SELECTED EXPLOSIVES PROCESSED BY RESS TECHNIQUE

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Particles of explosives need to have a defined particle size and a narrow particle size distribution. One promising and nowadays applied technique to produce such defined particles uses a supercritical fluid as the main process fluid during the crystallisation. The objective of this work is a screening experiment which allows to determine suitable process parameters (pressure, temperature and sc-fluid) for the particle formation of explosives. Within these experiments a new explosive FOX-7 achieved with the Rapid Expansion of Supercritical Solutions (RESS) using CO_2 as the sc-fluid.

Introduction

During the last decade, particle formation processes using supercritical fluids (scf) became more and more subject of interest. The most common techniques is the RESS process (Rapid Expansion of Supercritical Solution). The most obvious advantages of these techniques bases on the achievable small particle sizes and the narrow particle size distributions. Other interesting properties of the particles formed by supercritical fluid processes are based on the small amounts or the completely absence (if using the RESS technique) of organic solvents in the particles. As important parameters of the scf processes temperature, pressure, co-solvent and the supercritical fluid itself can be changed and in consequence may have influence on the particle size, particle size distribution, morphology, etc..

Processes applying sc-fluids under high pressure and increased temperature are cost intensive and have to deal with high safety standards, especially if they are applied to explosives. To reduce the costs for experiments and keep the risks as small as possible, small bench scale screening units for these techniques are introduced which need very small amounts of explosive material for every run.

To determine particle size and shape of the formed particles they were collected on smooth substrates, prepared and analysed by SEM.

Material and Methods

The raw FOX-7 (chemical name: 1,1-Diamino-2,2-Dinitroethene) is a product from Nexplo Bofors AB, Sweden. It is a crystalline odourless powder with a bright yellow colour. The mean particle size of the raw product is around 170 µm (Figure 1).

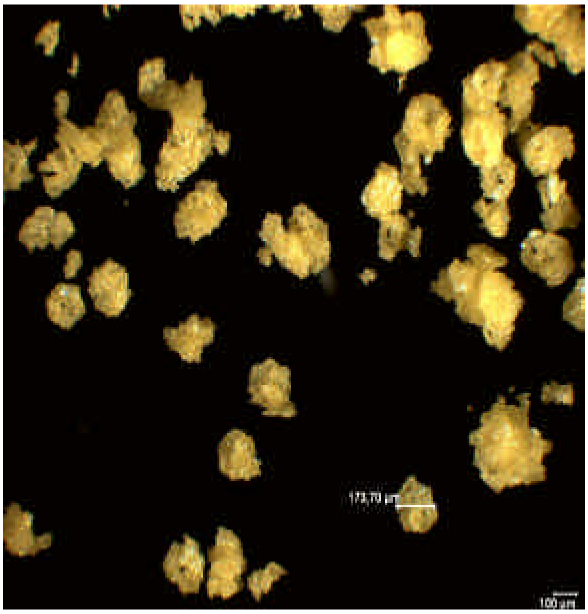


Figure 1: FOX-7 raw material

It decomposes without melting at 230°C. FOX-7 is a relatively insensitive explosive. The structural properties and the phase transfer behaviour is not completely understood yet, but the existence of different solid phases is common knowledge.
Figure 2 shows the XRD-spectra of the stabil solid α-phase of FOX 7 at room temperature.

