MICROPARTICLES GENERATION BY SUPERCRITICAL ASSISTED ATOMIZATION

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Supercritical assisted atomization (SAA) is a promising technique that can be used to produce micronic and submicronic particles of several kind of compounds, starting from water or organic solutions. It is based on the solubilization of supercritical CO_2 in the liquid solution formed by the solvent and the (solid) solute, and on its subsequent atomization using a thin wall nozzle. When the operation is properly conducted, two atomization processes take place: the first one produces the primary droplets at the exit of the nozzle, the second one destroys these droplets by the fast release of CO_2 from the solution.

In this work supercritical assisted atomization has been applied to Zinc Acetate and Aluminum Sulfate micronization that are ceramic and catalyst precursors. The influence of pressure, temperature and concentration of the liquid solution has been investigated. A good control of particle size in the submicronic and micronic range has been obtained for the treated materials. Spherical, non connected particles have been produced.

INTRODUCTION

Some properties of gases at supercritical conditions (mainly the large mass transfer rates and the modulation of solvent power) and the possibility to completely eliminate these process media from the products, make them particularly attractive to develop high performance micronization processes. Therefore, various micronization methods based on supercritical fluids have been proposed until now [1, 2]. Recently, atomization methods assisted by supercritical CO_2 have also been proposed [3-9] that promise to be particularly simple and effective in performing micronization.

Particle Generation from Gas Saturated Systems (PGSS) has been developed by Weidner and Knez mainly for polymers [4]. It is based on the solubilization of supercritical CO_2 in the melted polymer and on the atomisation of the formed solution. No liquid solvents are used in this process [5]. Micronic particles of some pharmaceutical compounds have also been obtained by PGSS [4] though, with partial thermal degradation of the pharmaceutical principles. Indeed, the major limitation of this process is the possibility of thermal degradation of compounds.

Supercritical Carbon Dioxide Assisted Nebulization- Bubble Drying (CAN-BD) process has been developed by Sievers and coworkes [10, 11] and can be considered the supercritical equivalent of the "effervescent atomisation" [12]. It consists of the dynamic mixing of supercritical CO_2 with a liquid solution in a contacting device characterized by an overall residence time ranging between 0.01 and 0.1 s. Then, the biphasic mixture is atomized using a capillary tube. The discontinuous liquid-gas system is particular effective in atomization. Various compounds have been successfully micronized using this technique, mainly from water solutions [6].

Supercritical Assisted Atomization (SAA) has been proposed by Reverchon [9, 13] and can be regarded as the supercritical evolution of the "flashing -liquid" atomisation [12]. Traditional flashing-liquid atomisation is based on the solubilization of a liquefied gas in the liquid solution prior to its atomization. The main limitation is that liquefied gases are released from the solution slowly; therefore, their contribute to atomization is limited. When supercritical CO_2 is solubilized in a liquid solution and the formed ternary solution (supercritical fluid + liquid + solute) is atomized through a nozzle (primary atomization), the gas expands from the droplet very rapidly (secondary atomization) and gives a determining contribution to the final dimension of droplets. In this process the solubilization step is performed in a contacting device with long residence times (up to some minutes) to assure the efficient solubilization of CO_2 in the liquid solution. Obviously, vapor-liquid equilibria (VLEs) in the saturator also control the feasibility of SAA process and its performance. Very small micronic or submicronic droplets are generated and controlled diameter micro particles or nano particles can be produced. This process has been until now applied to several pharmaceutical compounds and a superconductor precursor [9, 14-15].

In this paper, we apply the SAA process to the production of two ceramics/catalyst precursors: Zinc Acetate (AcZn) and Aluminum Sulfate (AlSu) to produce micronic particles with controlled particle size distributions (PSD). The influence of some process parameters on particle size and morphology of SAA produced powders will be assessed.

EXPERIMENTAL APPARATUS

The laboratory apparatus used for SAA is reported schematically in **Figure 1.** It mainly consists of three fed lines used to deliver supercritical CO_2, the liquid solution and warm N_2, and three vessels: saturator, precipitator and condensator. CO_2 is sent to a heated bath and then to the saturator where it solubilizes into the liquid solution. The liquid is pressurised by a high pressure pump, heated and sent to the saturator. N_2 is heated in a heat exchanger and then, it is sent to the precipitator. The saturator is a high pressure vessel (I.V. 50 cm^3) loaded with stainless steel perforated saddles, in order to assure a large surface for the contact between CO_2 and the liquid. The obtained solid-liquid-gas mixture at the exit of the saturator is sent to a thin wall stainless steel injector (I.D. 100 μm) in order to produce a spray of liquid droplets. The precipitator is a stainless steel vessel (I. V. 3 dm^3) operating at near atmospheric pressure. It receives the flow of heated N_2 that assists the evaporation of the liquid droplets to precipitate the solute in form of small particles. More details about the apparatus have been given elsewhere [9].

