Large scale production of tailored nano-oxides by advanced, high-output, high-versatility Flame Spray Pyrolysis

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Content:

1. EXECUTIVE SUMMARY

The aim of the project ADVANCE-FSP, funded by European Commission over the past four years, has been the design and construction of a prototype industrial Flame Spray Pyrolysis nanoparticle production line, one order of magnitude higher than whatever is currently available, suitable to achieve at a continuous and trouble-free production level of 5kg/h the same results regarding nature and size range (10-20 nm) of nanoparticles as obtained in the small FSP laboratory reactors currently used, validating the technology developed by the production in industrial operating conditions of nanoparticles of ZrO2, CeO2, CeO2/ZrO2, Pd/CeO2/ZrO2 and Pt/CeO2/ZrO2. In FSP nanoparticle synthesis, liquid precursors dissolved in a fuel or solvent are dispersed through a nozzle. The resulting spray is ignited and sustained by a pilot flame. Particles are produced within the spray flame, with aerosol formation, droplet evaporation, combustion, coagulation, sintering and even surface growth occurring in parallel. The fundamental problem in up-scaling the FSP technology from laboratory to industrial level is the fact that for larger productions an increase in feed rate and/or precursor concentration are required, both resulting in the formation of nanoparticles with bigger diameters.

The partners in ADVANCE-FSP have been an interdisciplinary consortium including European leaders in FSP technology, nanoparticles production, safety and engineering. The project has taken an approach based on subsequent incremental up-scaling processes, first to productions of 100g/h, second to 500 g/h and subsequently to 5 Kg/h, heavily relying on on-line measurements during FSP synthesis of temperature fields (FTIR), concentration of precursor species in the different flame fields (FTIR), evolution along the flame of the particle size and degree of agglomeration (thermophoretic extraction and TEM) and definition of velocity fields within FSP reactor (phase Doppler anemometry). The upscaling process was also supported by the use and further development during the project of computational Fluid Dynamics Simulations able to predict for FSP reactions the flow, temperature and specification fields, spray conditions, combustion dynamics and particle growth evolution.

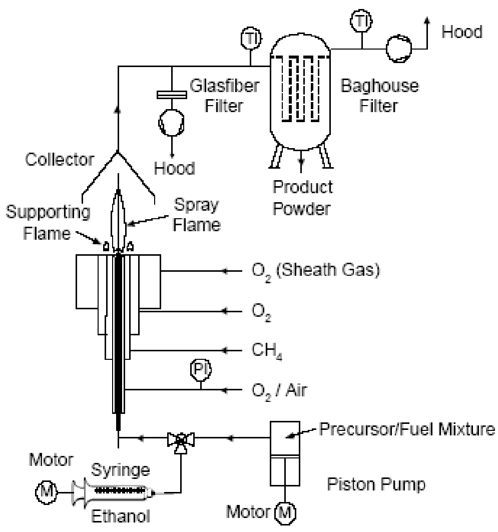
The upscaling process of the FSP technology has finalised in ADVANCE-FSP with the construction of a full industrial line for production of 5 kg/h of nanoparticles. The industrial line constructed in the project has been analysed in terms of safety aspects by HAZOP methodologies. In addition, risk assessment based on the nanoparticle risk management system CENARIOS was applied. Safety and implementation measures have been introduced in the final design and operation procedure of the industrial line. The FSP constructed system counts with a total automated feeding system in order to prepare the precursor mixtures up to 150 litres, two parallel filter chambers for collecting of nanoparticles which allow adapting the production in a range from 1 to 5 kg/h and a conveying and packaging system tailored designed for nanoparticles which avoids completely the contact with the nanopowders. Furthermore, two different FSP reactor systems has been researched during the project for industrial scales based on standard spraying systems and an innovative concept based on swirl flow which has been tested an validate for pilot scale production.

The full industrial line of 5 kg/h, installed in the facilities of Technological Centre Lurederra, has become in the larger FSP equipment for production of nanoparticles. The line has been tested validating its operability and production capacities by producing ZrO2 nanoparticles up to 5 kg/h. While previous tests during optimisation of the upscaling process at 5 kg/h had reached nanoparticles sizes in the range of 40 nm, nanoparticles have been obtained with size sin the range of 20 nm and with a good quality regarding purity in the combustion process. The full industrial line based on FSP developed has validated also as an economic and environmental friendly technology in comparison with other competitor. As evaluated in the project FSP technology is the most competitive technology in the production of nanoparticles such as nano-oxides especially for complex multicomponent oxides.

2. PROJECT CONTEXT AND OBJECTIVES

Context

Nanooxides are currently being produced at industrial level by diverse technologies, including traditional processes such as deposition-precipitation, impregnation, chemical vapour deposition or sol-gel methods. In general, the preparation routines using these technologies become more complex and the task more demanding if several components are present, such as, for instance, in supported multimetallic catalysts, or if calcinations are required to obtain a crystalline and defined metal oxide support. As example, in a sol-gel process the synthesis steps can imply, for instance, the dissolution of the proper amounts of precursor salts in water, mixing with an aqueous solution of citric acid as complexing agent, evaporation of water in vacuum, drying of the gel obtained and calcination of the dry solid. In both cases, these methods imply time consuming procedures, production of liquid by-products and presence of impurities in the final material. Although nanooxides produced by wet methods find nevertheless a market niche, gas-phase processes based on the hydrolysis of metal chloride vapours in an oxy-hydrogen flame (Aerosil process) are more competitive, where available for industrial mass production of nanooxides. The German company Evonik is currently producing by gas-phase processes fumed silica, alumina and titania at production rates up to several tons per hour, being also capable of producing other typologies such as indium-tin oxide and silica particles doped with iron oxide. However, this process is limited to the use of easily vaporizable chloride precursors, such as $TiCl_4$ and $SiCl_4$, which are available only for a few materials.



The spectrum of nanoparticles that can be produced in the gas-phase was enormously enlarged by the introduction of the Flame Spray Pyrolysis (FSP), process which relies on the direct introduction of liquid raw materials into the flame rather than in the use of chloride vapours. In a nutshell, FSP precursors, such as for instance cerium 2-ethylhexanoate or zirconium 2-ethylhexanoate are dissolved in a fuel or solvent, such as ethylhexanoic acid or xylene as examples, and dispersed through a nozzle. The resulting solid-cone spray is ignited and sustained by a pilot flame (see figure). Particles are produced within the spray flame, with aerosol formation, droplet evaporation, combustion, coagulation, sintering and even surface growth occurring in parallel. In flame synthesis, flames are used as a low-cost energy source to drive the nanoparticle formation mechanisms. The rapid succession of heating and cooling during combustion create materials with special structure, morphology, composition and high purity resulting in unique products.

