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OASIS

Open Access Single entry point for scale-up of Innovative Smart lightweight composite materials and components

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Catalogue of Up-graded performances for Pilot Lines for nanoscale structures (nanomaterials) in unprocessed form with intrinsic functionalities

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DISCLAIMER

Executive Summary

This deliverable (DEL D1.5) describes the upgrade of the 3 pilot lines (PLs) for *nanoscale structures* (nanomaterials) in unprocessed form with intrinsic functionalities products:

- **PL1: FUNCTIONALISED NP.** (SIO_2 NANO REINFORCED AEROGELS. Functionalised nanoparticles), owned by UCLM.
- **PL2: NANOWET.** (Wet chemical nanoparticles and nanomaterials syntheses), owned by CEA.
- **PL3: NANOCOMPOSITES.** (Magnetic and flame-retardant nanoparticles and nanocomposites), owned by FhG.

This deliverable describes:
- The purpose of each pilot line and the needs for the upgrade/upscale.
- An overview of the upgrade/upscale for each pilot line. Some insights on what the pilot lines can offer in terms of production and processing.

The delay in this deliverable was due to the COVID-19 crisis, which had stopped all activities in some of the PLs for few months.

Table of Contents

1. Content of the Deliverable

This deliverable DEL D1.5 is focusing on the development of a catalogue of up-graded performances for PLs for nanoscale structures (nanomaterials) in unprocessed form with intrinsic functionalities (FUNCTIONALISED NP. by UCLM, NANOWET by CEA, NANOCOMPOSITES by FhG).

Each one is described by an overview of the upgrade/upscale and the capability of the facilities within the OASIS OITB.

2. Objectives of the upgrade/upscale for the PLs for the nanoscale structures (nanomaterials) in unprocessed form with intrinsic functionalities.

The vision of OASIS is an ecosystem of 12 nanotechnology manufacturing pilot lines (PLs), operating under a common and demanding umbrella of Sustainable Production (OASIS framework). It aims at ensuring a competitive, quality, safe and environmentally friendly production, of nano-enabled products in compliance with the applicable regulation.

One major task of WP1 aims at upgrading the 12 PLs integrated in OASIS OITB to meet industrial needs:

- Upgrade of the 3 pilot lines for *nanoscale structures* (nanomaterials) in unprocessed form with intrinsic functionalities.
- Upgrade of the 5 pilot lines for *intermediate products* with nanoscale features.
- Upgrade of the 4 PLs for *nano-enabled products.*

This deliverable DEL D1.5 is focusing on the upgrade of the three PLs for *nanoscale structures* (nanomaterials) in unprocessed form with intrinsic functionalities:

- **PL1: FUNCTIONALISED NP.** (SiO_2 NANO REINFORCED AEROGELS. Functionalised nanoparticles), owned by UCLM.
- **PL2: NANOWET.** (Wet chemical nanoparticles and nanomaterials syntheses), owned by CEA.
- **PL3: NANOCOMPOSITES.** (Magnetic and flame-retardant nanoparticles and nanocomposites), owned by FhG.

The KPIs for the upgrade of the three PLs for *nanoscale structures* (nanomaterials) in unprocessed form with intrinsic functionalities in Table 1.

The upgrade of the pilot lines related to the intermediate products with intermediate products with nanoscale features and nano-enabled products are presented in DEL D1.6 and D1.7, respectively.