MATERIALS

Zinc Acetate (AcZn) and Aluminum Sulfate (AlSu) with a purity of 99.99% were supplied by Sigma-Aldrich (Italy). Water (H_2O, HPLC grade) and Methanol (MeOH, purity of 99.5%) were supplied by Carlo Erba Reagenti (Italy). CO_2 (purity 99.9%) was purchased from SON. The approximate solubility of the AcZn in H_2O was 320 mg/mL, measured at room temperature, in the case of AlSu it was of 250 mg/mL. AcZn solubility in MeOH resulted of 60 mg/mL at room temperature and pressure.

ANALYTICAL METHODS

Samples of the precipitated powder were observed by Scanning Electron Microscopy (SEM). Particle Size (PS) and Particle Size Distribution (PSD) were

measured using the Sigma Scan Pro software; about 1000 particles were considered in each PSD calculation.
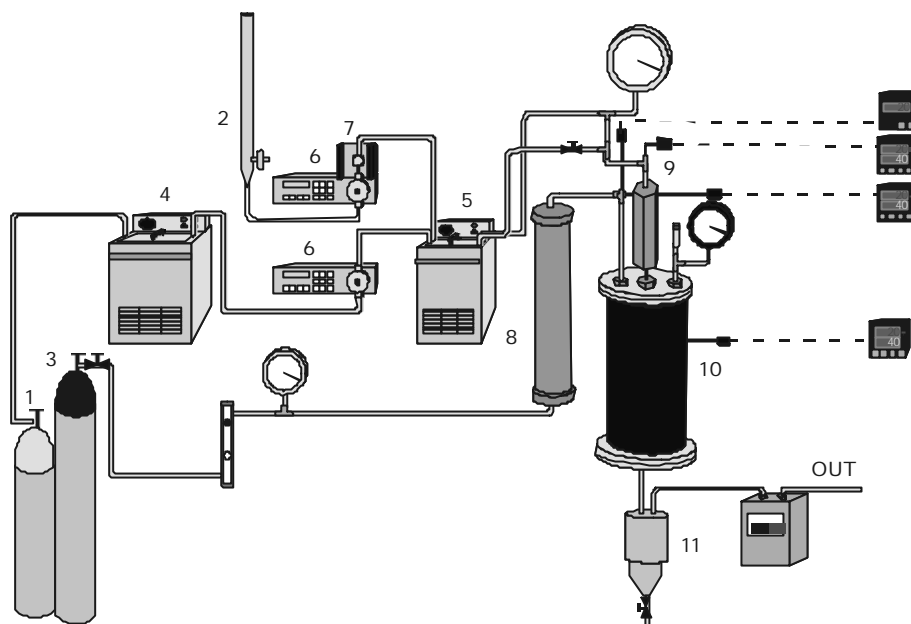

Figure 1: Schematic representation of the SAA apparatus: 1) CO_2 cylinder; 2) liquid solution; 3) N_2 cylinder; 4) cooling bath; 5) heating bath; 6) high pressure pumps; 7) dampener; 8) heat exchanger; 9) saturator; 10) precipitator; 11) condensator.

RESULTS

The solubility of CO_2 in water at the ordinary SAA conditions (60÷100 °C, 80÷150 bar) is relatively low (~2% max) if compared with CO_2 solubility in organic solvents at the same operating conditions [16]. The dissolved CO_2 (even at these conditions) is, however, able to induce liquid droplets explosion during atomization, thus allowing SAA processing [9]. In the case of MeOH and of several organic solvents, CO_2 solubility in the liquid can exceed 60%; in these cases, different operating conditions in the saturator can produce very different CO_2 solubilizations, influencing the final dimension of the atomized droplets.

The operating pressure and temperature conditions in the saturator explored in this study ranged between 90 to 110 bar and between 80 and 90 °C. The ratio of mass flow rates between CO_2 and the liquid solution was regulated between 1.2 and 1.8 w/w; i.e., we operated with an excess of CO_2 with respect to saturation conditions in water, to allow the pressurization of the saturator. The temperature of the precipitation chamber was maintained in the range between 65 and 80 °C. Warm N_2 with a flow rate of 60 Ndm^3/min was used.