FSP due to the enormously broad range of liquid precursors available, it is currently considered as one of the most promising techniques for synthesis in only one step of a very large diversity of sophisticated inorganic nanoparticles. Currently, nearly all periodic table elements can be produced by FSP in the form of oxide, phosphate, carbonate and other ceramic and salt nanoparticles. Mixing of precursors in the desired ratio prior to their introduction into the flame allows production of doped materials, binary and ternary oxides and even more complex multi-component nanoparticles. Examples of FSP-produced materials include solid solutions of CeO_2-ZrO_2 with and without Pt coating for automotive off-gas treatment, CeO_2-GdO_2 for solid oxide fuel cells, Pt/Al_2O_3 and Pd/Al_2O_3 enantioselective hydrogenation catalysts, Pt and $BaCO_3$ supported on Al_2O_3 for NO_x storage reduction catalysts, bioactive calcium phosphates, such as hydroxyapatite and tricalcium phosphate for repair of bone defects, FSP-made magnetic nanoparticles for separations in organic synthesis or bioseparation of proteins, highly soluble $FePO_4$ nanoparticles for food fortification, superconducting $YBa_2Cu_3O_{7-x}$ nanoparticles, and lithium-based spinel structures used for Li-ion batteries.

Only laboratory-scale flame reactors that produce nanopowders in milligram to gram quantities have been used for the development of these new materials and for studying the corresponding particle formation and growth processes. On the other hand, the similarity of the FSP process to the industrial flame synthesis of pigmentary titania and fumed silica points indeed at the capability for industrial upscaling of the FSP technology, and thus to its potential as a flexible tool for large-scale production of a new generation of complex nanomaterials.

FSP is therefore a technique that in principle should be suitable to be readily upscaled to produce nanostructured materials in high volumes at a relatively low cost. However, the fundamental problem in upscaling the FSP technology from laboratory to industrial level is the fact that for larger productions an increase in feed rate and/or precursor concentration are required, both resulting in the formation of larger nanoparticles. Previous studies developed by partners of the project such as Lurederra, with an FSP industrial plant of a sustainable capacity of 500 g/h, indicated that the minimum nanoparticle size which could be reached in this plant with a maximum capacity of 800 g/h was 25 nm, and attempts to go under that size by further increasing the dispersion gas flow rate resulted in incomplete combustion and formation of hollow spheres in the range of 80 nm. In this way, research in the upscaling of FSP technology under the constrains of maintain the properties of the nanoparticles synthesised in the same ranges of sizes as well as purity and nature than in lab-scale will enable to launch this technology to the market as a leading technology for producing nanoparticles for a large range of applications.

Objectives

The ultimate objective of the project ADVANCE-FSP was <u>to upscale to industrial use the production of nanoparticles by Flame Spray Pyrolysis.</u> In order to fulfil this ambitious and innovative objective, two major objectives were accomplished:

1) Development of a Computational Fluid Dynamics (CFD) model suitable for FSP production rates between 100 g/h and 5 Kg/h, fine-tuned and validated through on-line measurement to be used as support in the upscaling process as well as for the definition of the operation conditions to be set in industrial FSP reactors up to 5 Kg/h.

2) Design and construction of a prototype industrial FSP nanoparticle production line suitable for continuous, trouble-free operation at a production rate of 5 Kg/h, operating in accordance with the industrial standards regarding automation, safety, ease of operation, ruggedness, particle containment and waste control, and capable to produce at industrial-scale level nanoparticles with the same characteristics in nature and size as those obtained in the small FSP laboratory reactors currently used, demonstrating as well their superiority against possible competitor products by the relevant techno-economic and environmental evaluation.

In this way, the partial objectives to be accomplished during the different stages of the project *ADVANCE-FSP* consisted on the following:

⇒ In WP1, as a first step, the relevant partners defined the full set of industrial requirements for the nanoparticles to be produced and the starting conditions for their production in laboratory-scale reactors. The process of upscaling was defined to be carried out on CeO2, ZrO2, CeO2/ZrO2 with sizes in the range 10-20 nm, with a limited production of Pt/CeO2/ZrO2 and Pd/CeO2/ZrO2.

⇒ WP2 had as objective to obtain in a FSP laboratory-scale reactor with a production capacity of 100 g/h CeO_2, ZrO_2, CeO_2/ZrO_2, $Pd/CeO_2/ZrO_2$ and $Pt/CeO_2/ZrO_2$ fulfilling the requirements set by the industrial partner Johnson Matthey Plc including the development of a CFD model to be refined and validated through on-line measurements on FSP production at a lab-scale scale production.

⇒ Subsequently, the objective in WP3 was to obtain in a FSP medium-scale reactor with a production capacity of 500 g/h CeO_2, ZrO_2, CeO_2/ZrO_2, $Pd/CeO_2/ZrO_2$ and $Pt/CeO_2/ZrO_2$ meeting the industrial requirements set and including use of on-line measured data for medium-scale FSP reactors to fine-tune the CFD model previously developed in order to adjust it to a range of production rates between 100 g/h and 500 g/h.

⇒ Then, WP4 was focused on the design and construction, according to the data supplied by CFD modelling on small and medium FSP units, a prototype industrial FSP reactor suitable to produce the same nanoparticles in nature and size as obtained in laboratory-scale FSP units but with a production capacity of 5 Kg/h, and which was fitted into an existing FSP medium-scale line in order to produce CeO_2, ZrO_2, CeO_2/ZrO_2, $Pd/CeO_2/ZrO_2$ and $Pt/CeO_2/ZrO_2$ nanoparticles meeting the industrial requirements set as well as to further fine-tune the CFD model developed by introduction of on-line measurements in order to model production rates between 100 g/h and 5 Kg/h.

⇒ After the complete upscaling process, WP5 had as main objective the design, based on the large-scale prototype FSP reactor built, tested and optimised, a full FSP industrial line suitable for production of nanoparticles with similar properties to those obtained in existing FSP laboratory units but with an industrial production capability of 5 Kg/h, and to construct its different components, namely automation system, precursor delivery system, FSP reactor unit, nanoparticle filtering unit and collection system.

⇒ The objectives in WP6 were to assemble the individual units constructed into a fully operative prototype FSP industrial line with a production rate of 5 Kg/h, to identify the health risks associated to the upscaled FSP process developed through a hazard and operability study (HAZOP) and to implement a CENARIOS-like nanotechnology risk management systematic in the operation of the prototype industrial FSP line constructed.

⇒ Finally, in the last technical WP7, the objective was the successfully production using the industrial FSP line developed of industrial batches of nanoparticles. As defined, these were 10 Kg of CeO_2, 10 Kg of ZrO_2, 20 Kg of CeO_2/ZrO_2 in different proportions, 5 Kg of $Pd/CeO_2/ZrO_2$ and 1.5 Kg of $Pt/CeO_2/ZrO_2$ according to the specifications set by industrial partner Johnson Matthey. In addition, the final objective was to demonstrate the superiority of the nanoparticles synthesised against competitor products by the development of the relevant techno-economic and environmental evaluation.

3. DESCRIPTION OF THE MAIN S&T RESULTS/FOREGROUND

CFD modelling and on-line characterisation techniques for FSP production

One of the main results obtained in the project was the development of a Computational Fluid Dynamics (CFD) model to describe nanoparticle formation by Flame Spray Pyrolysis and to be used in order to predict particle sizes as a function of reactor operation parameters. This model was developed for laboratory conditions to medium and pilot scales. This model was useful for optimisation and research of the process parameters and also was used in the design and upscaling of the FSP reactors reducing the time and resources needed for experimental testing.

