IN SITU CHARACTERISATION OF A NANOPARTICLE JET FROM THE RESS PROCESS

Robert Lindner[1*], Michael Türk[2], Pierre Panine[3] , Martin Steurenthaler[2]

[1]European Space Agency, Keplerlaan 1, 2200AG Noordwijk, The Netherlands
[2]Institut für Technische Thermodynamik und Kältetechnik, Universität Karlsruhe, Engler-Bunte-Ring 21, 76131 Karlsruhe , Germany
[3] European Synchrotron Radiation Facility, ESRF, Polygone Scientifique Louis Néel, 6 rue Jules Horowitz, 38000 Grenoble, France

*Fax : +49-71-5655430, Email: Robert.Lindner@esa.int

A nanoparticle-gas jet system from the RESS process has been interrogated with Small Angle X-ray Scattering (SAXS) on a Synchrotron high brilliance beamline. The solvent is CO_2 and the different solutes are benzoic acid and $Cu(TMHD)_2$ (Bis(2,2,6,6-tetramethyl-3,5-heptanedionato) copper(II)). It is shown that such a highly diluted and weak scattering system can be investigated and particle sizes resolved near the exit of the aerosol jet.
Axial scattering curves as a function of height and time above the nozzle exit of a batch type RESS setup were obtained. Mean radii of approx. 26.6nm for benzoic acid, 26.3nm for $Cu(TMHD)_2$ and between 50nm and 26nm for pure CO_2 were obtained 1 mm above the nozzle exit in the center of the jet, being in good agreement with 2D LIF measurements. Measurement for pure CO2 showed droplet formation in the jet. The obtained data suggest a high polydispersity or asymmetry in this region.

INTRODUCTION

The production and utilization of nanoparticles is an increasing field for industrial and scientific applications, such as advanced materials, catalysts, semiconductors, optical components and precursor materials used in ceramic and pharmaceutical industry. Several new processes are promising for the production of particles, avoiding the disadvantages of classical techniques, like milling, crystallization and subsequent cleaning. The Rapid Expansion of Supercritical Solutions (RESS) process is such an environmentally compatible process [1,2,3,4]. It uses supercritical fluids (e.g. CO_2), which are characterized by densities very close to those of liquids and mass transfer properties (viscosities and diffusivities) lying between those of gases and liquids. This makes them attractive solvents for separations and reactions. The key idea behind RESS is to dissolve the solute of interest in a compressed fluid, followed by an extremely fast phase change from the supercritical to the gas-like state caused by the rapid expansion from supercritical to ambient pressure through a capillary nozzle. Due to the very high attainable super saturation in the free jet, particle formation occurs by homogeneous nucleation in the initial formation stage. After nucleation the particles grow either by coagulation or by condensation until super saturation disappears.
The on-line characterisation of the jet and the particle genesis in the transonic and supersonic regime is difficult, due to high jet velocities and gradients in small dimensions. Only integral (with respect to the jet dimension) on-line measurements by means of light scattering and ex situ analysis of the collected particles have been performed so far.

Small Angle Light Scattering (SAXS) is a standard technique to resolve size and shape in the mesoscopic scale for e.g. colloids and polymers. This technique has been applied to this highly diluted particle gas system for the first time. Recent publications dealing with fluid particle systems in gas flame synthesis [5] and soot flames [6] showed the feasibility of performing in situ measurements on particle gas systems.

MATERIALS AND METHODS

Experimental Setup

During 2004, first experiments were carried out at ESRF with a batch type setup (V = 0.5l), which allows for experiment duration of several minutes [4]. A schematic representation of the apparatus is shown in **Figure 1**. This apparatus is designed for experiments in the temperature range from 270 to 370 K and pressures up to 25 MPa. Pure CO_2 is condensed from a solvent reservoir (6 MPa) into the thermostatic extraction unit (high-pressure cell (5), V=500ml, with basket insert (4)) at T=270K. Closing valve 6 after filling and heating the liquid CO_2 to the desired supercritical temperature pressurizes the system up to 22MPa. Thereby the supercritical solvent is loaded with the solute and thermal equilibrium is reached usually within 15 minutes. Thereafter, pure CO_2 flows through the bypass section of the extraction unit (2) and the capillary nozzle (1) to minimize the unsteadiness of the flow and to accelerate thermal equilibrium.