	UPSCALING: Production rate	UPGRADING: In-line control target
Nanomaterials	**PL#1. Functionalised NP**. SiO_2 Nano-reinforced Aerogels. Functionalised nanoparticles. Functionalities: thermal insulation	
	Current production rate 0.36 m^2/batch in 4 days	In-line humidity measurements to enable monitoring of the drying process to achieve time effectiveness of the process
	OASIS target 2.16m^2/batch in 4 days	
	PL#2. Nanowet. Wet chemical nanoparticles and nanomaterials syntheses. Functionalities: tracing, thermal/electrical conductivity.	
	Current production rate 10 L/day reaction in water or organic solvents	20 nm to 1 mμ analysis of nanoparticles to enable accurate in situ monitoring of the synthesis. Upgrading of the reactor (cryostat, pump and agitating system) to enhance volumetric productivity and fine control of the reaction
	OASIS target 25 L/day semi-continuous processes	
	PL#3 Nanocomposites. Magnetic and flame retardant nanoparticles and nanocomposites. Functionalities: Inductive heat, Flame, corrosion-inhibition	
	Current production rate 5 kg/hour batch	Nano-building blocks: 5 to 100 nm Supraparticles: 0,5 – 50 μm
	OASIS target 10kg/hour Half continuous processing	

Table 1. KPIs of nanoscale structures (nanomaterials) in unprocessed form with intrinsic functionalities.

3. Upgrade of the 3 pilot lines for *nanoscale structures* (nanomaterials) in unprocessed form with intrinsic functionalities

OASIS	**Datasheet for pilot lines- FUNCTIONALISED NP**
OITB Member	University of Castilla La-Mancha
Name of Pilot line	Functionalised NP SiO_2 Nano Reinforced Aerogels Functionalised Nanoparticles
Number of the Pilot Line	PL1
TRL of pilot line	TRL6

Description of the pilot line:

The pilot line consists in a semi-industrial Freeze-Dryer (Fig.1) that permits to obtain aerogel panel materials with exceptional properties such as: ultra-light density (<80 kg/m^3), high porosity and low thermal conductivity (<0.05 W/m·K). The porous material is firstly frozen and consequently sublimated under vacuum by a primary and secondary drying process. The pilot line is a compact unit with casters, constructed in a steel stove-enameled cabinet. It is equipped with a vial stoppering and spacing device, isolation valve chamber to condenser, micro suite software and a vacuum pump with exhaust filter. The system permits to control the freeze-dryer functions by a Human Machine Interface that offers: i) information about system elements such as: valves, motors, indicator, ii) output alarm information, iii) modifying the parameters of the freeze-dryer cycle, iv) protecting the system from unauthorized use and v) recipe development. As well, a vacuum sensor is in the chamber to control the pressure of the product environment, enabling the evaluation of the final scale-up results. To fully understand the physicochemical properties of the final product is possible to monitor the experimental conditions. Additionally, this opportunity allows controlling and improving the energy consumption during the freeze-drying process.

Picture

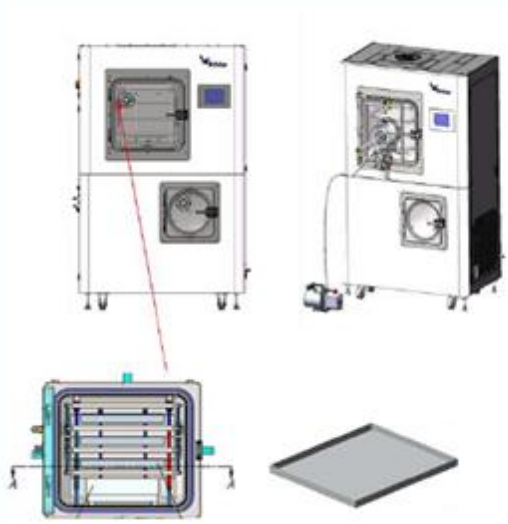


Fig.1 Freeze-drying Pilot Line. Lyobeta 6PL.

