

# SPRAY DRYING OF ENERGETIC MATERIALS BY THE EXAMPLE OF AMMONIUM NITRATE AND AMMONIUM DINITRAMIDE

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## **Abstract**

Spray drying technology is a method of producing high-quality particles from solutions, emulsions or suspensions on an industrial scale. The gentle process is preferably used in the processing of sensitive substances from the food, pharmaceutical and chemical industries. Advantages are in particular the moderate process temperatures and the low mechanical load on the products. Due to the continuous processing, only small quantities of products are in the direct processing zone. These advantages in terms of quality and safety were transferred to the processing of energetic materials through the conception and procurement of a combined spray drying and spray congealing process at Fraunhofer ICT. By varying spray formation, process temperatures, solvents and solids concentrations, product properties such as particle size and morphology can be influenced. The continuous process control offers the possibility of sample production on a 100 g scale up to production on a technical scale of several kilograms per day.

For the safe processing of propellants and explosives, the following additional features have been implemented: explosion protection in accordance with ATEX, closed inert gas operation with nitrogen, solvent resistance, solvent recovery, remote control and installation of the process unit in a safety working area.

The spray drying plant was applied for two oxidizers used in solid propellants. By the example of phase stabilized ammonium nitrate (PSAN) the feasibility of the process was proofed. The processing of ammonium dinitramide (ADN) showed some well-known challenges. The transferability of this manufacturing technology for particulate products to numerous other oxidizers and explosives is realistic from the technical point of view.

## **Motivation**

Particle technology of energetic materials is based on generation, production, refining and characterization of particulate products. These intermediates were applied in propellant, explosive or pyrotechnical formulations. Concerning the generation of particles the particle size, the morphology and the purity are of major interest.

Spray drying and spray congealing are well known processes for food, chemical and pharmaceutical applications [1, 2]. The goal of this work is to transmit this particle processing technologies to energetic materials like oxidizers and explosives.

## **Spray Drying and Spray Congealing Processes**

The basics on spray drying are described by Anandharamakrishnan et al. [1] and Vehring et al. [3]. The spray congealing process is described by Winters et al. [2]. These two types of spray processes are considered for the application of energetic materials. Figure 1 shows both principles. The liquid feed may be a solution or a melt of the solid product. This liquid is pumped to a nozzle system where it is atomized and liquid droplets are generated. In case of a solution, the solvent is evaporated in a hot process gas, whereas the solid part is remaining as particles. In case of a melting, the droplets are congealing in a cold process gas, whereas the particles retain the same volume and shape as the melt.