In addition to the CFD model developed, another important result of the project was the definition, set up and adjustment of instrumentation for on-line characterisation of the events occurring in the FSP reactors. The on-line characterisation was applied during the project along the upscaling process and was also a support for the validations of the CFD simulations.

On-line characterisation techniques for FSP production

In the initial stages of the project, for characterisation of lab-scale reactors, systems for temperature and spray measurements as well as nanoparticles sampling were applied.

For on-line temperature diagnostics, a Fourier-transform infrared spectroscopy (FTIR) system for measuring the emission, transmission and background spectra of the burning spray was built and used to obtain the average temperatures of the lab-scale flame spray reactor. The method employed for the measurements is schematically shown in the Figure 1. Briefly, line-of-sight flame temperatures were obtained by comparing the best match of the blackbody Planck function and the measured infrared (IR) emission and absorption spectra of hot CO2 present in the measurement volume, where self-absorption of the flame was taken into consideration. Temperature measurements of flames burning ethanol and toluene without precursor and in the absence of particles were made in order to establish the diagnostic technique and to validate the basic CFD combustion model at lab-scales.

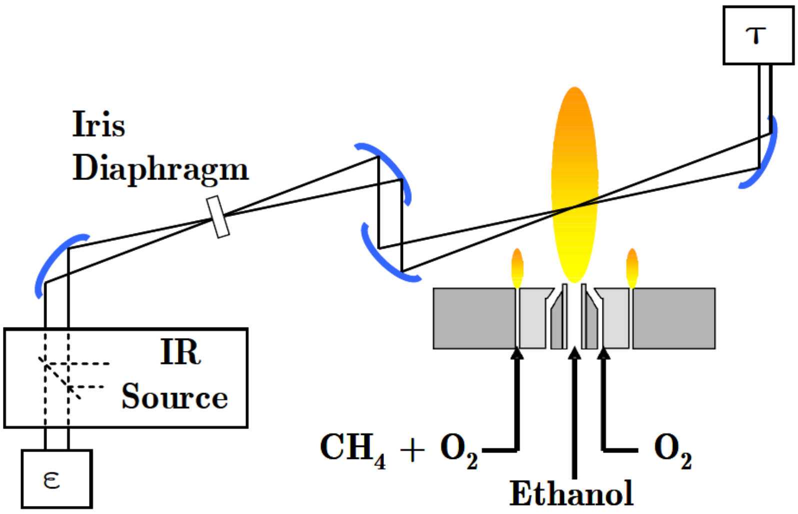


Figure 1: Schematic of the FTIR set-up for flame temperature measurements, where ε stands for emission and τ for transmission detector.

Temperature profiles were successfully compared to data reported in the literature in order to validate the experimental set-up and measurement procedure. Then, FTIR measurements were conducted at different FSP operating conditions of interest to this project. The flame temperature diagnostics showed that with increasing dispersion oxygen flow, the flame temperature decreases, which is in agreement with more oxygen and entrained air diluting and cooling the flame. Also, temperature characterisation of the flame showed as expected that increasing the solvent flow rate resulted in increased flame temperature similarly to changing the solvent from ethanol to toluene, since in both cases more enthalpy is supplied to the flame.

The FTIR temperature measurement technique was successfully established and provided a profound data basis for CFD model validation in a non-intrusive way.

A two dimensional Phase Doppler Anemometer (PDA) was installed for non-intrusive determination of droplet velocity, concentration and size in the spray of the lab-scale FSP reactor. The methodology employed for measurement is shown in the Figure 2. The laser beam is divided and frequency-shifted in a Bragg cell and guided by fiber optics to the emitter which focuses the beams into the measurement volume inside the flame. A detector records the refracted light.The PDA was initially calibrated by measuring the droplet size of a monodisperse aerosol. Droplet size and velocity diagnostics were carried out with the PDA for the spray flame of the lab-scale reactor.

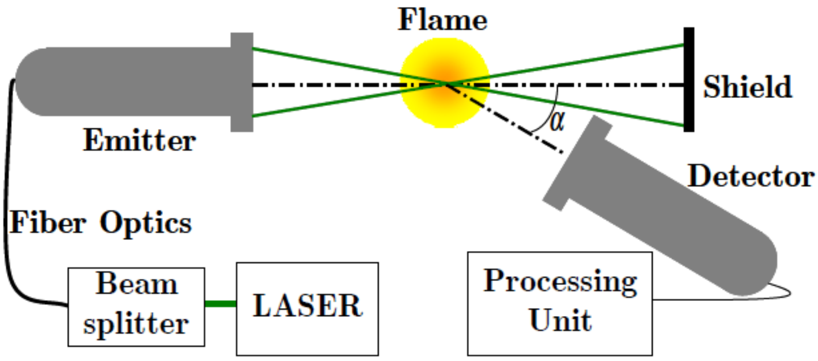


Figure 2: Schematic of the experimental set up for droplet size and velocity measurement in-situ the FSP flame using PDA.

The centerline velocity profiles of 4 ml/min ethanol spray flames at different dispersion gas flows between 5-7 L/min were measured. Close to the burner, similar velocity contours were observed for different employed dispersion O2 flows. This might be explained by the same initial velocity in both cases since sonic conditions are always reached with the lab-scale reactor at a pressure drop of 0.9 bar across the nozzle. After this, lower velocities were found for spray flames with higher dispersion oxygen at lower heights above the burner due to the much lower temperature of this flame at this location. However, for higher dispersion oxygen involves also a higher momentum flux, in this way, it was found higher velocities at locations where the temperature of the two flames is almost similar.

In addition, the Sauter mean droplet diameters for the spray flame conditions at lab-scale were determined also at the different height above the burner (HAB), from 5 to 30 mm.The biggest droplets of about 20 µm diameter were observed at the edges of the spray while 5 µm droplets are in the center. Initially the droplets have a large radial velocity component which is preserved in the bigger ones due to their inertia while the smaller droplets follow the gas which loses its radial velocity rapidly. The droplet concentration revealed that the lab-scale FSP reactor produces a hollow-cone spray. Measurements of the droplet size and number as well as gas velocity were performed reliably with the PDA for HAB = 5, 10, 25, 30 and 35 mm. This allowed a detailed three dimensional investigation of the flame spray characteristics.

Evolution of particle characteristics in the FSP flame was investigated by thermophoretic sampling. For lab-scale, zirconia synthesis was studied. Particles were sampled on carbon-coated copper TEM grids at different heights above the burner (HAB = 40 – 200 mm). The TEM grids are placed in a stainless steel holder such that the grid surface is exposed through an opening on both sides of the holder. Here, the particles are deposited by thermophoretic force which is independent of particle size in free molecular regime. The sampling grids are subsequently analysed by Transmission Electron Microscopy.

The thermophoretic sampling technique could only be applied above a certain height in the flame since droplets present in the flame destroyed the sample grids at lower locations. Several aspects were found after statistical analysis of the results. The primary particle diameter is seen to increase with increasing HAB, as can be expected. Initially, it was observed that the primary particle size distribution might still be widened by particle formation. Then, the number-based geometric standard deviation, σg, of primary particles decreased to 1.3 further suggesting that sintering, which narrows the primary particle size distribution, takes place after a certain height in the flame.

