale nanoparticle synthesis.

Ideally, the nanoparticle production unit should be placed in a designated and fully enclosed room that is only accessible to personnel with appropriate personal protection equipment via an air lock, as is shown in Fig. 8 by the example of the FSP pilot system at Johnson Matthey Technology Center (UK). The control of the process is performed from outside the nanoparticle production space, and all workplaces requiring nanoparticle handling inside the room are
additionally equipped with glove-box isolators.

4. Economic Considerations

Production cost estimates for the FSP-manufacture of nanopowders at the pilot or even industrial plant level are difficult due to the lack of available raw material prices, their market-dependent variability and the geographically varying labor costs. Here, we make an attempt to analyze the cost structure for the continuous production of bismuth oxide from bismuth-nitrate and zirconium oxide from zirconium-2-ethylhexanoate nanoparticles based on a pilot plant with 1.25 kg/h production rate located in Switzerland. Prices for precursors and solvents are current market prices for ~200 kg barrels. Gases (methane, oxygen, air) are assumed to be delivered from a pipeline network in an industrial chemical production setting. Continuous operation with 4 shifts (1 person per shift plus partial supervising and assistance) over 330 days per year and 24 h/day is assumed, resulting in ~8000h of production and 10t annual production rate. A capital investment of 750,000 EUR is considered for the pilot plant, linearly depreciated over ten years. Costs for maintenance, utilities, supplies, laboratory charges and packaging (combined “Others”) are estimated as fractions of the capital investment or labor costs according to Peters, Timmerhaus and West (2003). For comparison, the cost structure for a small production plant with a ten-times-higher production rate is shown in Fig. 9 as well.

Even though both materials are based on different precursors, relatively low-cost bismuth nitrate and the more expensive zirconium-2-ethylhexanoate, the combined precursor and solvent costs have approximately the same share, namely ~45% for the 10t/yr plant and ~80% for the 100 t/yr production. This is due to the requirement of additional solvents such as 2-ethylhexanoic acid for the conversion of the nitrate precursor while these are already present in the zirconium raw material. At 10 t/year production rate, expenditures for labor constitute about 40% of the total production costs but only 10% for 100 t/year. This is due to the fact that the fully automated pilot plants require approximately the same number of operators independent of their production rate. Expenses for gases are almost negligible in all cases but will be much higher if cylinders or liquid oxygen are used. Depreciation of the capital investment costs accounts for 3 – 7% while maintenance, consumables such as filter bags, packaging, utility and laboratory charges (“others”) are 6 to 7% of the total costs.

Uncertainties in raw material price estimates thus have a huge influence on the total production costs and purchasing in larger quantities will significantly reduce costs. Furthermore, the aim should be the use of low-cost solvents such as ethanol or acetic acid and operation at a metal concentration in the precursor solution that is as high as possible. It should be possible by optimization of the precursor solution and processing conditions to produce oxide nanomaterials at costs of some tens of euros per kg at pilot plant level. Economy of scale will help to reduce these costs in industrial manufacturing units, but it will be hard to beat the production costs of the current chloride process for fumed silica or titania, since FSP precursors and organic solvents will remain more expensive than the metal chlorides, hydrogen and oxygen.
5. Conclusions

Nanoparticle synthesis by flame spray pyrolysis has been successfully transferred from the laboratory to the pilot plant level with production rates of a few kilograms per hour, as several examples have shown. The process can be operated continuously in a safe manner with the help of process automation. Pilot plant production costs for simple oxides can be estimated at below 100 EUR/kg with raw materials being the largest cost factor.

Prime research needs are the design of low-cost precursor solutions with higher metal-to-carbon ratios, a better utilization of the heat generated during combustion and strategies for more efficient flame quenching. This would reduce the amount of organic solvents supplied to the system and lead to a reduction of raw material costs and CO₂ emissions. Furthermore, this would reduce the volume flow of cooling gas, allowing more flexible operation with smaller nanoparticle collectors, e.g. baghouse filters. These challenges should be tackled by a combined experimental and modeling approach. The latter must include process fluid dynamics, combustion as well as droplet and particle dynamics, and should guide the design of new FSP reactors and the next scale-up step.

Furthermore, strategies for contained product nanoparticle packaging and handling must be developed in view of industrial nanoparticle manufacture. The identification of hazards associated with FSP synthesis of nanoparticles must be identified more systematically. The existing pilot units will be used to carry out hazard and operability studies aiming at the development of design and operational guides for larger FSP systems.

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Author's short biography

Karsten Wegner

Karsten Wegner studied process engineering at the University of Karlsruhe (Germany), graduated in 1998 and then obtained his Ph.D on gas-phase synthesis of nanoparticles from ETH Zurich in 2002. He was co-founder and CEO of the start-up company FlamePowders that focused on industrial flame synthesis of nanopowders. Since 2005 he works as a consultant for aerosol manufacturing of nanomaterials and counts major industries, research centers and the start-up Tethis (Milan, Italy) to his customers. Together with his partners, he has designed and built customized FSP pilot plants around the globe. Karsten Wegner also holds a position as lecturer and senior researcher at ETH.

Björn Schimmöller

Björn Schimmöller received his diploma in process engineering from the University of Karlsruhe (Germany) in 2005. He then joined the Particle Technology Laboratory at ETH Zurich for his Ph.D thesis with focus on the “Structure of Flame-Made Mixed-Metal Oxide Catalysts”. After receiving his degree in 2010 he stayed at ETH as a postdoctoral fellow and has recently joined Cabot Corporation in Boston, USA. His research interests lie in flame synthesis of mixed-metal-oxide and metal nanoparticles focusing on control of material properties and their performance as well as process scale-up.

Bénédicte Thiebaut

After obtaining her PhD from Heriot-Watt University, Edinburgh (UK), Bénédicte Thiébaut joined Johnson Matthey 13 years ago. Since then, she worked on numerous projects specializing in the nanotechnology area including flame spray synthesis of nanoparticles. The technique proved of interest to various Johnson Matthey businesses and her work was then dedicated to the investigation of catalyst preparation and novel products by this method. Bénédicte led the successful creation of a development scale Flame Spray Pyrolysis unit and now is in charge of the new facility as well as the various projects associated with the technology.

Claudio Fernandez

Claudio Fernandez is managing director of the Technological Centre Lurederra in Los Arcos, Spain as well as president of TECNAN Nanoproducts. He developed a rich background in materials technology, management, and entrepreneurship e.g. through positions at the Royal Institute of Technology in Stockholm (Sweden), Gaiker and LEIA Technology Centers (Spain), and Commercial Laminate Iberia SA (Akzo Nobel Group). His latest venture, TECNAN, provides custom-manufacture of nanopowders by FSP, nanodispersions as well as other final nanoproducts and caters to customers worldwide. With Lurederra, Claudio Fernandez has managed and coordinated numerous European Research Projects, the latest of which is “Advance-FSP” focussing on the scale-up of flame spray synthesis of nanoparticles.
Tata Narasinga Rao

Tata Narasinga Rao is leader of the Center for Nanomaterials at the International Advanced Research Center for Powder Metallurgy and New Materials (ARCI) in Hyderabad, India. He holds a MSc degree in physical chemistry and obtained his Ph.D. in electrochemistry from Banaras Hindu University (BHU), Varanasi, in 1994. After working at IIT Chennai, he moved to the University of Tokyo as a JSPS postdoctoral fellow and was appointed assistant professor in 2001. His center at ARCI is equipped with several techniques for nanoparticle synthesis, among them a FSP pilot plant capable of continuous nanoparticle production at semi-industrial level allowing to pursue application-oriented nanomaterials development in an industrial context.