Features of the Pilot Line

Input material	Up to 21,600 mL
Output/Yield material	Up to 2 m^2 of material/batch
Production time	4 days
Energy consumption	170 kW·h
Name of the Process	Freeze-drying process
Keywords of the process (max.5)	Quality control, Sustainable process
Keywords of the product (max.5)	Ultra-light material; high thermal insulating material; high porous material
Technological offer	Develop of innovative materials; optimization of synthesis conditions; obtain experimental data that allow to model and simulate the process at industrial scale
Operating mode	Automatic; semi-automatic and manual
Language	English; Spanish and French

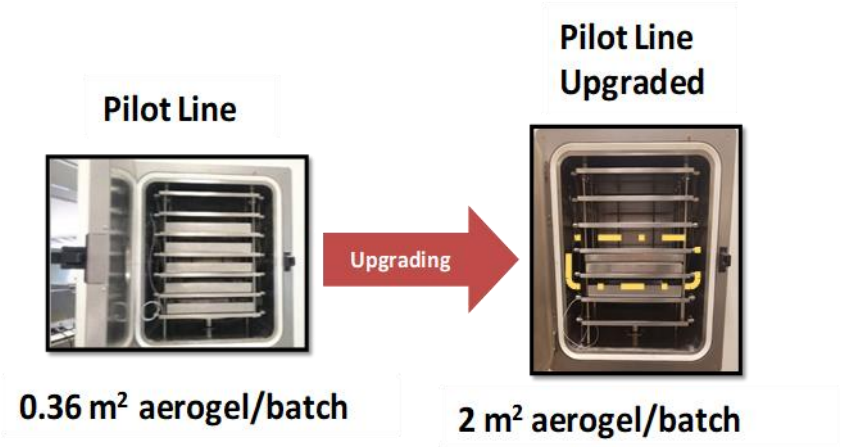
<table>
<tr><th colspan="2">Upgraded Technology</th></tr>
<tr><td>Parameters of the process</td><td>1. Installation of the Lyologger software for data supervision, control, and data acquisition in order to control the different operational variables during the process.
2. Installation of Pirani and MKS Baratron type 626 devices to detect the end of the primary drying process and consequently upgrading de energy production.
3. Upgrading production of the final aerogel panels per batch (Fig.2).
4. Installation of an apparatus to measure the energy consumption of the process (Fig.3 left), saving up to the 50% of the total energy used (Fig.3 right).</td></tr>
<tr><td>KPI achievement</td><td>1. Production from 0.36 to 2 m^2 of aerogel/batch
 

Fig.2 Upgrading production of the resulting aerogel amount per batch.

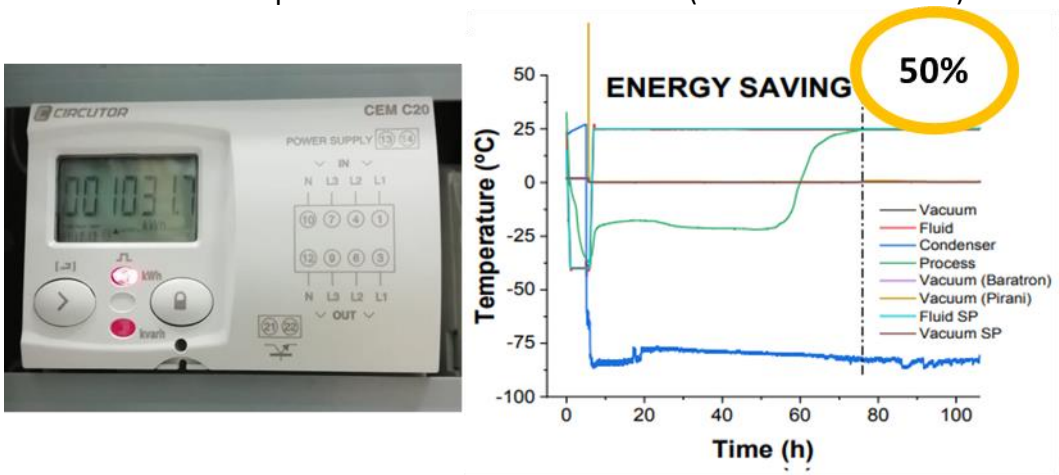
2. Saving of the energy consumed up to 50%. At the moment, the energy consumed is optimized from 330 to 170 kW·h (50% at the moment).
 