The medium-scale FSP reactor was characterized for flame temperatures, droplet size, concentration and velocity applying Fourier-Transform Infrared Spectroscopy (FTIR) and Phase Doppler Anemometer (PDA) on-line diagnostics. Therefore, the measurement set-ups were adopted to operate with the medium-scale reactor. Medium scales reactors were tested at 27.1 ml/min ethanol feed and 50 l/min dispersion O2.

Temperature profiles of the medium-scale Flame Spray Pyrolysis (FSP) reactor were determined by Fourier-Transform Infrared Spectroscopy (FTIR) using a similar approach as for the laboratory-scale unit. However, as in medium scales the investigated flames were larger and thus the FTIR signal to noise-ratio is decreased, the method had to be adapted by increasing the sampling time to obtain reliable results. The effect of precursor and nanoparticle formation on the FTIR flame temperature was investigated by comparing results with pure solvent flames of lab-scale and medium-scale reactors. In both cases the presence of precursor was found to be negligible on the temperature profiles, allowing FTIR temperature characterization with pure solvent in absence of nanoparticle formation which makes easier the characterisation.

In addition, to facilitate process scale-up and allow comparison with the CFD model, temperature profiles were investigated in order to study effects of dispersion gas and solvent flow rate as well as dispersion gas pressure drop and composition.

Also, for medium scale, the velocity, droplet concentration and droplet size profiles of FSP ethanol sprays were characterized by Phase Doppler Anemometry (PDA) following the same approach than in lab-scale reactors. On-line characterization of medium scale reactors represented in a good manner the real events in the flame and following similar trends than in lab-scale reactors. A complete characterisation of flame events was developed at this stage.

On-line characterisation was also applied by ETH in the latter stage of the project in order to characterise the new industrial reactor designed for production of 5 kg/h. In this case, FTIR temperature measurements were not able to be measured in industrial reactor due to the larger amount of heat generated by this flame. Also PDA was challenging but it was measured. The spray pattern of the industrial-scale FSP reactor was characterized in terms of velocity, droplet size and concentration. Therefore Phase Doppler Anemometry (PDA) measurements were applied to the burning spray flames. Industrial designed FSP reactor was operated with a xylene flow rate of 64 ml/min and a dispersion O2 flow rate of 80 l/min. These conditions were used in order to compare with the medium-scale FSP reactor operated and validate the design of the new reactor in the formation of the flame spray.

Axial gas velocity profiles were determined from the velocity of the smallest droplets that closely follow the gas streamlines of the two burners for height above burner (HAB) = 5 - 50 mm. Qualitatively, the shape and extension of the spray cones were similar for the two reactors. Both sprays seemed to have solid cones. For all heights above the burner, the gas velocities were slightly higher and the flame was more symmetric with the industrial-scale burner. The latter was attributed to an optimized centering of the two-phase atomizer in the larger geometry of the industrial-sale burner. This could lead to more homogeneous growth region for the nanoparticles and might result in more homogeneous product powders.

Also spatial distribution of Sauter mean droplet diameters was measure for HAB = 5 - 50 mm. The average droplet sizes of the whole spray again are very similar for both nozzles and the large droplets were consistently located at the spray edges while in the flame region around the centreline the droplet size were small. For all measurements, in both reactors, the large droplets are noticeably concentrated at one side indicating that radial symmetry of the flames could be improved. As well as velocity fields were found rather symmetric, it was depicted that the asymmetry in droplet sizes is not due to the flow field but due to combustion phenomena. An optimization of the pilot flame in terms of homogeneity might improve the results.

Lastly, by comparing the normalized droplet number concentrations results confirmed that both sprays were of a solid-cone type, which was conserved up to a certain height. The spray cones were very narrow. This indicated that the influence of the dispersion gas swirl is rather weak, as swirl typically broadens a spray. Again, results for both nozzles were highly similar. At a height in the flame, the evaporation was nearly complete (~95 %) and only a few droplets were detected, resulting in increased asymmetry of the measured data.

In conclusion, the scale-up from medium- to industrial-scale reactor nozzle could be considered successful since at same operating conditions flame characteristics were maintained. In addition, the new design for the industrial-scale FSP could improve the spray flame symmetry as observed from the velocity fields.

CFD modelling for FSP production

CFD models were developed from lab-scales up to pilot scales in order to be used at industrial production optimisation of conditions and upscale reactor designs. In the first stage of the project, initial conditions for modelling were set at precursor flow rate in the range of 3-6 ml/min oxygen and dispersion flow rates between 3-7 L/min. CFD simulations were done with the commercial ANSYS Fluent v.12.1.4 axisymmetric solver. For aerosol dynamics simulations a population balance model was implemented where evolution of particle volume, area, and number concentration were solved by CFD.

Good and accuracy results were been obtained with the CFD models developed at lab-scale, simulated values of temperature fields, velocity and droplet number concentration were in good agreement with on-line measures developed in lab-scale reactors. Finally, integration of a particle-dynamics model into CFD simulation was realized for the prediction of nanoparticles properties.

For a comparison of primary particle size predictions in toluene flames, data reported by experiments was used. The agreement of the CFD-model with measured CeO_2 primary particle sizes by nitrogen adsorption (BET) was within less than 2 nm. The model followed the trends of increasing particle size with increasing precursor concentration. In the same way, comparison of experimental and simulated values was done for zirconia synthesis in ethanol flames. Predicted primary particle diameter for ZrO_2 was in close agreement with BET measurements suggesting correct description of the flame aerosol process.

The model developed at lab-scale demonstrated to have the required level of accuracy to be transferred to pilot-scale reactors. Finally, with the use of very detailed models, it was depicted also, that these details not impacted on the results obtained with the model, and this indicated that in this FSP reactor system comparable results could be obtained also with a simplified approach at less computational cost.

CFD model for medium scale was adjusted and refined in order to describe better the flame temperature. During the early phases of the project, it was adopted a combustion model that was based on a reaction that generates CO and CO_2 as a function of local thermodynamic equilibrium. The maximum temperatures this approach yields always seemed rather high, in this way, at this stage for the development of the model at medium-scales, it was made a reassessment of the model in order to be optimised and describe better the temperature and combustion process. The analysis, indeed, showed that the model was deficient in the early rapidly changing conditions of FSP flames. The lack of reversibility in the CO2 to CO reaction turned out to be the main drawback. In this way, it was reassessed a model already tested at the start of the project, which at that time was discarded as it was not managed in order to obtain a proper converged solution. At this stage, it was turned back to that scheme, and with some effort finally, it worked. The extended model provides a more detailed representation of the combustion processes in the flame. With the renewed model, much lower maximum temperatures were obtained. The new model got to a better agreement between the measured data and the predictions. The improved model for medium scale-reactors was used at this stage in order to investigate different designs of the reactor for the upscaling.

In parallel, another CFD computational model used to simulate medium scale reactors. Case studies were carried out to demonstrate the effects of geometries of reactors and processing parameters, which built a foundation for medium and large scale process design. This model was used also to simulate quenching rings and results showed that these could be effective to control the temperature profile of the flame and the particle size produced in medium and large reactors if needed to avoid nanoparticle size increment.