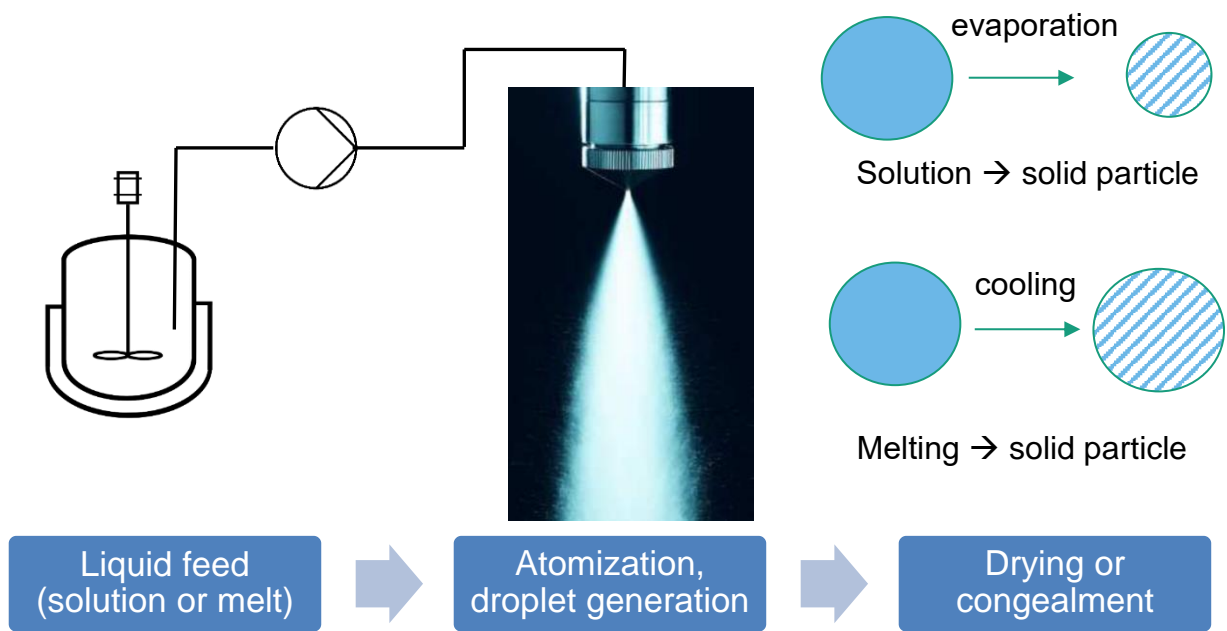


Figure 1: Principle of particle formation with spray processes, picture taken from [4]

Concerning the particle generation of energetic materials from a solution (spray drying) or from a molten stage (spray congealing) the process characteristics of the ICT pilot plant are listed in table 1.

Table 1: Process characteristics of spray drying vs. spray congealing

Spray drying	Spray congealing
Solutions of energetic materials (with variable solid concentration)	Molten energetic materials
Low temperatures of the solutions (feed)	High temperatures of the melt (feed)
High temperature of the process gas (evaporation of the solvent)	Low temperature of the process gas (cooling of the atomized melting)
Moderate risk	Higher risk
Short-term thermal stress	Longer thermal stress

Batch process, scale-up is possible by semi-continuous processing	Batch process, preparation and handling of melt is challenging
Smaller particles are producible by low solid concentrations of the solution	Particle size is predicted by the droplet size of the atomized melt
Compact or spherical particle morphology, determined by the evaporation of the solvent	Spherical particle morphology

Due to environmental reasons (solvent recovery) and safety reasons (inert gas process), a closed loop process, as it is schematically depicted in figure 2, is preferable.

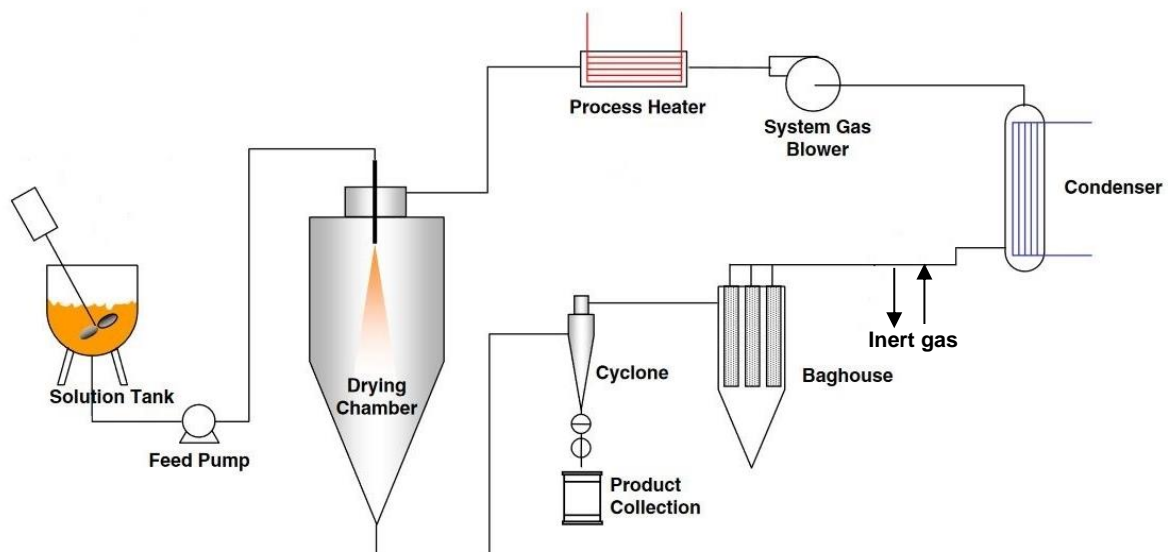


Figure 2: Closed loop plant for processes with organic solvents, modified picture from Dobry et al. [5]

### Combined Process Unit

A combined pilot plant for spray drying and optionally for spray congealing was established at Fraunhofer-ICT. The closed loop process unit (Fa. VetterTec, type SDL 02) is shown in figure 3.