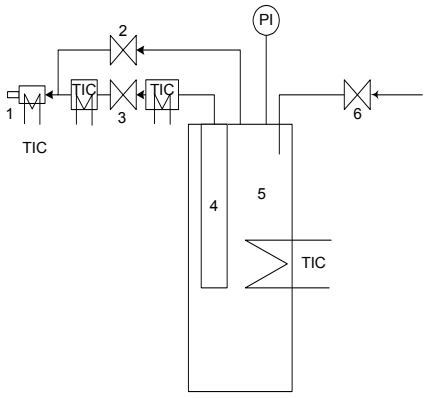

Figure 1: The mobile RESS batch reactor

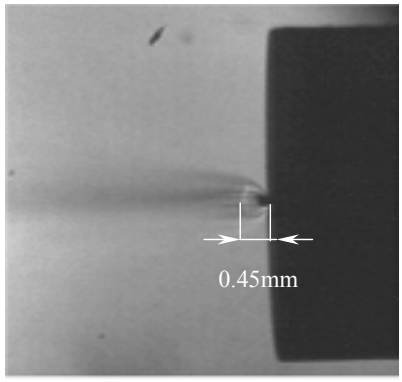

Figure 2: Schlieren picture of the jet

After equilibrium, the valve (3) at the top of the high-pressure cell is carefully opened and the supercritical solution (CO_2 and solute) flows through the thermostated duct to the capillary nozzle (50µm diameter). By adjusting the temperature of the high-pressure cell the pressure is maintained above 18-20 MPa for about 10-15 minutes, providing a jet of conical shape with widths of 0.05-2 mm, lengths of 0.5-5mm (**Figure 2**).

Diagnostic Method

Experiments were carried out at the ESRF ID02 high brilliance beamline using the SAXS pinhole camera setup with a CCD X-ray image intensified detectors (XRII), offering a high dynamic range and temporal resolution. Beamline parameters consisted of intensities between $1.2 \cdot 10^{12}$ and $1.9 \cdot 10^{12}$ Photons at a wavelength of 1Å, the beam size was 200 µm x 400 µm.
Figure 3 shows the schematic setup of the beamline with the two experimental hutches for USAXS and for the combined SAXS/WAXS measurements. The latter was used during the RESS-experiments.

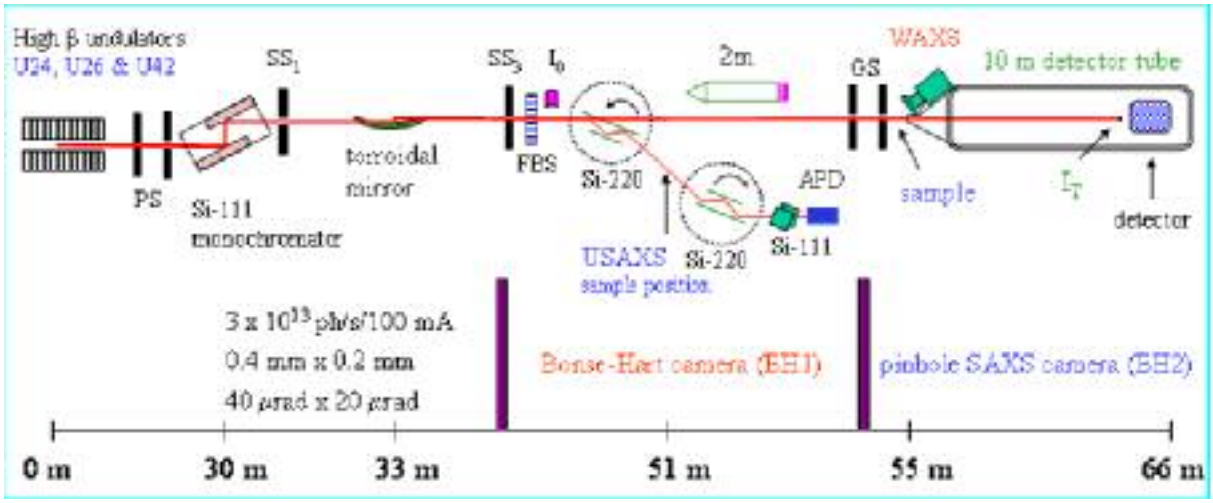

Figure 3 Schematic of the ESRF ID2 beamline

Data Treatment

In order to derive radii of gyration and hence the particle radius, the global unified scattering function [6] has been used to derive the particle radius from the scattering intensity profile, under the assumption of spherical particles. This approach uses directly both the local scattering laws for the Porod regime (high q) and Guinier regime (low q). By fitting the unified scattering function, values for R, B and G are retrieved.