In the later stage of the project, model predictions of flame temperature, height, velocity as well as initial droplet size, BET-equivalent particle size, evolution of primary particle diameter, physical properties of precursor solutions and pumping pressure during FSP were evaluated by detailed comparison with the measured data and published in literature for ZrO2. The simulation results showed that the numerical models are in very good agreement with on-line characterization at low and medium zirconia production rates up to 600 g/h, thus, they were used for equipment design, process optimization and prediction of particle properties at industrial scale production rates from 1 to 5 kg/h.

A commercial CFD code (ANSYS Fluent) was used to solve the multicomponent droplet evaporation, combustion and gas flow field in FSP. The CFD code was coupled with an in-house Fortran code to simulate the particle growth during FSP. The FSP apparatus with an axisymmetric geometry and a two-dimensional model were employed to reduce the complexity and computational time.

The computer models developed in FSP project were used to investigate the effect of reactor geometries and the processing parameters on the behaviour of flame and the formation of nanoparticles in medium and industrial scale reactors. Control parameters required for large reactors were predicted. For a large scale reactor (up to 5 kg/h), for the production of ZrO2 with an isopropanol solution of zirconium n-propoxide diluted in ethanol, the simulation results showed that the primary particle diameter could be controlled at ~ 20 nm, while the production rate was increased from 1 to 5 kg/h.

Industrial FSP line for production of nanoparticles up to 5 kg/h

An industrial line for production of nanoparticles has been constructed in ADVANCE-FSP project, this line is the largest one in the world with a capacity up to 5kg/h for the production of nanoparticles by liquid feed Flame Spray Pyrolysis.

The full design and construction of the 5 kg/h industrial line of FSP production of nanoparticles during the project was divided in its main components or parts:

- An automation system was developed and constructed in order to make easier the operation of the line and ensure a safety control of the system. Different operation modes are available in the industrial line for production of nanoparticles and maintenance labours. In addition, alarms, faults and safety stop sequences were implemented as a result of a Hazard and Operability Study developed during the project.

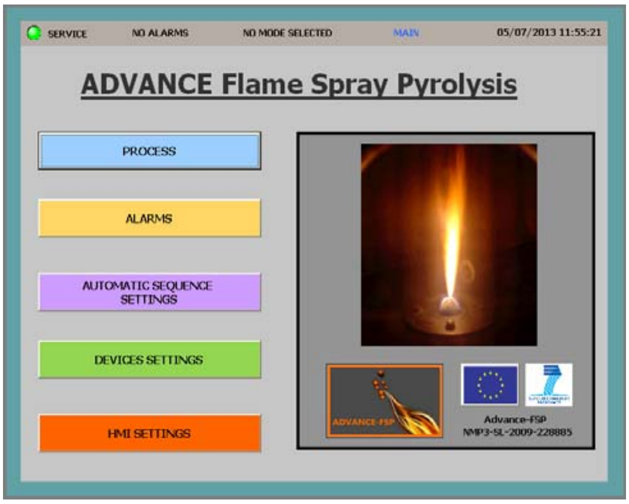


Figure 3. Main menu screen of the PLC interface

- A feeding system, including the stirred tank, liquid feeding piping, pump, flow meters, sensors, etc. has been designed and constructed. In order to ensure the operability of the system and also the safety procedures, it was studied the flammability of the possible mixtures in the operation conditions and defined the safe operation mode. Also, it was defined needed extra equipment such as carbon filters which are needed for avoid the release and recover of flammable vapours.
- FSP reactor chamber was constructed for confinements of the flame reactor. The reactor chamber included a long sight glass and an access door for cleaning and maintenance. The system was also designed taking into consideration easy access to all the media connections to the reactor as well as required adjustments. In addition, diameters of the cooling air piping were designed as well as diameter of the hot aerosol tubing was chosen for minimization of particle deposition. The large scale FSP reactor was based on standard nozzle using gas for spray formation. In addition, a new nozzle based on swirl flow was designed as alternative FSP reactor.
- The filter system constructed for nanoparticles collection from the aerosol was based on bag house filters with reverse pulsing. Two filter modules has been constructed in order to operate based on the production conditions with one or two modules in parallel. Filters of ePTFE were selected in order to withstand a temperature of 190 ºC. The equipment was designed to monitory the temperature, to include CIP system and to access to clean and dirty spaces.

- Finally, after collection system, the FSP line included a conveying and packaging system in order to handle with the nanoparticles avoiding contact with the operator or ambient. This system mainly consists of a suction shoe, a conveyor with Washing In Place equipment, a buffer vessel and a bin filling station. Nanoparticles are sucked from the suction shoe into the buffer vessel via the pneumatic conveyor. From there, they are filled into plastic bags using a continuous liner filling head.

Figure 4. Conveying and packaging system

After design and construction of the different parts, the line was assembled in the facilities of Technological Centre Lurederra in Los Arcos (Spain) where tests runs were developed.

Assembly of the 5 kg/h industrial line was made progressively in order to ensure the suitable fixing of all the elements. The first elements which were placed in the line were the bag house filter as being the bigger elements defined the situation of the rest of the elements. Once located the bag house filters, the off gas piping was installed. Next step was the installation of all the feeding lines for liquids and gases. After this, burner chamber, including the FSP reactor and air cooling piping were installed. In Figure 5, it can be seen the evolution of the line assembled.

Other elements which were also assembled in the line were the carbon filter for treatment of organic vapours, a video circuit for monitoring of the flame, systems for taking sample in the production, etc.

In parallel to the mechanical installations of all the elements, the wired up of the line and electric connections of all the equipment, including sensors, valves, emergency pushbuttons, beacons, etc. were made.

Figure 5. Installation of filters, off-gas piping, platform, burner chamber and aerosol piping

The full industrial line was analysed in safety aspects for design and operation with a HAZOP methodology as described previously. In addition, a risk and hazard evaluation following the nanoparticles risk management system CENARIOS (Certifiable Nanospecific Risk Management and Monitoring System) was applied for the production of ZrO2 and CeO2 nanoparticles. This risk assessment concluded in the following recommended nano risk reducing measures for industrial production of nanoparticles with the line developed:

- Dust Mask P2: While working in the area is essential to wear a dust mask of the quality P2.
- Maintenance, Avoidance of leakages: A regular maintenance of all parts of the plant is obligatory. Special attention should be given to leakages to minimize contamination of the air.
- Surveillance of Air Contamination: Additional to the obligatory dust mask the air contamination should be monitored all the time. From a given concentration of hazardous substances the area should be evacuated. It is recommended to work out the thresholds together with local authorities.
- Protection clothes including protection glasses should be weared to avoid skin and eye contact. It is recommended to cover the whole skin effectively. If the skin is injured is recommended to avoid the working area. Especially at the filling, protection clothes are strongly recommended.
- Operation instructions: Operation instruction to ensure a safe use of the nanomaterials should be prepared carefully. Especially all safety measures should be written down. It should be mentioned that a cleaning of the working area is obligatory regularly. The hazard of different paths of incorporation should be considered. It should be mentioned that a cleaning of all

contaminated parts of the body, especially the hands after a stay in the working area is mandatory.

