PARTICLE NUCLEATION AND MIXTURE FORMATION CHARACTERIZED BY A COMBINATION OF RAMAN AND MIE SCATTERING

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A two-dimensional optical laser based Raman and Mie scattering setup is used to enlighten the different steps of mixture and particle formation in the supercritical antisolvent process. Here, paracetamol was used as a model substance dissolved in liquid ethanol and injected into supercritical CO_2. During particle formation, an increase in partial density of CO_2 and a change in phase behaviour by the formation of the particles were observed. A change in concentration of the injected solution resulted in different location of particle formation depending on the concentration of the solution.

INTRODUCTION

One of the challenges in the SAS process is to tune the process conditions appropriate to the desired product requirements. The morphology of the produced particles covers spherical, crystalline, amorphous or even hollow spheres and the particle size and its distribution is also dependent on the process conditions [1]. There have been several attempts to describe the SAS process in a mathematical model to predict particle shape and size according to the process conditions but due to a lack of knowledge, an overall general concept without idealization has not been proposed yet. In this work, our aim is to show the concentration distributions depending on the solute concentration, the location of particle formation and give information about the increase in partial density of CO_2 for certain process conditions. All this information is obtained two-dimensionally using an optical laser based Raman and Mie scattering setup.

MATERIALS AND METHODS

The experiments were carried out using an optically accessible SAS chamber. The details of the SAS chamber and the Raman and Mie scattering process are outlined elsewhere [2]. A schematic of the experimental optical setup for the simultaneous detection of Raman and elastically scattered light signal (Mie scattering) used for the visualization of the CO_2 mole fraction distributions and the particle formation process is shown in Figure 1. On the Raman detection side, perpendicular to the laser sheet, the Raman signals were detected using three electron multiplying CCD (EMCCD) cameras equipped with CCD chips of 658 x 496 pixels. Superpixels were formed by binning the available pixels 2 x 2 resulting in a better signal-to-noise ratio but also reducing the maximum local resolution of the cameras. The mixture and particle formation area was imaged on 128 x 134 superpixels with a local resolution of 135 µm x 135 µm close to the laser sheet thickness of about 200 µm. For the separation of the Raman and the elastically scattered signals, two dichroic long pass mirrors were used. As the elastic scattering process has a much higher signal level compared to Raman scattering, the elastically scattered light had to be attenuated by neutral density filters with an optical density of 6.3 in order to not swamp the camera.

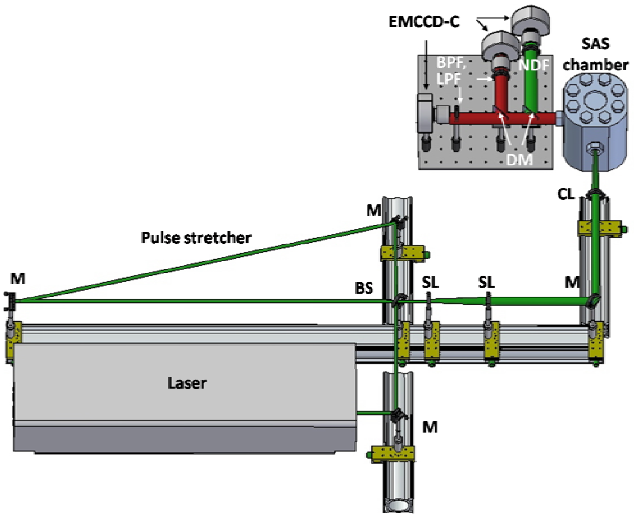

Figure 1: Schematic of the optical setup; M: Mirror, BS: Beam splitter, SL: Spherical lens, CL: Cylindrical lens, DM: Dichroic mirror, BPF: Band pass filter, LPF: Long pass filter, EMCCD-C: Electron-Multiplying-Charge-Coupled-Devise-Camera

The Raman signals of ethanol and CO_2 were separated by a dichroic long pass beam splitter, was transitive for the signal wavelength of the CH-vibration of ethanol at 630 nm and reflective for the signal wavelength of CO_2 at 574.4 nm. To guarantee the detection of pure Raman signals, the suppression of interferences onto the Raman cameras had to be carefully performed. This was realized by a combination of filters for the desired signal wavelength.