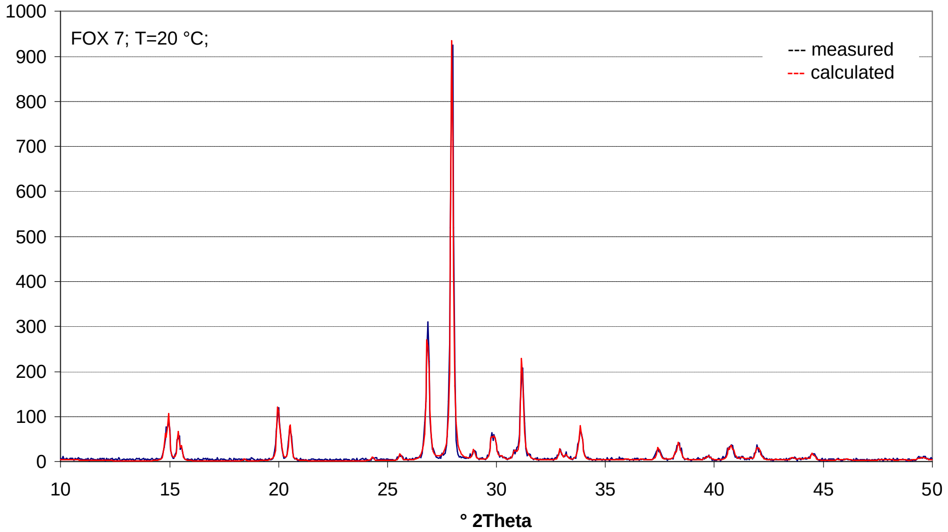


Figure 2: XRD spectra of the α-phase of FOX-7 at room temperature

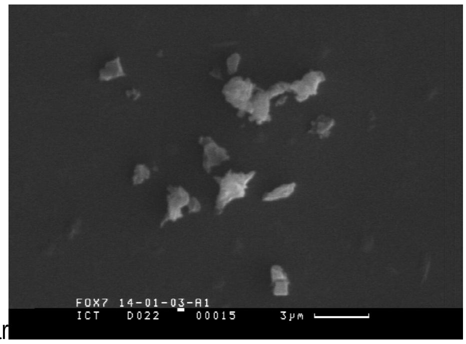
The RESS unit consists for the most part of input and control (p, T, flow rate) of components from what was previously a supercritical fluid chromatography instrument (Dionex SFC/GC 600). During the process the sc-fluid is pressurized by a syringe pump, passes an extraction cell and pre-expansion zone, both temperature controlled and expands as a free jet. The particles were collected directly on a suitable substrate for subsequent examinations by SEM.

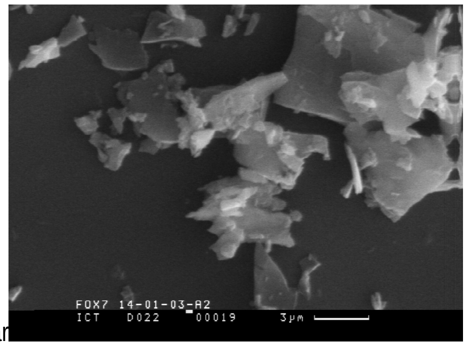
Results and Discussion

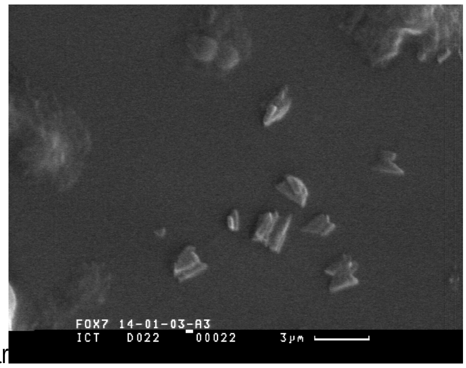
It was subject of this contribution to investigate the influence of pressure and temperature on the crystal properties like size and shape. Therefore both parameters were varied systematically: At isothermal conditions (50°C, 100°C and 150°C) the process pressure was increased in 50 bar steps from 100 bar to 250 bar.

Results from experiments carried out at 50°C

On account of the fact, that only particles can be identified on the SEM-picture in Figure 3 it can be assumed, that either the solubility of FOX-7 in supercritical CO_2 at 50°C is low or the solvation cinetics is slow.