- Nanomaterial in a closed system: Though the most of the process is in a closed system, a release of nanomaterial cannot be excluded totally. Especially at the filter and at the filling of the bags, nanomaterial can be released. Nevertheless it should be guaranteed that the rest of the system is closed.
- Air exchange: As it is not possible the enclosure of the nanomaterials completely, an effective air exchange is recommended. As harm to the environment for the nanomaterials within the scope was not examined sufficiently it is recommended to filter the air to the outside.
- No staff on site during process: As especially for inhalation the risk is not negligible it is recommended that staff avoids the area while process running. If observation is necessary it is recommended to stay in a sheltered area. This is strongly recommended when zirconium oxide is produced.
- Regular cleaning: The working area should be cleaned carefully regularly. Visible contamination should be removed immediately. It is clear that for the cleaning staff protection clothes including gloves and protection glasses is obligatory.
- Air filter to the environment are designated in the given design. It is recommended to check regularly the function of these air filters. Measurements to demonstrate their appropriate function can be executed in coordination with local authorities.
- Low amount: Though many possibilities of contamination are given during the process, in regular operation mode – that means without any leakages, accidents and unwanted release – the amount released is low.
- Underpressure: To protect adjacent offices and labours it is recommended to place the production line in an area where it is possible to apply a slightly underpressure in the working area.

Finally, here, is presented the characteristics of the industrial FSP line developed in the project (Figure 6). This equipment allows a production capacity up to 5 kg/h of a wide range of nanoparticles including metal oxides, from simples to mixed and doped oxides, carbonates, phosphates, sulfates and noble metals.

Figure 6. Industrial FSP line with 5 kg/h production

Main strengths of the new system are:

- Industrial production capacity up to 5 kg/h of wide range of nanoparticles.
- Fully automated production line including a Programmable Logic Controller (PLC) and Human Machine Interface (HMI).
- Stirred tank for preparation and pre-heating of the precursor mixtures with a capacity of 150 l.
- Automatic use of the liquid feeding system for precursor, purge, pump priming with the use of automated valves which avoids the contact of the operator with the solvents and precursors.
- Filter bag-house system with two modules which can be used individually or in parallel allowing adapt the production capacity to the filter collection area for a range between 1-5 kg/h.
- Conveying and packaging system for nanoparticles storage and filling of bins avoiding the contact of the operator with the nanopowders.
- Monitoring of pressure in liquid and dispersion gas lines, liquid level, liquid and gas flow rates, temperature of liquid and aerosol stream, filter pressure drop, etc.

Production of nanoparticles (ZrO2) at 5 kg/h

The industrial FSP line developed in the project was used for the production of ZrO2 nanoparticles. Selection of production parameters was made based on CFD model predictions. Industrial productions were made with zirconium octoate 24 % in M.S. (CDR) in xylene. Capacity of the industrial line was checked by producing at 3 kg/h nanoparticles using only one filter chamber. After that a production was made with both filter chambers at 5 kg/h. The properties of the nanoparticle obtained are presented here:

ZrO2 nanoparticles-3 kg/h

Chemical Formula	ZrO2
Colour	White
Particle size range	15-25 nm

N_2 Physisorption:

The specific surface area of the powder analysed by N2 physisoprtion (BET) was 46.6 m2/g, indicating a primary particle size of 22.67 nm.

Transmission electron microscopy (TEM):

Images obtained from TEM shows the morphology and size distribution. Nanoparticles sizes are in the range of 20 nm or less, which indicate a result slightly inferior to BET calculations.

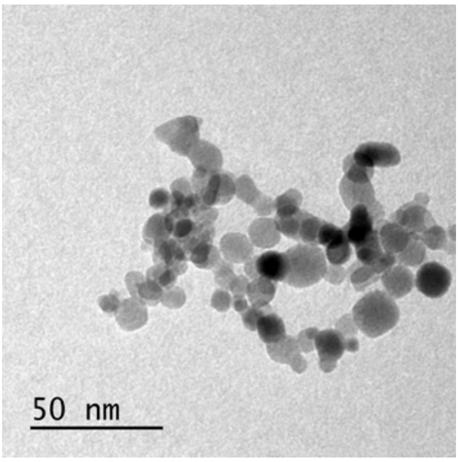


Figure 7. TEM of ZrO2 nanoparticles (3 kg/h)

X-Ray Diffraction:

The diffraction pattern in Figure 8 indicates the presence of a bimodal distribution with a 53 wt-% of crystalline tetragonal zirconia and a 47 wt-% amount of monoclinic Zirconium Oxide. There is no evidence to support the presence of any additional crystalline phases.

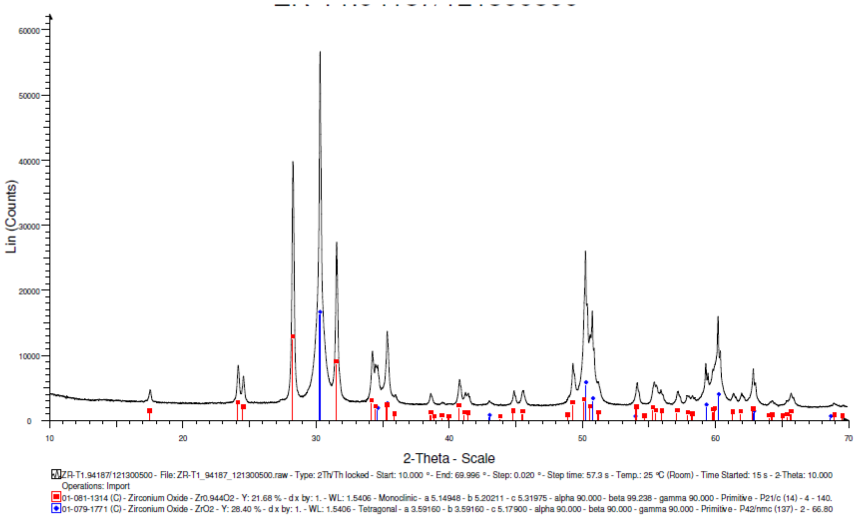


Figure 8. XRD of ZrO2 nanoparticles produced at 3 kg/h

Thermo gravimetric analysis (TGA):

ZrO2 produced nanoparticles has less than 1.0% moisture (Tª=150ºC) and around 1.77 % of carbon impurities (Tª=500ºC). Purity was also checked by loss of ignition test (300 ºC, 4 hours) and results showed a loss of weight of 1.10 % also according to TGA results.

ZrO2 nanoparticles-5 kg/h

Chemical Formula	ZrO2
Colour	White
Particle size range	15-25 nm

N_2 Physisorption:

The specific surface area of the powder analysed by N2 physisoprtion (BET) was 36.3 m2/g, indicating a primary particle size of 29 nm.

Transmission electron microscopy (TEM):

Images obtained from TEM shows the morphology and size distribution. Nanoparticles sizes are around 20 nm or slightly superior, which indicate a result slightly inferior to BET calculations.