When we performed the experiments at various AcZn concentrations in water, we experienced problems due to the solution viscosity; highly viscous solutions were obtained when we operated at concentration larger than 50 mg/mL. For example, when we injected a solution with a concentration of 150 mg/mL, we observed two morphologies in the precipitator: microspheres and crystals. In **Figure 2** a SEM image of AcZn large crystals obtained at 150mg/mL is reported. Sometimes we also observed the blockage of the injector [17].
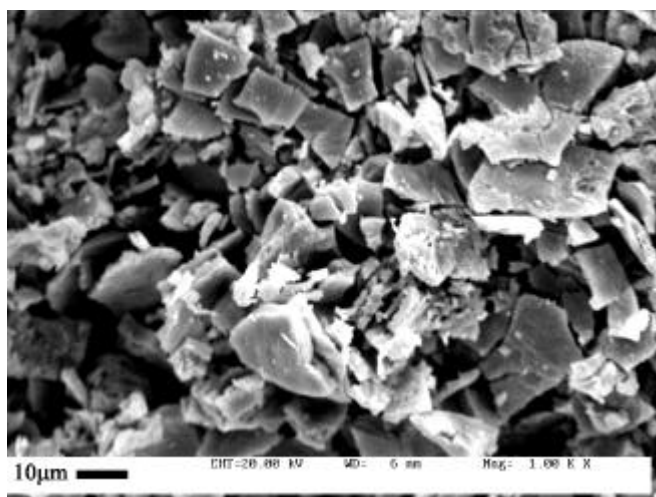
Figure 2: SEM image of AcZn precipitated by SAA from water; concentration of the liquid solution 150mg/mL.

As a consequence of these problems, we decided to explore a limited range of concentration and varied the AcZn concentration in the solution between 20 and 50 mg/mL. Operating in this concentration range, we observed in all experiments single non aggregated spherical particles. A marked influence of liquid solution concentration on the mean particle size and on the particle size distribution of the precipitated powders was also observed. In **Figures 3a and 3b**, SEM images of micronized AcZn at 20 and 50 mg/mL are reported. These images were produced using the same enlargement (5K); therefore, their comparison gives a qualitative indication of the PS variation with concentration. They show that by increasing the solute concentration, a continuous increase of the mean particle size and a broadening of the particle size distribution were obtained.
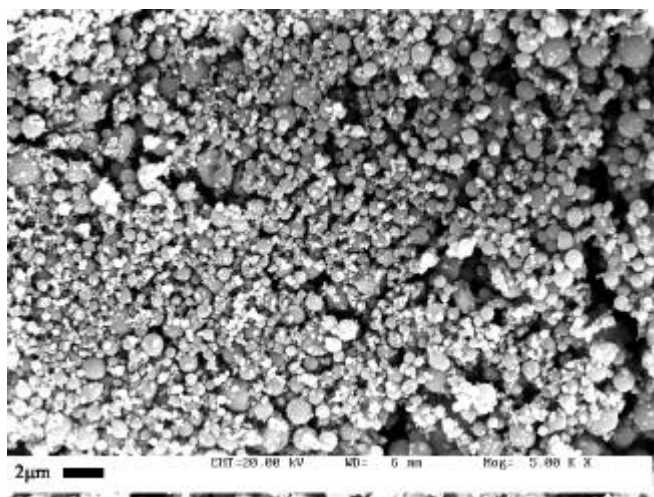

Figure 3a: SEM image of AcZn precipitated by SAA from water; concentration of the liquid solution 20 mg/mL.
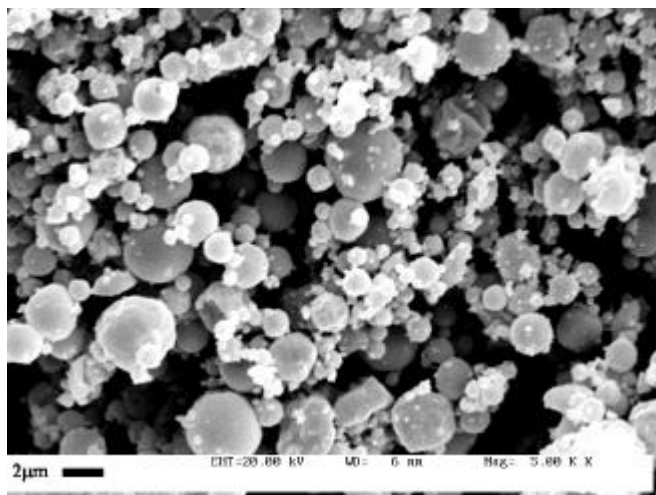
Figure 3b: SEM image of AcZn precipitated by SAA from water; concentration of the liquid solution 50 mg/mL.