$$I(q)=G\exp\left(\frac{-q^2R_g^2}{3}\right)+B\left(q^*\right)^4,\ q^*=\frac{q}{\left[erf\left(\frac{qR_g}{6^{0.5}}\right)\right]^3},$$

$$G=Nr_e\rho_e^2V^2,\ B=2N\pi r_e^{\ 2}\rho_e^2S$$

$G=Nr_e\rho_e^2V^2$

$B=2N\pi r_e^{\ 2}\rho_e^2S$

$N=Number\ density\ of\ \ primary\ particles$

$r_e=electron\ radius$

$\rho_e=Average\ electron\ density$

$q=Scattering\ vector$

$R_g=Radius\ of\ \ gyration$

$S=average\ surface\ area$

$V=average\ particle\ volume$

The polydispersity index PDI introduced by Beaucage [5] describes the width of the particle size distribution

$$PDI = \frac{B}{1.62\,G} R_g^{\,4}$$

RESULTS

Figure 4 shows typical results of SAXS measurements for pure CO_2, Benzoic acid/CO_2, and Cu(THMD)$_2$/CO_2. Graph A, B and C show log-log plots of the scattering intensity as a function of the scattering vector q = $(4\pi/\lambda)$* sin(Θ), with λ being the wavelength of the incident light and Θ being the scattering angle.