100 bar


150 bar


200 bar


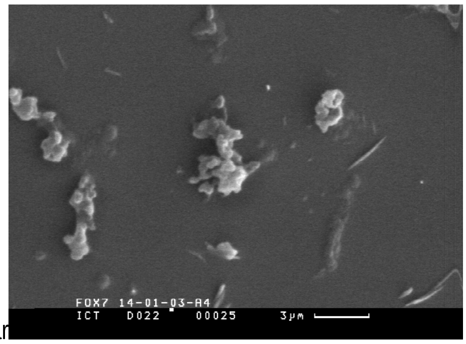
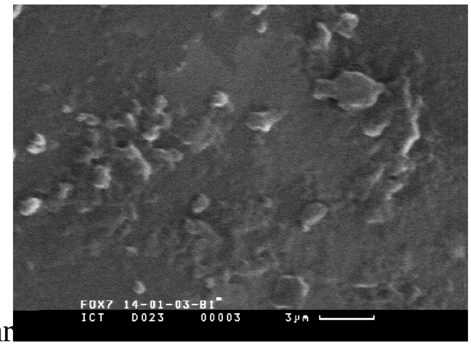
250 bar


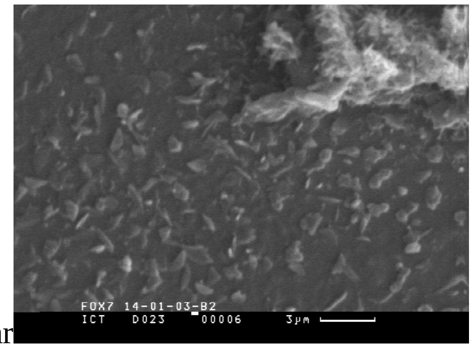
Figure 3: FOX-7 processed at 50°C at different pressures

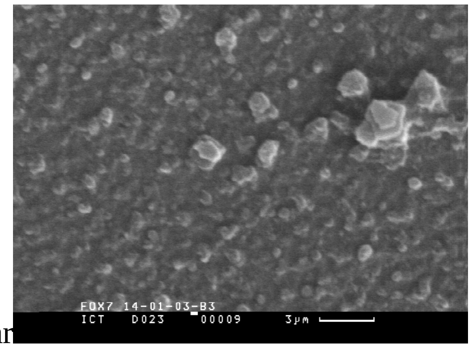
The particles formed at 100 bar and 200 bar are more or less isolated wherelse the particles formed at 150 bar and 250 bar are partly agglomerated. The particle size is around 1 µm to 3 µm, regarding the particles from the 150 bar experiment some significantly bigger particles can be observed. Comparing the 200 bar particles to those from the 250 bar experiment the particle size seems to be slightly smaller. The primary particles of the agglomerates derived fom the 250 bar experiment seem to bo in the sub-micron range.

Results from experiments carried out at 100°C

Usually, with increasing temperature at isobaric conditions the density of supercritical fluids decrease and therefore the solubilities of solutes decrease too. On the opposite, the solvation cinetic incrases with rising temperature and sometimes predominates the lowered solubility. As shown in Figure 4 the amount of particles sprayed at 100°C is significantly higher comparing to the 50°C experiments shown in Figure 3.

100 bar 

150 bar 

200 bar 

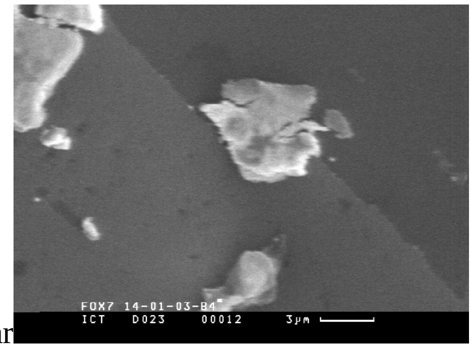
250 bar 

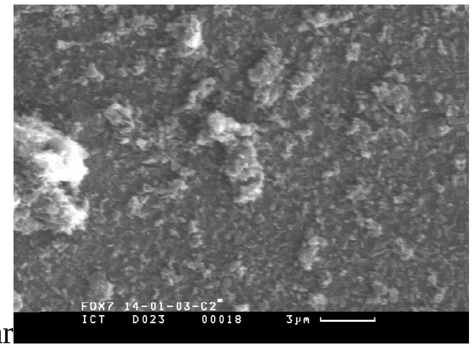
Figure 4: FOX-7 processed at 100°C at different pressures

