

Formation and Coatings of Fine Particles in Jets of Supercritical Fluids

A. Gokhale^{*}, Y. Shen^{**}, B. Khusid^{***}, R. Dave^{****} and R. Pfeffer^{*****}

^{*} Department of Mechanical Engineering, aag6@njit.edu

^{**} Department of Mechanical Engineering, ys4@njit.edu

^{***} Department of Mechanical Engineering, khusid@adm.njit.edu

^{****} Department of Mechanical Engineering, dave@adm.njit.edu

^{*****} Department of Chemical Engineering, pfeffer@adm.njit.edu

New Jersey Institute of Technology, Newark, NJ 07102

ABSTRACT

We present experimental studies of supercritical anti-solvent (SAS) processes for the formation of polymer particles and the polymer coating of fine particles in jets of supercritical fluids. The inner diameter of nozzles utilized in experiments on the particle formation varied from 10 μm to 127 μm . The coating of particles was studied on jets injected through a coaxial ultrasonic nozzle of 300- μm inner diameter.

Keywords: Supercritical Fluids, micronozzle, ultrasonic nozzle, nanoparticles, nanocoating

1 INTRODUCTION

Conventional technologies for manufacturing micrometer- and nanometer-sized polymer particles, such as dry and wet grinding and solution precipitation, do not provide required flexibility to tailor the particle properties as well as to control the particle size distribution, morphology and purity. Methods utilizing supercritical fluids for the formation of particles demonstrate potential to overcome these drawbacks. The supercritical antisolvent (SAS) process is an emerging technology for the production of polymer particles for a wide variety of biomedical and pharmaceutical applications. In this method, an organic liquid solution of the polymer of interest is injected through a nozzle into a chamber containing a highly compressed gas or supercritical fluid (inexpensive and environmentally benign carbon dioxide is a common choice), which is miscible with the solvent, but is an antisolvent for this polymer [1]. Similarly, SAS coating can be realized by injecting a suspension of host particles in liquid solutions of polymer. Supercritical fluids offer a “solvent-free” approach for the production and coating of nanometer and submicrometer particles by eliminating the use of large amount of environmentally harmful organic solvents.

Recently published studies of the SAS formation of polymer particles are limited to the use of good organic solvents or their mixtures and relatively wide nozzles. In contrast, we use the new concept of mixing thermodynamically “good” and “poor” solvents and

micronozzles to regulate the precipitation of a polymer from the injected solution [2]. Binary mixtures of dichloromethane (DCM) and acetone, which are respectively “good” and “poor” solvents for Polyvinylpyrrolidone (PVP), were used to prepare PVP solutions [2]. Utilizing this concept, we also demonstrated the feasibility of polymer coating of silica particles.

2 SETUP AND MATERIALS

A setup shown schematically in Fig. 1 is mainly used for the visualization of the breakup patterns of liquids injected into supercritical CO_2 . The visualization system comprises microscope zoom lens (Edmund Industries), a high-speed CCD camera (Flow Master, LaVision), a computer with the image capture software (Davis 6.2, LaVision) and a Nd:YAG dual cavity pulsed laser (Solo III, New Wave Research). To produce a larger amount of PVP particles for analysis, the view cell in this apparatus is replaced with a 910-mL high-pressure chamber placed inside a water bath. Fused silica capillaries of 10- μm , 20- μm , 40- μm , and 127- μm (Polymicro Technologies) are used as micronozzles in experiments on the particle formation. The operational temperature is maintained at 35°C while the operational pressure varies from 79 to 120 bar.

A customer designed coaxial ultrasonic nozzle shown in Fig. 2 was fabricated by Sono-Tek Corporation (Milton, NY). It comprises two coaxial nozzles. The smaller nozzle inside has an inner diameter of 300 μm and the wall thickness of 130 μm . The remaining part of a bigger nozzle is a ring-shaped geometry with an inner diameter of 560 μm and outer diameter of 760 μm . A small mixing zone having a length of 1.02 mm is located between the tips of two nozzles. The nozzle is designed to operate at a fixed frequency of 60 kHz [3]. The inner nozzle is used to inject a polymer solution, whereas the outer nozzle is used to inject CO_2 .

High pressure CO_2 cylinders (Bone Dry, 99.9% pure) are purchased from MG Industries. Acetone (HPLC Grade, 99.5+ %), DCM (HPLC Grade, 99.7+ %), PVP (MW 1,300,000 and 360,000) are purchased from Alfa Aesar and EUDRAGIT (E100, MW 150,000) is purchased from Rohm GmbH. All materials are used as received. SEM,

LS230, N4 Plus, FTIR and TEM are used for characterization of the particles.

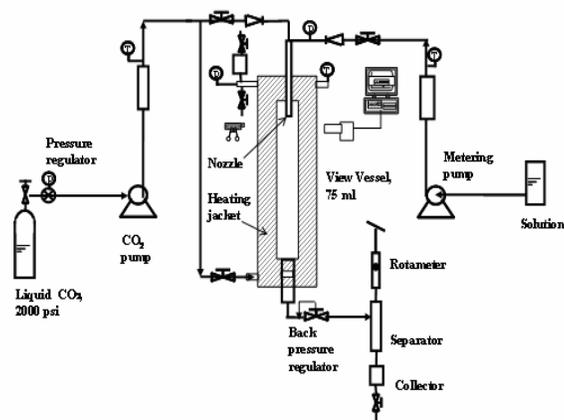


Figure 1: Experimental setup for the visualization of the liquid breakup injected into supercritical CO₂.

detach the jet tip at some distance downstream of the nozzle because of the growth of disturbances leading to the eventual jet breakup. The Rayleigh breakup, the first wind-induced breakup, and the second-wind-induced breakup, were also clearly identifiable in our experiments. Increasing the acetone content in the solvent is found to suppress the particle aggregation, decrease the average particle size, and eliminate the surface irregularities of the PVP particles (Fig. 3). However, increasing the operational pressure well above the critical point is found to increase the average size of the PVP particles and broaden the particle size distribution.