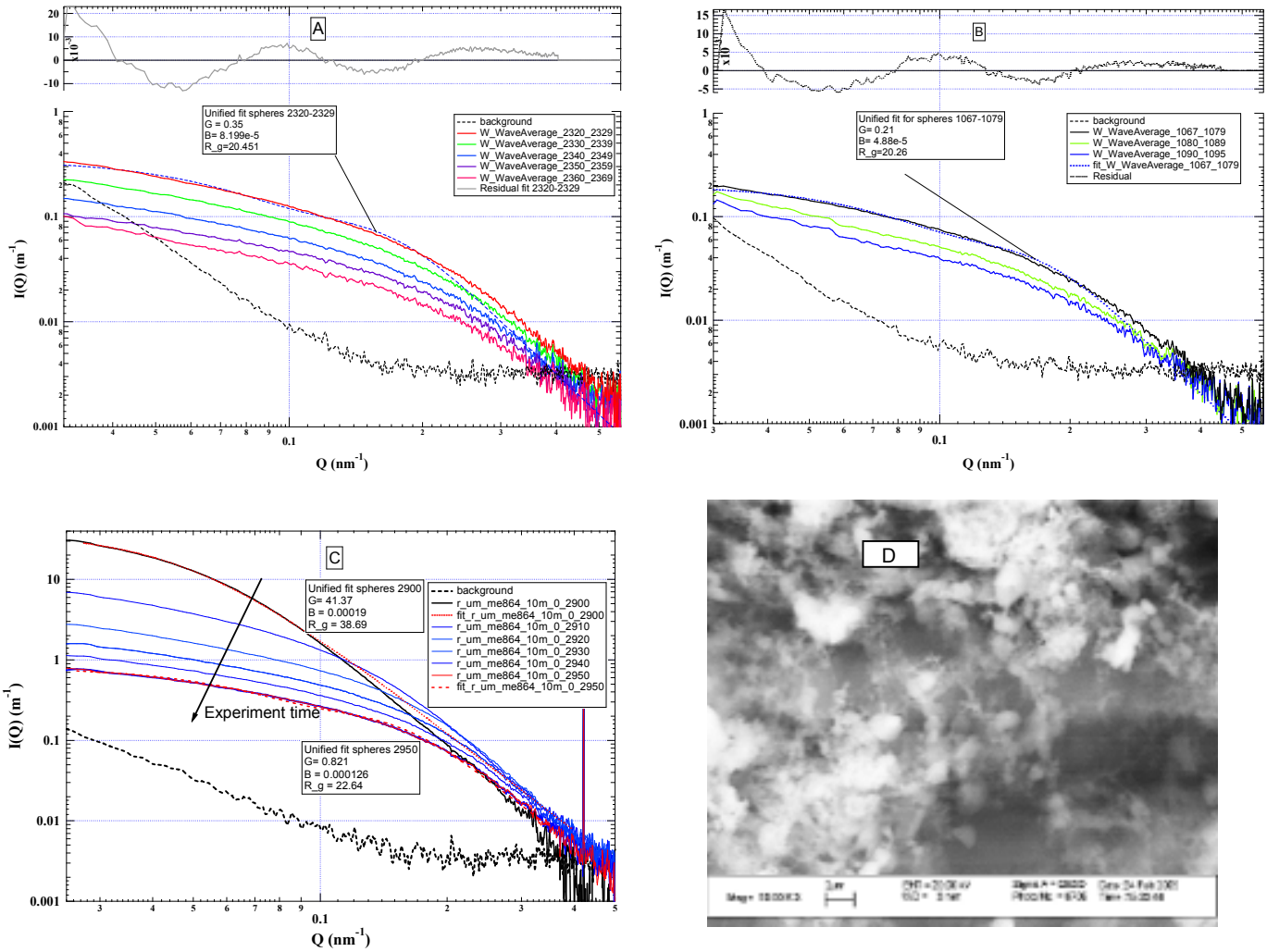

Figure 4 Background corrected log-log plots of small angle scattering at ID02 of A) CO_2/Benzoic acid, B) CO_2/ Cu(TMHD)$_2$ C) pure CO_2 at different times. Radial (x) and axial (z) position in the jet: x= 0mm, z=1mm, initial extraction pressure p=24MPa (CO_2, benzoic acid) and p=21MPa (Cu-complex), nozzle temperatures 70-80°C. For A) and B) each curve is averaged over consecutive 0.5s measurements, the residual of the fit from the first averaged I(q) is shown in the top part of the graphs. The black dotted lines represent the background intensities. C) depicts single measurements for pure CO_2 without fit. D) shows a Field Emission Scanning Electron Microscope (FE-SEM) picture of the copper complex(Cu(THMD)$_2$) collected with a needle inserted in the jet some mm from the nozzle exit. SEM chamber pressure was limited to p=10Pa min. due to the vapour pressure of the complex. The sample was not sputtered.

Graph **A** and **B** show as well a fit on the first averaged measurements. The global unified scattering function was used [5], assuming spherical geometry as the SEM picture of the

particles, sampled at the end of the jet, suggests in graph **D**. The quality of the fit is reasonably good. However, for high q the consistency is less good. A fit in these regions is hampered by the degraded quality of the signal. As a first evaluation with $R = 1.3*R_g$ [5], these fits would yield a primary radius of 26.6nm and a polydispersity index of 25.3 for benzoic acid, for the copper complex a primary radius of 26.34nm and a PDI of 24.5 respectively. The radii obtained are in good agreement with LIF measurements which yielded particle radii of about 27nm 1mm centered above the nozzle for benzoic acid [**7**]. Graph **C** shows a set of measurements of pure CO_2 at the same position and with similar P and T. Applied to the scattering curves of pure CO_2, the fit on the initial measurements would result in a radius of 50nm and a PDI of 6.3 for the last recorded measurement a radius of 29.4nm and a PDI of 24.9 for CO_2 droplets or particles which were formed in this jet. The values for the first measurement is in good aggreement with earlier simulations on pure CO_2 jets [4].
It is very likely that the two-phase region and the solid line of CO_2 has been crossed, creating droplets and ice, with a relatively high concentration, yielding a high signal (N.B, with pure CO_2 as a comparatively "weak" scatterer). A difference in photon flux can not explain this high signal (before start of measurement, 1.6 10^{12} ph/s for pure CO_2 experiment, 1.7 and 1.9 10^{12} ph/s for benzoic acid and the copper complex experiments).
With the solutes on the other hand, the jet was much less visible suggesting that we expanded directly from supercritical into gas, only having solute particles with a lower concentration on one side, on the other side being hampered with the problem of clogging. This resulted in a smaller jet, lower concentrations and hence a lower signal.

CONCLUSION

The feasibility of in situ SAXS measurements on a highly diluted nanoparticle jet from the RESS process has been shown, despite the low signal intensity. Particle radii of approx. 26nm were retrieved from the SAXS evaluation, which is in good line with LIF measurements [7]. Results for the polydispersity index suggest either that a high polydispersity is existent at this stage in the nucleation process. It could arise as well from particle shape asymmetry of contrast gradients within the particles [8]. This is subject to further investigations. Additional experiments using an optimised continuously operating setup will enable a mapping of the jet, including the investigation of aggregates using a Bonse-Hart camera for Ultra Small Angle X-ray Scattering (USAXS) measurements.
A comparison with BET measurements determining the Surface to Volume ratio of the particles can substantiate SAXS and USAXS data. However, due to the small dimensions, it is difficult to sample particles at exactly the same measurement location.

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