Fig.3 Apparatus to control the energy consumed during the freeze-drying process and energy saving figure with the different operational parameters.</td></tr>
</table>

OASIS	**Datasheet for pilot lines- NANOWET**
OITB Member	CEA
Name of Pilot line	SYNTHETIC NANOPARTICLES AND NANOMATERIALS FOR NANO-REINFORCEMENTS
Number of the Pilot Line	PL2
TRL of pilot line	TRL5

Description of the pilot line:

The PL2 is composed of 3 main items: a large unit of connected reactors for semi-continuous process (Fig.4), an *in situ* monitoring probe by UV/vis spectroscopy (Fig.5) and an automated semi-industrial freeze-dryer with process control interface (Fig.6). Overall, The PL2 gathers tools for synthetic chemistry in solution, including synthesis, separation and purification processes. Mainly dedicated to the synthesis of nanomaterials and associated advanced materials, the PL2 is operating in a secured environment to ensure best practices for the fabrication and handling of nanoparticles, mainly in solution. Exploiting this PL2, the synthesis of a large panel of nanomaterials can be considered such as oxides (ZnO, SiO_2, TiO_2, Al_2O_3…), carbides (TiC, SiC, B_4C…), and metals (Ag, Cu, Au nanowires). Coatings by oxidation reaction, grafting procedures and electroless deposition protocols may also be carried out to produce core-shell nanoparticles with high benefit to be incorporated in diverse matrices.

The unit for large-scale nanoparticle synthesis consists in two 20 L connected reactors with injection by dosing pump (Fig.4). Furthermore, 10 L and 5 L reactors are available for disposing of the adequate volumetric productivity. Advanced control of the synthetic parameters such as temperature with the cryostat, injection/flow with the pump (maximum flow 85 L/h) and mechanical stirring with motorized system enhance volumetric productivity, fine control of the reaction and limit the coproduction of undesired side-products. Moreover, the present unit offers improvements of the reaction yields and of the well-defined nanoparticles' mean size. The Julabo 1000F circulator is intended for temperature control applications of liquid media. Working temperature ranges from –40 °c up to 200 °C for the latter equipment presenting the following dimensions: 42 x 49 x 70 cm (W x D x H). The RW 20 digital overhead stirrer is used for mixing or stirring liquids with low to high viscosity (maximum 10 Pa.s) by using various stirring tools available in the laboratories. The operating speed ranges from 60 to 2400 rpm with a speed setting accuracy of 1 rpm.

Pictures

Fig.4. Unit of large connected reactors (20 L on the left, 10 L on the right).

Fig.5. The AGILENT CARY 60 UV/vis spectrophotometer

Fig.6. Semi-industrial Freeze-dryer unit

Features of the Pilot Line	
Input material	Nanopowders (*e.g.* Al_2O_3 / TiC /SiC / ZnO) or nanomaterials precursors
Output/Yield material	25 L/day of nanoparticles / coated nanoparticles / nanowires / core-shell nanoparticles / phosphors / hollow nanoparticles
Production time	Typically, a few hours - one day (in progress)
Energy consumption	To be determined
Name of the Process	Synthetic nanoparticles and nanomaterials for nano-reinforcements
Keywords of the process (max.5)	Quality control, Sustainable process, Wet-end chemistry, Coatings, Nanoparticles
Keywords of the product (max.5)	Core-shell, nanomaterials, dimension control, nanopowders, well-dispersed
Technological offer	The pilot line 2 gathers tools for synthetic chemistry in solution, including synthesis, separation and purification processes. Mainly dedicated to the synthesis of nanomaterials and associated advanced materials, the pilot line 2 is operating in a secured environment to ensure best practices for the fabrication and handling of nanoparticles, mainly in solution. Exploiting this pilot line 2, the synthesis of a large panel of nanomaterials can be considered such as oxides (ZnO, SiO_2, TiO_2, Al_2O_3…), carbides (TiC, SiC, B_4C…), and metals (Ag, Cu, Au nanowires). Coatings by oxidation reaction, grafting procedures and electroless deposition protocols may also be carried out to produce core-shell nanoparticles with high benefit to be incorporated in diverse matrices.
Operating mode	Manual
Languages	English and French.