Figure 3: Spray tower (left) and solvent recovery system (right)

The following process characteristics are realized:

- Combined pilot plant: spray drying / spray congealing
- Suitable to generate particles from solvents, suspensions and melts
- Batch size: 100 g up to kg-scale
- Process temperatures up to 250°C
- Variable atomization systems (top-spray, bottom-spray, rotation atomizer)
- Target particle size range: Spray drying 1 – 200  $\mu\text{m}$ , spray congealing 20 – 150  $\mu\text{m}$
- Equipment features: ATEX, closed loop of inert process gas, solvent recovery, remote control
- CIP (cleaning in place)
- Solvent resistant
- Suitable for processing energetic materials and dangerous goods

## Experiments and Results

The experiments were conducted with typical oxidizers for rocket propellants. We started our experiments with the setup for spray drying. First, we used an aqueous solution of ammonium nitrate with 7 % potassium nitrate for phase stabilization. The goal was to produce phase stabilize ammonium nitrate (PSAN) from a solution and not as usual from a melt [6].

The total amount of solid was 20 %. The process gas temperature was 150 °C. The feed rate was about 2 kg/h. Figure 4 shows the particle size distribution of the spray dried product with a mean particle size of 48 µm, measured by laser diffraction spectroscopy (Malvern Instruments, type Mastersizer 2000). Figure 5 shows a SEM picture of the product.

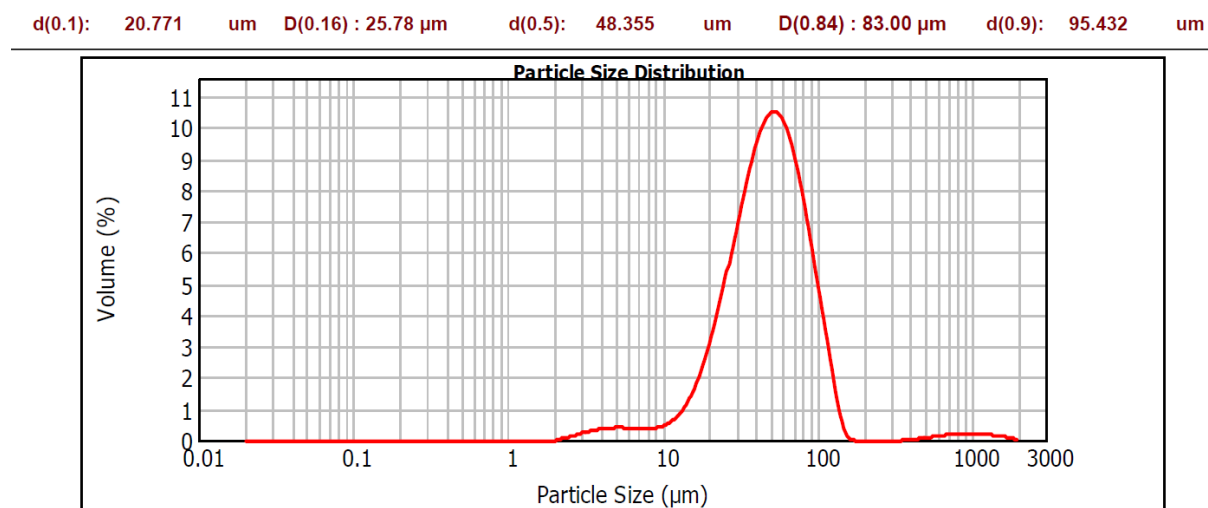


Figure 4: Particle size distribution of spray dried PSAN with 7 % potassium nitrate