RESULTS

The aim is to show the influence of the solute paracetamol on the mixture formation process, the particle nucleation and the partial density distribution of CO_2. Therefore, pure ethanol without the solute paracetamol, a 3 wt % and a 5 wt % solution are injected into the antisolvent CO_2 at conditions above the MCP. For process conditions above the MCP, jet mixing is expected which means that mixing is a gas-like process characterized by turbulent flow and vortices structures within the jet [3]. Below the MCP, the liquid ethanol is disintegrated into droplets with the instantaneous absorption of CO_2 into the droplets. In Figure 2, averaged mole fraction distributions for a chamber pressure $p_{CO2} = 10.0$ MPa and an injection pressure of the solution $p_S = 20.0$ MPa are given. The mole fraction images were obtained by conducting a calibration to calculate mole fraction distributions out of the Raman intensity single shot images. Basically, all mole fraction distributions shown in Figure 2 indicate a rapid mixture formation at steady state conditions. By adding the solute paracetamol, an increase in the mole fraction distributions is obvious. This phenomenon will be explained in the following by the Mie scattering images in **Erreur ! Source du renvoi introuvable.** and by the partial density distributions of CO_2 obtained from the Raman intensity images in **Erreur ! Source du renvoi introuvable.**.

We found a relationship between particle nucleation and the change in phase behaviour depending on the amount of solute added to the ethanol solution. The images in **Erreur ! Source du renvoi introuvable.** give information on the start of particle formation depending on the concentration of the solution. Light scattering directly at the nozzle outlet can be observed for all three solution concentrations and appears only due to the phase interface between the injected liquid solution and the supercritical CO_2.

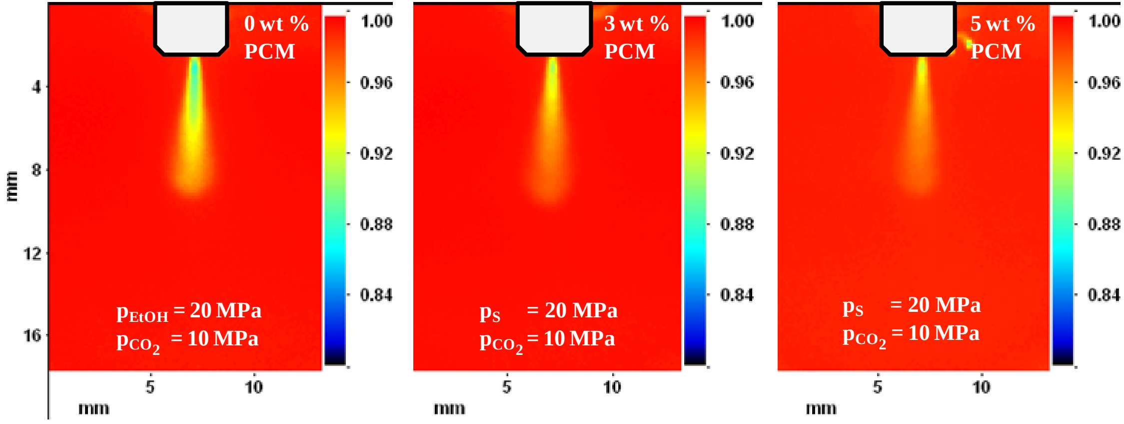

Figure 2: Averaged mole fraction distributions from 50 single shot images at different solution concentrations at 313 K.

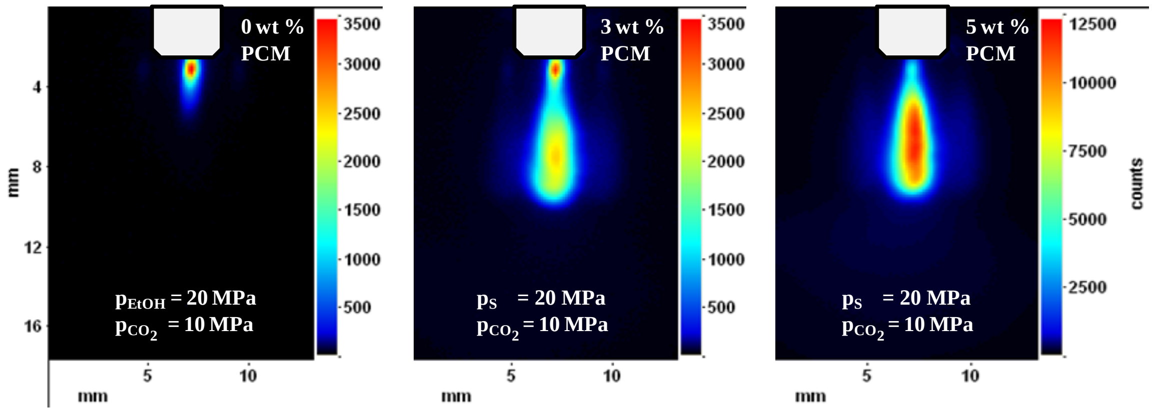

Figure 3: Averaged elastically scattered light intensity images of pure ethanol, a 3 wt% solution and a 5 wt % solution of paracetamol dissolved in ethanol injected into supercritical CO_2 at 313 K.