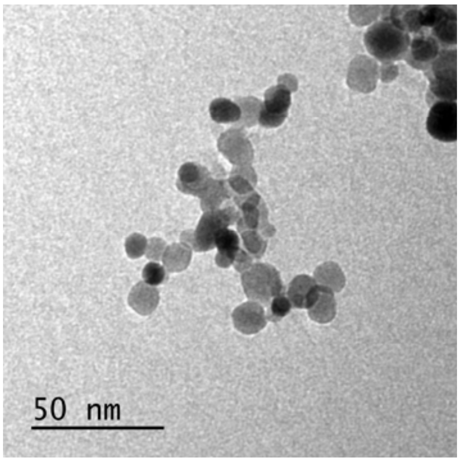


Figure 9. TEM of ZrO2 nanoparticles (5 kg/h)

X-Ray Diffraction:

The diffraction pattern showed that crystalline phases of ZrO2 are present.

Loss of ignition:

Purity was checked by loss of ignition test (300 ºC, 4 hours) and results showed a loss of weight of 0.89 %.

Characterizations developed for production tests at 3 and 5 kg/h indicate that the ZrO_2 nanoparticles obtained fulfill in a great way the objectives initially defined in the project. Nanoparticle sizes observed in TEM images demonstrate that the ranges of sizes are only slightly superior to the range of 10-20 nm defined at the beginning of the project. In addition, regarding purity objectives, in all cases, the carbon content of the nanoparticles produced is lower than 2 %, also defined as maximum in the project. Upscaling of the production from 100 g/h up to 5 kg/h has been developed successfully only with an increment of size of 10 nm. These results demonstrate the capability of the technology for production of high quality nanoparticles at large scale. In addition, upscaling strategies are extrapolable to other nanoparticles, as well as other precursor systems.

4. POTENTIAL IMPACT, DISSEMINATION & EXPLOITATION

Potential impact and exploitation

Impact on industrial competitiveness

The most important results of the project is the upscaling of Flame Spray Pyrolysis technology for the production of nanoparticles, demonstrating this process by the construction of a full industrial production line with a capacity up to 5 kg/h. These capacities have never been before achieved with this technology, so it represents a total advance in the field. Summed to the production capacity achieved, another important result has been that the nanoparticles obtained at industrial scale by the adjustment of the required conditions in FSP have similar properties than the ones which are synthesised at lab-scales. This is also a differential aspect from other technologies such as wet methods. In addition, it is important to consider that the industrial technology developed has been assessed in terms of safety of the production process and regarding nanoparticle handling incorporating the actions and recommendations needed in order to makes this technology able to the introduction in the market and industry.

The global market for nanomaterials is estimated at 11 million tonnes at a market value of €20 billion. However, the nanomaterials market is still dominated by materials which have been in use for decades, such as carbon black (mainly used in tyres) or synthetic amorphous silica (used in a wide variety of applications including tyres, as polymer filler but also in toothpaste or as anticoagulant in food powders). In the past years, many new nanomaterial-related applications have been developed. Those include a number of consumer products such as UV-filters in sun creams and anti-odour textiles. However, many medical and technical applications such as tumour therapies, lithium-ion batteries which can drive electrical cars, or solar panels also exist. Those applications have the potential to create major technological breakthroughs, and therefore in order to open the market for these applications, an industrial technology for its production has to be available. FSP, after the consecution of this project is set as a leading technology for production of nanoparticles.

In addition to the capacity of the new technology developed in the project, impact in ensured as it has been demonstrated the economic competitiveness in terms of production costs. Techno-economic analysis developed in the project based on the 5kg/h industrial production line developed have analysed the costs of the production of nanoparticles for ZrO_2. Comparing marketable prices of FSP produced ZrO_2 with other current commercial prices from competitors has been realised that nanoparticles with similar properties produced by FSP technology are more competitive. Prices found in competitors indicate that FSP technology can obtain at least a reduction of current commercial prices of 50 %. For ZrO_2 nanoparticles, the commercial calculated prices for this technology are in the range of 50-60 euros/kg. For other nanoparticles, the final price will depend finally of the cost of the metal precursor, which will depend on the scarcity of this material, but the trend will be maintained as well, obtaining reduced prices for FSP in comparison with other competitors.

Also, it has been noticed that FSP is not competitive when the nanoparticles can be synthesised by gas phase synthesis processes developed by Evonik, however, this is not an inconvenient as only very few oxides such as SiO_2, TiO_2 and Al_2O_3 are produced by this competitor technology. FSP technology is likely the most versatile technique known for production of nanoparticles, including very complex types, in a single step, of nearly all periodic table elements in the form of oxides, phosphates, carbonates or others, as well as complex multicomponent materials. In this way, this will be the main market of FSP technology reaching typologies which gas phase processes cannot reach. Indeed, as also concluded in the project regarding economic potential, the prices of nanoparticles made by FSP will be more competitive in comparison with other technologies when increasing the complexity of the composition, for example for mixed and doped oxides. Cost of production of these typologies for competitor technologies such as wet methods is considerably larger than for the simple oxides, as these technologies require an increased number of steps.

Socioeconomic impact on European Union

Conservative market estimates for metal oxide nanoparticles in 2020 are of 1663168 tons. In this way, the exploitation of the ADVANCE-FSP project results will allow to capture directly a large segment of the market. Additionally, success in the project will result in reinforcement of the European nanotechnology-based products industry, promoting the development of a diversity of multidisciplinary areas focused in research, development and commercialisation of new efficient and competitive applications. In addition, taking into account that the current direct employment in the nanomaterial sector in Europe is estimated at 300 000 to 400 000, introduction in the market of this production technology will also represent a considerable benefit in the society by the creation of new jobs.

Impact on environment

Flame Spray Pyrolysis technology has been assessed in environmental terms resulting in a considerably lower impact than other competitor technologies. Comparison with wet methods, more specifically sol-gel processes has been developed for ZrO2 nanoparticles. FSP process proved to be more environmental friendly than sol-gel processes as depicted by LCA analysis for the same production capacity. The total environmental impact of the production of 5 kg of ZrO2 nanoparticles by FSP quantified in terms of Ecopoints and kg of CO2 equivalent respectively was 12.5 EcoPt and 191 Kg of CO2 equivalent, while for sol-gel process, this quantity amounted to 49.3 EcoPt and 626 Kg of CO2 equivalent. Mainly, the large volumes of solvents required for sol-gel synthesis resulted in larger impact than FSP processes.

To summarise the potential impact of the ADVANCE-FSP projects are:

- Development and validations at industrial scale of a nanoparticle production technology with demonstrated competitiveness regarding costs and quality of the nanoparticles produced.
- Potential increase of final applications of nanotechnology by the development of an industrial technology for production and commercialisation of a very wide range of different typologies of nanoparticles.
- Increase competitiveness of nanotechnology market in Europe and potential increase of related employment.
- Development of production technologies for nanoparticles with low environmental impact and following safety considerations in the design of the equipment, operation procedures and specific related nano-risks.

The overall objective is to maximize the uptake of the project results and potential impacts by the commercialisation and exploitation of the results. There are two main sectors that are targeted in the commercialisation strategy: the academic research community working on the use of the computational code and the methods for on-line characterization of the flame where main sector of application will be companies producing nanoparticles, environmental fine particle emission and also for research work and the commercial companies which have worked in the design of equipment or in the upscaling of industrial production.

Main dissemination activities

A project identity set consisting of the project logo as well as the ADVANCE-FSP website (http://www.advance-fsp.eu/) was created at the beginning of the project in 2010 and updated with data from all the partners.