The quantitative effect of concentration is shown in **Figure 4**, where particle size distributions calculated on the basis of the number of particles are reported. The mode of the particle size largely increases with the concentration from about 0.26 μm at 20 mg/mL to about 2.82 μm at 50 mg/mL, confirming the qualitative observations obtained from **Figures 3a and 3b**. Therefore, even if the range of concentrations explored is relatively limited, an effective control of particle size over about one order of magnitude is possible.
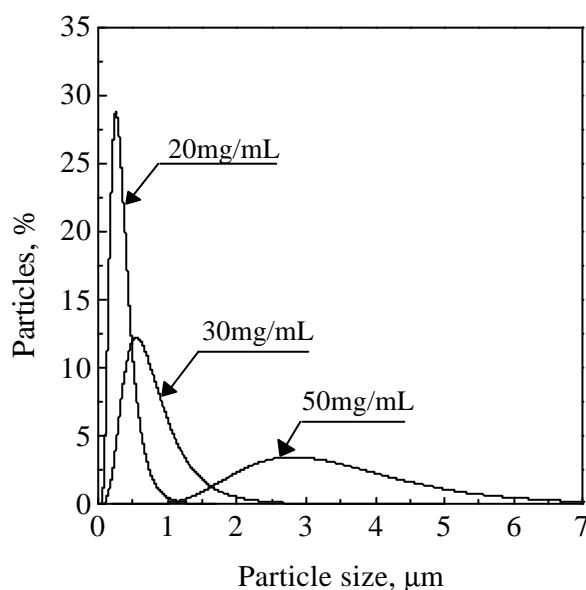

Figure 4: Distributions based on the number of AcZn particles, produced by SAA from H_2O varying solute concentration from 20 to 50 mg/mL.

MeOH-AcZn solutions with concentrations ranging between 20 and 60 mg/mL were also tested by SAA. In these experiments the operating conditions were similar to the ones of H_2O-AcZn tests. In all experiments, the observed morphology was represented by spherical particles that in same cases where connected in small groups. Considering the particles distributions, we observed that mean particles size was 0.5 μm

at 80 mg/mL. Particle size increased again with concentration; therefore, these results confirm the trend observed for the SAA of AcZn-H_2O.

The comparison of the experimental results obtained precipiting AcZn in the same operating conditions from Water and Methanol shows that in the case of precipitation from Methanol sharper PSDs were obtained when compared with those obtained from water.

Using AlSu/water solutions we obtained similar results in terms of morphology and control of PS and PSD as for AcZn. In this case, concentration ranged from 20 to 200 mg/mL. The morphology of AlSu particle was in all the experiments spherical, with single particles having well defined boundaries. Two examples, of these microparticles are reported in **Figures 5a and 5b**. These samples were taken from experiments with the concentration of the liquid solution set at 20 mg/mL and 200 mg/mL, respectively. Since the two images have been taken at the same enlargement (5K), it is possible a qualitative evaluation of the effect of concentration on the dimensions of particles produced: also in this case particles diameter increases with concentration.

The results on AlSu are summarized in **Figures 6 and 7**, where the particle size distribution of the powders obtained at different solute concentrations is shown in terms of number of particles and their volume, respectively. In volume based particle size distributions, the contribution of the larger particles is enhanced since the volume and not the diameter is the relevant parameter of the distribution. Particles with a mode of about 3 μm were obtained operating at 20 mg/mL. The mode moved to 3.5 μm at 200 mg/mL but also a PSD enlargement was observed. If the mode is calculated on particles volume, at the same concentrations as in the previous calculations, it moves from about 4 μm to about 7 μm (**Figure 7**).
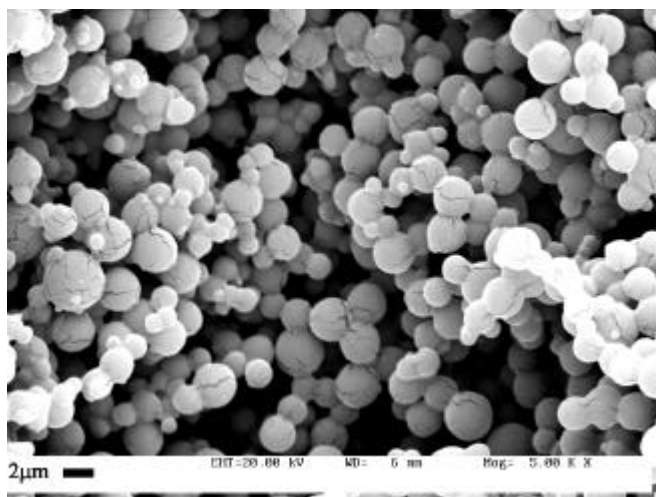