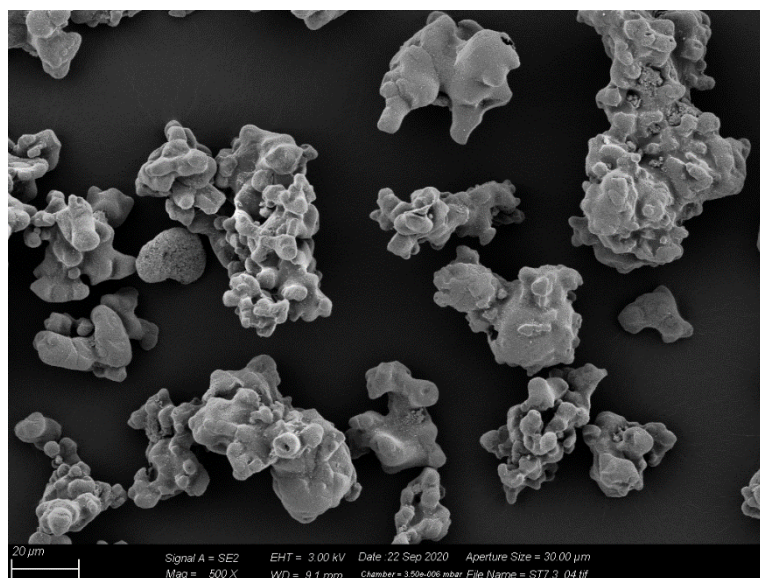


Figure 5: SEM picture of spray dried PSAN with 7 % potassium nitrate

Figure 6 and 7 show the thermal analyses by DSC (differential scanning calorimetry, TA Instruments, type Q2000) of the spray dried and phase stabilized product and as comparison the DSC-plot of pure ammonium nitrate. The phase stabilized ammonium

nitrate has no phase transition below 100 °C as it is typical for products with 7 % potassium nitrate. For comparison, the pure ammonium nitrate has a phase transition at about 53 °C. This phase transition is unfavourable as it is accompanied by a density change [6] at a moderate temperature that may be exceeded occasionally during storage.