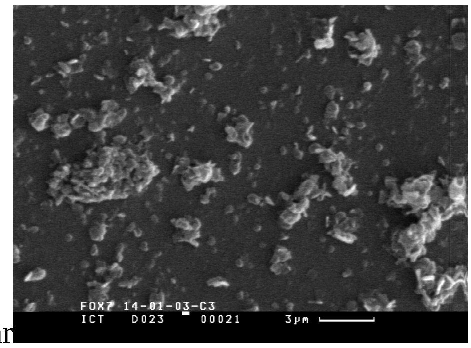
Every substrate shown in Figure 4 is covered by a layer of particles. At 100 bar the particles sem to be agglomerated and like grown together, the particle´size is around 1,5 µm to 3 µm. The experiment carried out at 150 bar formed particles which are more isolated and with a size of about 1 µm. The agglomerate seen in the upper right corner of this SEM picture seems to be an artifact and not a product formed by the RESS process. The number of particles in the SEM picture increases comparing the 200 bar with the 150 bar experiment. The contour of the particles seem softer than at lower pressures. The size of particles derive from the 200 bar experiment can be estimated to be in the submicron range down to 0.5 µm. The experiment, carried out at 250 bar is not interpretable referring to the process. It might have been, that the nozzle touched the surface of the substrate during the experiment.

Results from experiments carried out at 150°C

The highest temperature for the experiments was set to 150°C. The particle formation at 100 bar failed, possibly because of a blocked nozzle. The SEM images of the particles formed at higher pressures provide enough information for interpretation (Figure 5).

100 bar (particle formation failed)

150 bar


200 bar


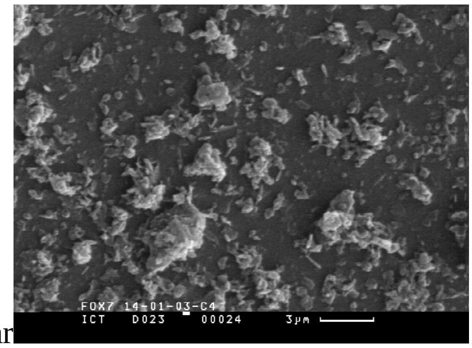
250 bar


Figure 5: FOX-7 processed at 150°C at different pressures

The highest amount of particles can be observed in the image of the 150 bar experiment, nevertheless the experiments carried out at 200 bar and 250 bar covered the substrate with a sufficient amount of particles, too. The degree of agglomeration is nearly in the same order of magnitude regarding the partilces from the 150 bar, 200 bar and the 250 bar experiment. The primary particle size seem to be slightly increased with increasing pressure. The size of the primary particles seem to be in the submicron area.

Comparing the individual temperature steps one can genarally state that the particle size decreases with increasing the process temperature. Comparing the experiments carried out at 150 bar at 50°C, 100°C and 150°C respectively, the particle size decreases They decrease from around 2 µm to 3 µm at 50°C to a range of 1 µ at 100°C to submicron range between 0,3 µm and 0,5 µm.

Conclusions and Outlook

The experiments presented in this contribution demonstrate the solubility of FOX-7 in supercritical CO_2. The experiments show as well, that the particle formation by the RESS process was successfully done. Concerning the influence of the process parameters on the particle size, it could have been shown, that the particle size decrease while increasing the process temperatures. Further examinations will aim on the formation of higher amounts of material which allow to be analysed by X-Ray diffraction. In consequence, the focus of further examination will be set on the identification of the structural properties of RESS processed FOX-7. In order to investigate the influence of different sc-fluid polarity on the particle formation process, supercritical Trifluoromethane will be used as process fluid.