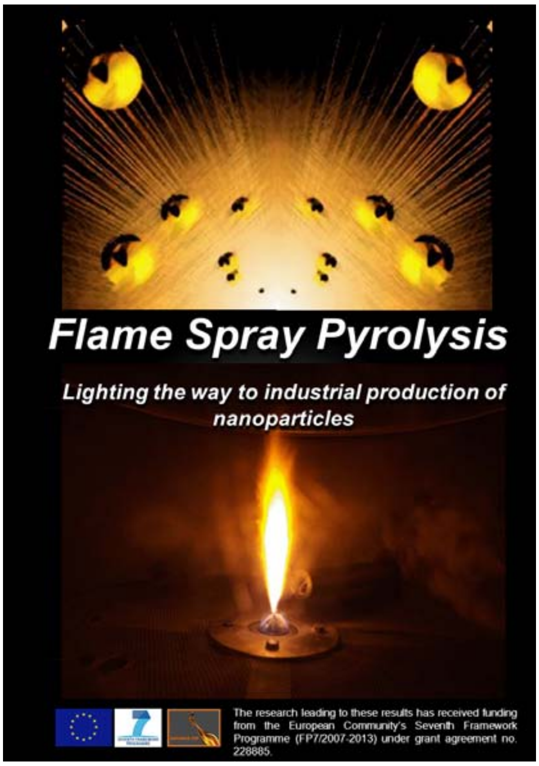
Articles were published at the beginning of the project in the popular press in order to let know the project in economic newspapers of the region of the coordinator: Nueva Gestión, Negocios en Navarra, etc.

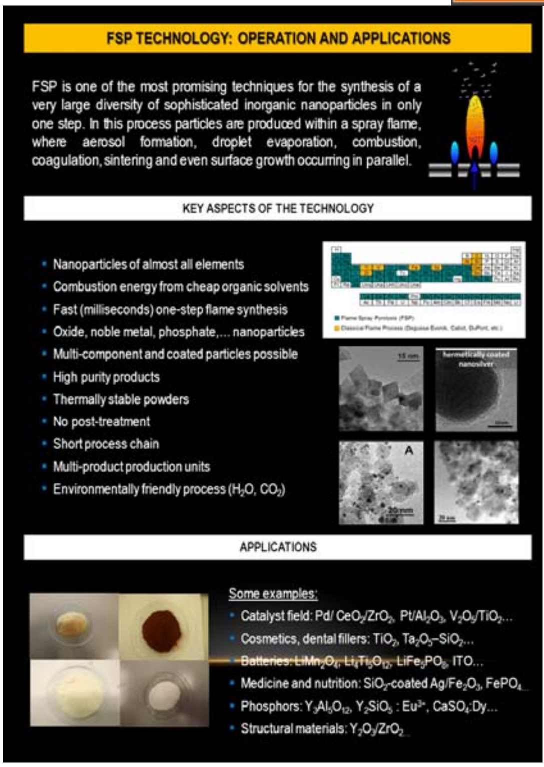
In addition during the project, posters and oral presentations were made by the project partners at different conferences in Europe (Portugal, Zurich, Nuremberg, Duisburg, Prague, Kreta, Bremen), USA (Minneapolis, Santa Clara, Pittsburgh, Boston, Portland and San Francisco) and in China (Shenzhen).

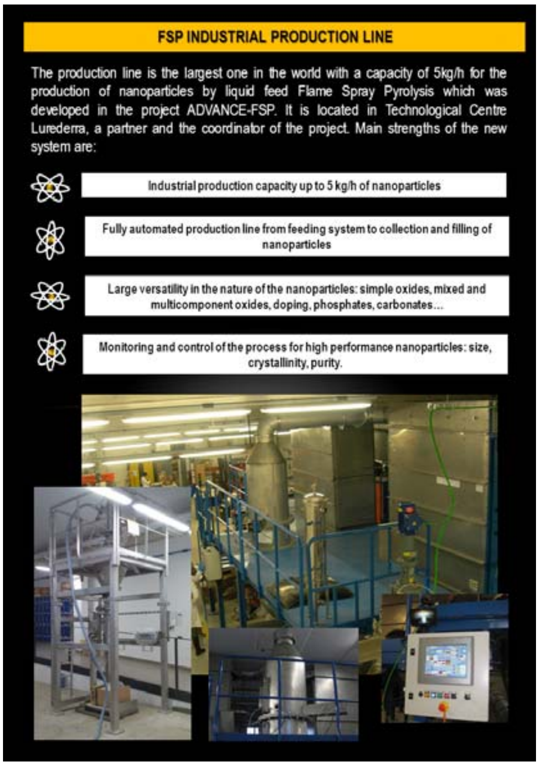
Two workshops were hold in Los Arcos (Spain) in the beginning and at the end of 2013 in order to promote the applications of nanoparticles as well as the potential of the Flame Spay Pyrolysis technology. Second workshop was held in order to present the new industrial line constructed to interested groups, making a demonstration of the operation.

Workshops held in Technological Centre Lurederra (Los Arcos)

Divulgation of information was made also through preparation of brochures containing primarily characteristics of the technology developed and the industrial line constructed.







Brochures for dissemination of Flame Spray Pyrolysis technology

In addition, publications in well-known international papers were made by the partners of the project. The following scientific papers have been published already or are pending to be published in the short term:

Arto J. Gröhn, Beat Buesser, Jorma K. Jokiniemi, and Sotiris E. Pratsinis. Design of Turbulent Flame Aerosol Reactors by Mixing-Limited Fluid Dynamics. Ind. Eng. Chem. Res. 2011, 50, 3159–3168.

Karsten Wegner, Björn Schimmoeller, Bénédicte Thiebaut, Claudio Fernandez and Tata N. Rao. Pilot Plants for Industrial Nanoparticle Production by Flame Spray Pyrolysis. KONA Powder and Particle. 2011, 29, 251-265.

Arto J. Grohn, Sotiris E. Pratsinis, Karsten Wegner. Fluid-particle dynamics during combustion spray aerosol synthesis of ZrO2. Chemical Engineering Journal. 2012, 191, 491– 502.

M.L. Eggersdorfer, A.J. Gröhn, C.M. Sorensen, P.H. McMurry, S.E. Pratsinis. Mass-mobility characterization of flame-made ZrO2 aerosols: Primary particle diameter and extent of aggregation. Journal of Colloid and Interface Science. 2012, 387, 12-23.

H. Torabmostaedi, T. Zhang, P. Foot, S. Dembele , C. Fernandez. Process control for the synthesis of ZrO2 nanoparticles using FSP at high production rate. Powder Technology, 2013, 246, 419-433.

H. Torabmostaedi , T. Zhang. Effect of nozzle geometry and processing parameters on the formation of nanoparticles using FSP. Chemical Engineering Research and Design, 2014 (In press).

H. Torabmostaedi , T. Zhang. Computational study of the effect of processing parameters on the formation and growth of ZrO2 nanoparticles in FSP process. Chemical Engineering and Processing, 2014, 78 1-10.

H. Torabmostaedi, T. Zhang. Optimization of quenching efficiency in flame synthesis of ZrO2 nanoparticles at industrial scale production rate by CFD. Particuology 2014 (In press).