Upgraded Technology	
Parameters of the process	1. *Large connected reactors*: two 20 L connected reactors with injection by dosing pump (pump flow max. 85 L/h) with 10 L and 5 L side reactors 2. *In-situ monitoring*: accurate UV-vis spectrophotometer Agilent Cary 60 UV-Vis with fibre optic probe (working at 190-1100 nm) with fast data collection 3. *Nanopowder drying*: automated freeze dryer with process control interface from Cryotec for non-aggregation of nanoparticles
KPI achievement	1. Production unit for nanoparticles synthesis, separation and purification processes up to **25 L batch with 500 g of nanoparticles** per day. Previous process could deliver 30- 40 g per batch for a 5 L reactor ✓ 2. **In-line** nanoparticle doping **analysis by UV/vis spectroscopy** ✓ 3. ***In-situ* detection of optical properties** informing the operators on the **size of the nanoparticles** and thus allowing **perfect control during the production** at large scale and **repeatability with very low deviation figures** ✓ 4. **Automated freeze-drying unit** allowing the **production** of large amounts **of dried nanopowder** by sublimation process **without exhibiting aggregation** ✓

OASIS	**Datasheet for pilot lines- NANOCOMPOSITES**

OITB Member	Fraunhofer ISC
Name of Pilot line	Nanocomposite: Magnetic and flame-retardant nanoparticles and composites
Number of the Pilot Line	PL3
TRL of pilot line	TRL 5-6

Description of the pilot line:

The modular pilot line PL 3 is an open access infrastructure for companies, which was implemented for the production of high quality (multi-)functional nanocomposites (supra-particles) on a pilot scale. Essential elements of the pilot line in Wuerzburg are the particle synthesis in batches up to 100 liters (5 kg of nanoparticles per hour), modification and separation methods such as semi-continuous operating centrifuge and in-line analysis and techniques for the uniform and agglomeration free incorporation of nanoparticles into composites. The 100 L reactor can be stirred, fast heated, fast cooled and also used under reflux. It is also possible to apply pressure and low vacuum to the reactor. Complimentary to this high volume batch reactor, continuous reactions can be carried out in an ultrasonic dispersion / reaction unit. Supplementary to the semi continuous centrifuges, lab to technical scale spray-dryers can be used for separating particles from the solvent.

Picture

Fig.7 Modular pilot line PL3: 100-Liter batch reactor; half-continuous centrifuge; magnetic drum separator; spray-dryer

Features of the Pilot Line	
Input material	Up to 100 L
Output/Yield material	Up to 10 kg of material/h
Production time	1-5 day
Energy consumption	5 - 50 kW·h
Name of the Process	Synthesis, Separation, Spray-drying
Keywords of the process (max.5)	Wet chemical synthesis, Sustainable process
Keywords of the product (max.5)	Nanoparticle, Supraparticle, Flame retardant, Inductive heatable additive
Technological offer	Up-scaling of wet chemical nanoparticles synthesis; Combination of nanoparticles to multifunctional supra-particles; Flame retardant and inductive heatable additives
Operating mode	semi-automatic and manual

Language	English; German

Upgraded Technology	
Parameters of the process	1. Inert-loop for spray drying of flame able solvents. 2. Ultrasound nozzle for spraying micro-particles. 3. Continuous heating equipment for magnetic particles synthesis
KPI achievement	1. Continuous production of magnetic nanoparticles for inductive heating and fast curing during pultrusion.