Figure 5a: SEM image of AlSu precipitated by SAA from water; concentration of the liquid solution 20 mg/mL.
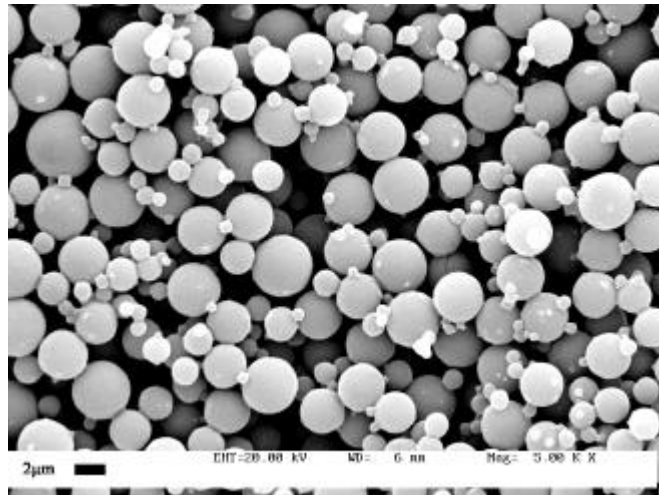
Figure 5b: SEM image of AlSu precipitated by SAA from water; concentration of the liquid solution 200 mg/mL.

The comparison of PS of AcZn and AlSu obtained at the same concentrations (for example at 20 mg/mL) shows that in the case of AcZn, submicronic particles were efficiently produced, whereas micronic particles were obtained for AlSu. Since the experiments were performed at similar conditions, this marked difference should depend on the interactions among solutes, water and CO_2 system.

In previous works we have shown that the contribute of secondary atomization (secondary droplets produced by the release of CO_2 from the internal of primary droplets) is decisive in SAA. The present results seem to confirm our statements; therefore, the quantity of dissolved CO_2 and viscosity and surface tension control the final droplet dimensions. As a consequence, process parameters that can modify these characteristics of the ternary solution are expected that can be used to obtain an efficient control PS and PSD of the powders produced.
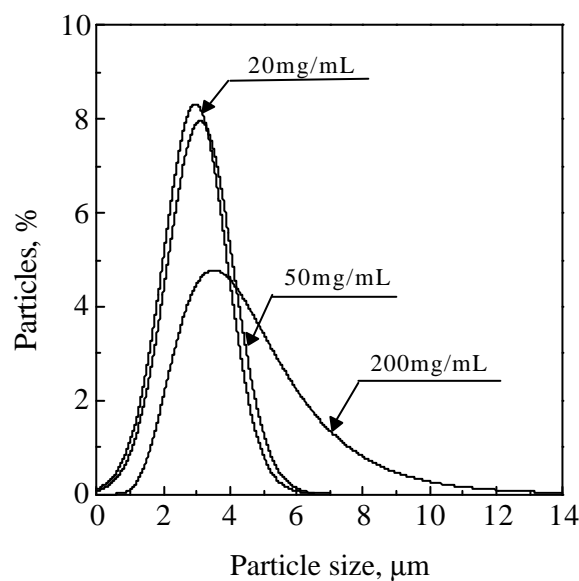

Figure 6: Distributions based on the number of AlSu particles, produced by SAA from H_2O varying the solute concentration from 20 to 200 mg/mL.
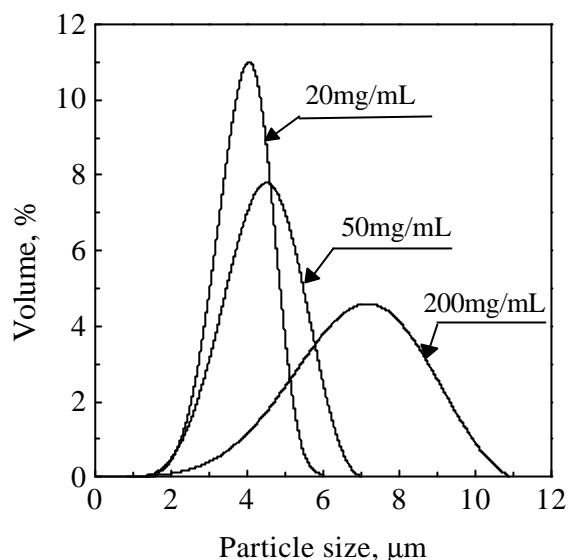
Figure 7: Distributions based on volume % of AlSu particles, produced by SAA from H_2O varying the solute concentration from 20 to 200 mg/mL.

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