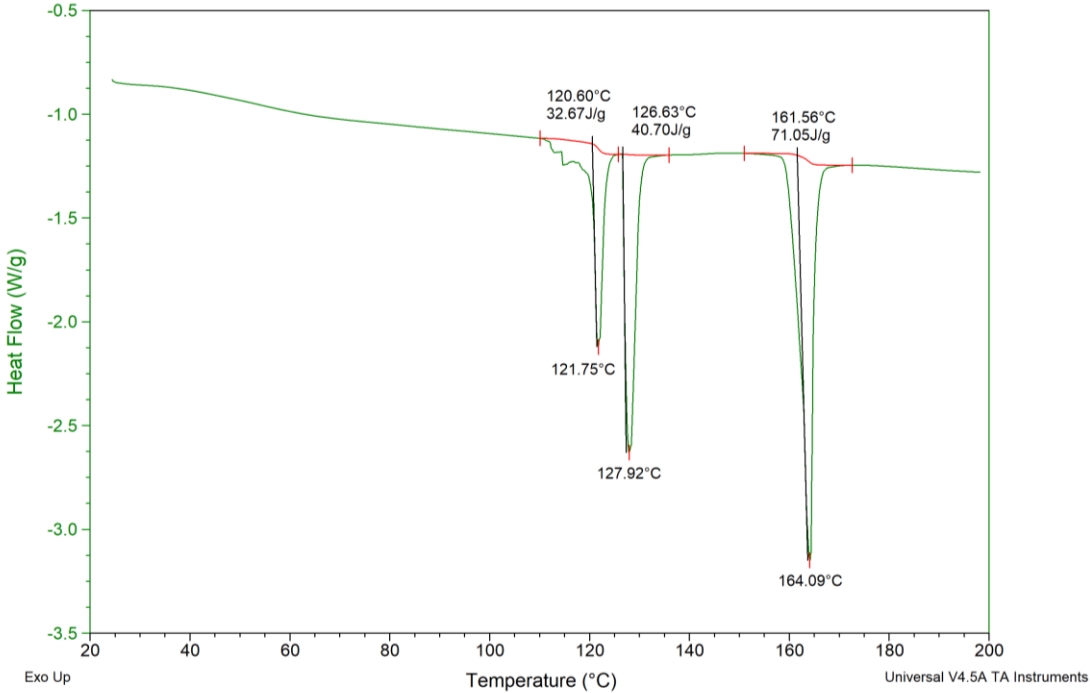


Figure 6: DSC measurement of spray dried PSAN with 7 % potassium nitrate

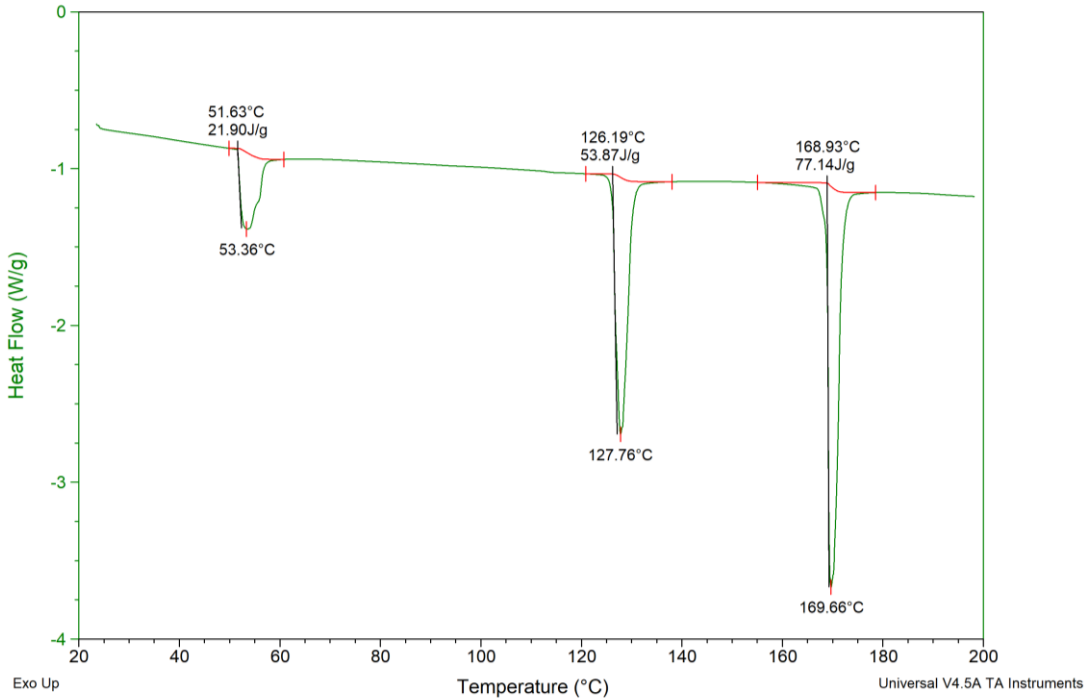


Figure 7: DSC measurement of pure ammonium nitrate

The spray drying experiments with ammonium dinitramide (ADN) were made with an organic solution and a concentration of 20 % ADN. The moderate process temperature was set to 100 °C. The experiments have shown that the special material properties of ADN to build super cooled liquids [7] were also observed for the spray drying process. A lack of crystallisation seeds prevents the droplets from solidification, which leads to agglomeration and caking inside of the process plant. There are ongoing investigations concerning the inhibited crystallization behaviour of ADN that will address this challenging material property.

## **Conclusions and Future Work**

Further parameter studies have to be made by varying the materials and process parameters. The goal is to adjust the particle size and to improve the morphology.

Top spray and rotation atomizer setups of the process shall to be tested for the spray formation.

Most challenging of all is the awareness that it is necessary to found a crystallization seed or mechanism for ADN.

Application of the spray processes with other energetic materials are promising. Materials with good solubility in volatile solvents are suitable for spray drying. Materials with low melting temperature and higher decomposition temperature are suitable for spray congealing.

## **Literature**

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