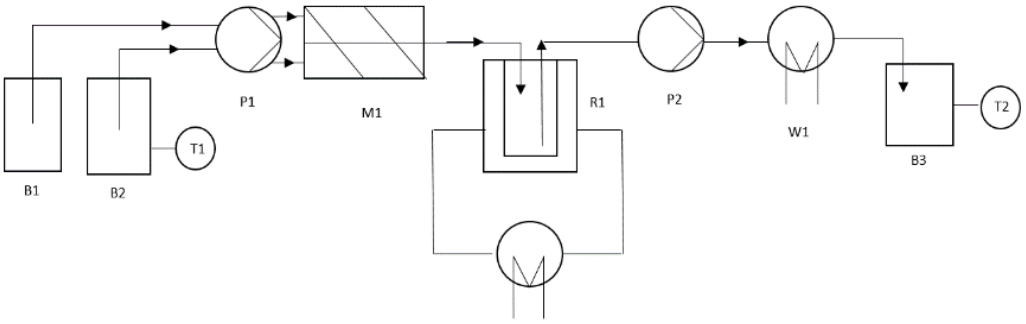


Fig.8 Flowchart of the upgraded continuous production of the magnetic particle synthesis.

2. Wastewater and solvent-savings (~20%) installment of an inert-loop to the spraydrying equipment.

Fig.9 Spray-dryer with an inert-loop

4. Conclusions

These pilot lines are part of an ecosystem of 12 nanotechnology manufacturing pilot lines, providing nanomaterials, nano-intermediates, nano-enabled products and associated services for the development and commercialization of lightweight multifunctional products based on aluminium and polymer composites.

The up-graded performances for PLs for nanoscale structures (nanomaterials) in unprocessed form with intrinsic functionalities have successfully been performed. The pilot lines are fully operational and ready to start the democases' development. This document can be used as a public catalogue of technical information from the PLs for the Single Entry Point (SEP). The OASIS Open Call will provide free access to all successful applicants in which the winners of the Call will benefit from the upgraded facilities.

Additionally, this public catalogue of technical information reflects a state of the PLs from the OASIS project for dissemination purposes (WP7).

5. Degree of Progress

This deliverable is a 100% complete

6. Dissemination Level

This deliverable is public.

7. Appendix

The presentation of the Up-graded performances for PLs for nanoscale structures (nanomaterials) in unprocessed form with intrinsic functionalities are presented:

liten cea tech

PL2. SYNTHETIC NANOPARTICLES AND NANOMATERIALS FOR NANO-REINFORCEMENTS

OASIS

TECHNOLOGICAL OFFER

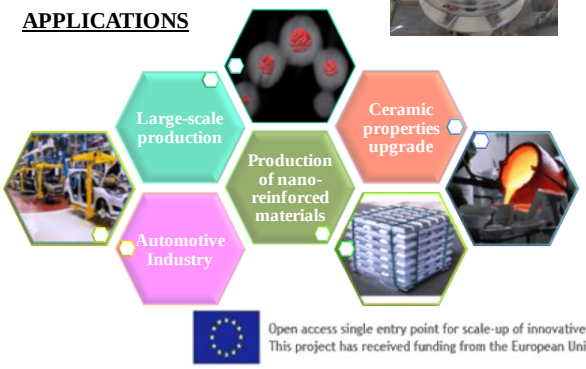
The Pilot Line can be used to:

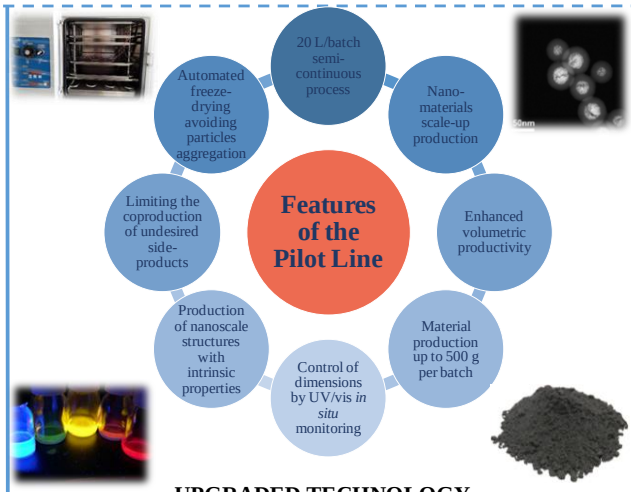
- Perform large-scale synthetic chemistry.
- Control the key synthesis parameters "in line".
- Develop advanced nanoparticles and nanomaterials.
- Ensure high-quality production of nanomaterials in compliance with the applicable regulations.

COMPETITIVE PRODUCTS

- Nanoparticles large-scale production.
- Coating/Encapsulation improving matrix incorporation.
- Properties enhancement.
- Synthesis repeatability.

APPLICATIONS





UPGRADED TECHNOLOGY

- *Large connected reactors*: two 20 L connected reactors with injection by dosing pump (pump flow max. 85 L/h) with 10 L and 5 L side reactors.
- *In-situ monitoring*: accurate UV-vis spectrophotometer Agilent Cary 60 UV-Vis with fibre optic probe (working at 190-1100 nm) with fast data collection.
- *Nanopowder drying*: automated freeze dryer with process control interface from Cryotec for non-aggregation of nanoparticles.

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Fraunhofer ISC

PL3. NANOCOMPOSITES: MAGNETIC AND FLAME RETARDANT NANOPARTICLES AND COMPOSITES

OASIS

TECHNOLOGICAL OFFER

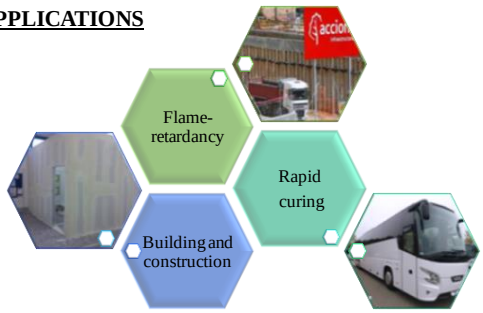
The Pilot Line can be used to:

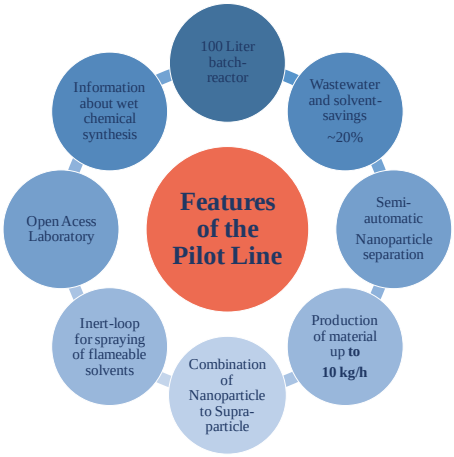
- For wet chemical synthesis of nano- and micro-particles.
- Upscailing of wet chemical synthesis.
- Separation of magnetic and non magnetic nanoparticles.

COMPETITIVE PRODUCTS

- Inductive heatable additives.
- Flame retardant additives.
- Combined additives through supra-particle design.

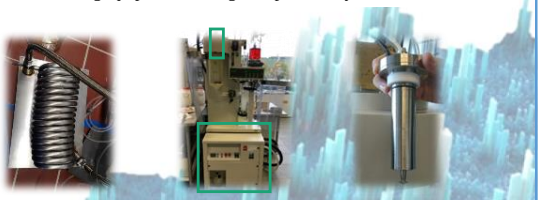
APPLICATIONS





UPGRADED TECHNOLOGY

- Inert-loop for spray drying of flame able solvents.
- Ultrasound nozzle for spraying micrometer particles.
- Continuous heating equipment for magnetic particles synthesis.



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