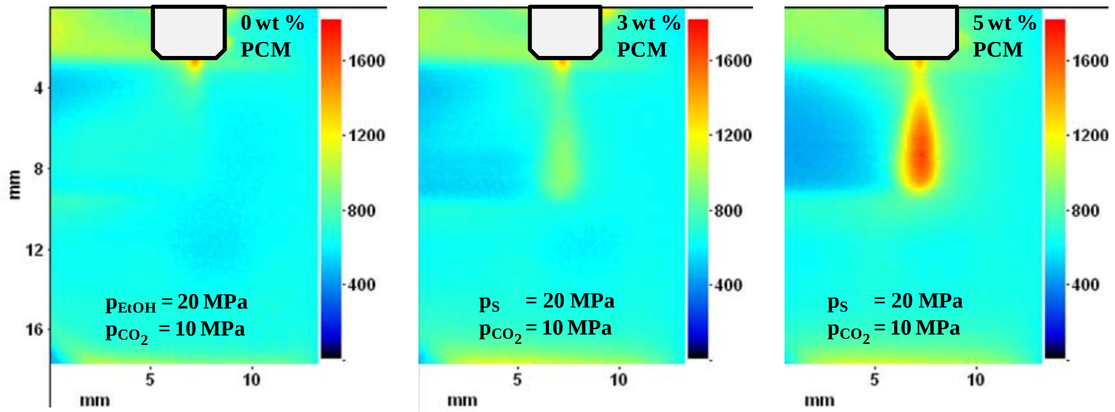

Figure 4: Averaged partial density distributions of CO_2 during the injection of pure ethanol (0 wt %), a 3 wt % solution and a 5 wt % solution of paracetamol dissolved in ethanol at 313 K.

With increasing distance from the nozzle outlet, the interface tension between the liquid ethanol (also for the 3 wt % and 5 wt % solution) and the surrounding supercritical CO_2 decreases. As the intensity level of the scattered light does not change with respect to the solution concentration but is constant even for 3 wt % and 5 wt % solute, just light scattering from the liquid phase interface is observed without the formation of particles in this region.

Mixing between the injected ethanol without solute and the antisolvent CO_2 leads to the formation of a supercritical phase without any phase boundary, hence no scattered light can be observed. For both solutions with solute, a significant intensity increase in the Mie signal intensity due to solid particles which exhibit a phase boundary is obvious. However, there is a considerable difference recognizable for the two concentration solutions. There is a strong increase in the signal level at a short distance to the nozzle outlet for the 5 wt % solution but an even posterior increase for the 3 wt % solution. This behavior evolves from the higher supersaturation of the 5 wt % solution resulting in an earlier start of nucleation compared to the 3 wt % solution. As the Mie scattering signal is dependent on both, the size of the particles and the number density of the particles, the measurement technique is not appropriate for the determination of the size or the quantity of the particles, but exhibit qualitative information on particle formation in the jet.

In **Erreur ! Source du renvoi introuvable.**, the partial density distributions of CO_2 indicate an important further characteristic of the particles. Without the solute, the partial density distribution of CO_2 is almost homogenous after the liquid phase at the nozzle outlet has vanished. By injecting liquid 3 wt % or 5 wt % solutions, the formation of the particles leads to an intensity increase in the partial density distributions of CO_2 at different distances to the nozzle outlet. A similar intensity increase was also found below the MCP, where particle formation from the liquid solution is well known [2]. Therefore, the formation of the solid particles leads to a phase change of the system and a change in precipitation from a supercritical solution to precipitation from a liquid solution. The amount of solute added to the solvent strongly influences the phase behaviour and also the location of the liquid phase appearance. From the images in **Erreur ! Source du renvoi introuvable.** and **Erreur ! Source du renvoi introuvable.**, it is apparent that liquid phase formation is strongly dependent with the process of particle nucleation. A crosstalk of the scattered light from the particles or from the Raman signal of paracetamol was considered and can be excluded. In further studies, the increase of the chamber pressure reduced the elastically scattered light signal but did not change the location of particle formation. This characteristic just depends on the amount of solute added and on the supersaturation of the solution.

CONCLUSION

One promising feature of the SAS process is the very high supersaturation depending on the solution concentrations. This is evidenced by the very high mole fractions of CO_2 obtained by the Raman measurements. With the knowledge on the location of particle formation and the change in partial density of CO_2 by the appearance of the solid particles, a much better process control can be achieved. If particle formation from a supercritical solution is the aim, higher pressures or instead smaller solution concentrations are necessary. As a higher amount of the solute leads to an earlier production of particles, they remain even longer in the supersaturated liquid region and will possibly grow to larger and even more aggregated particles.

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