The use of the coaxial ultrasonic nozzle is found to facilitate coating of nanometer and submicrometer silica particles for the modification of their surface. Evenly coated silica particles and a thin layer of polymer coating can be easily observed from Fig. 4. The concept of “good” and “poor” solvents also results in a morphology variation of the obtained coated silica particles from the coaxial ultrasonic nozzle.

4 CONCLUSION

The variation of the acetone content of a solvent, the nozzle diameter, and the jet velocity is demonstrated to provide an efficient method to vary surface morphology of the PVP particles and their size from several tens of nanometers to several hundreds of nanometers. Operation at pressure slightly above the critical point is shown to favor the formation of a narrow particle size distribution.

The ultrafine silica particles are successfully coated with polymer by using coaxial ultrasonic nozzle. The coaxial ultrasonic nozzle possesses potentials for the future scale-up of SAS coating process.

5 REFERENCES

- [1] J. Jung and M. Perrut, “Particle design using supercritical fluids: Literature and patent survey”, *The Journal of Supercritical Fluids*, 20(3), 179-219, 2001.
- [2] A. Gokhale, B. Khusid, R. Dave, and R. Pfeffer; “Formation of Polymer Nano-particles in Supercritical Fluid Jets”, NANOTECH 2005, Technical Proceedings of the 2005 Nanotechnology Conference and Trade Show, Anaheim, CA, May 8-12, 2005, v.1, 215 – 217.
- [3] H.L. Berger, “Ultrasonic liquid atomization: Theory and application”, Partridge Hill Publishers, New York, 1998.

3 RESULTS AND DISCUSSION

The breakup of liquids injected into supercritical CO₂ appears to be similar to that observed for the injection of a liquid into an immiscible liquid (Fig. 3). For low flow rates, drops are formed individually at the tip of the nozzle and break off when they attain a particular size (dripping flow). In the jetting mode, which occurs at larger velocities, drops

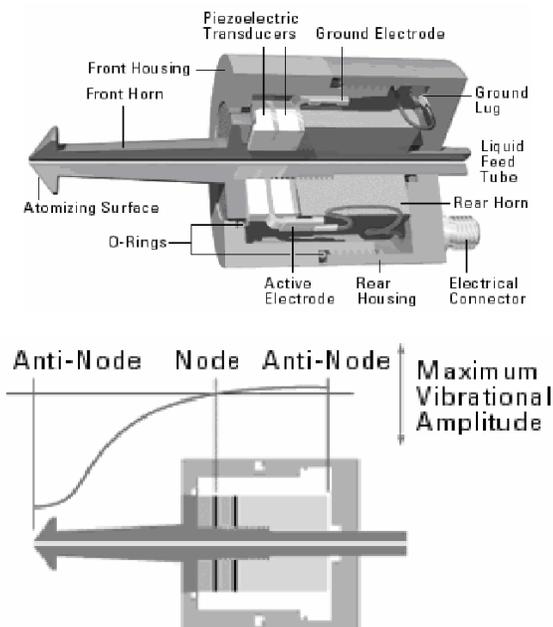


Figure 2: Schematics of an ultrasonic nozzle for coating submicrometer particles (upper pane) and a standing wave pattern (lower pane) [3].

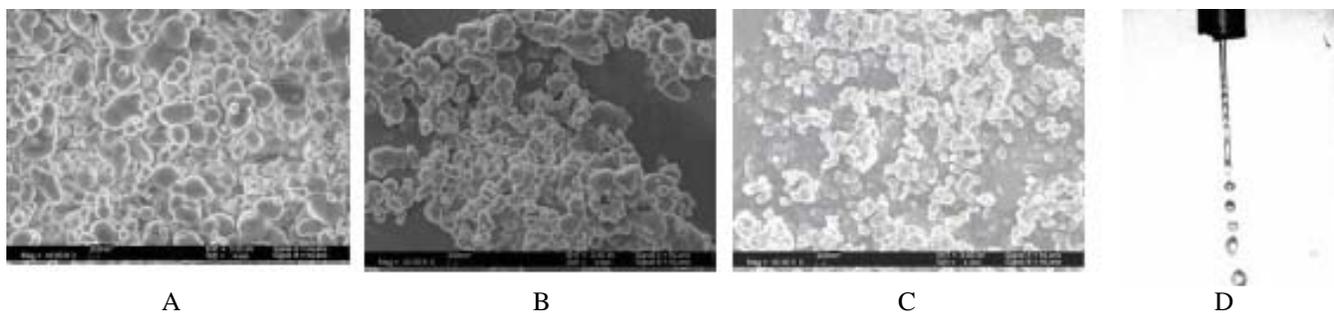


Figure 3: Effects of the solvent composition on the particles morphology. SEM photos of synthesized PVP nanoparticles. Nozzle ID 40 μm , pressure 79 bar, temperature 35°C, solution injection rate 0.2 ml/min; DCM/acetone (v/v) solvents: (A) 100/0; (B) 80/20; (C) 60/40; (D) the jet breakup of DCM into supercritical CO_2 .

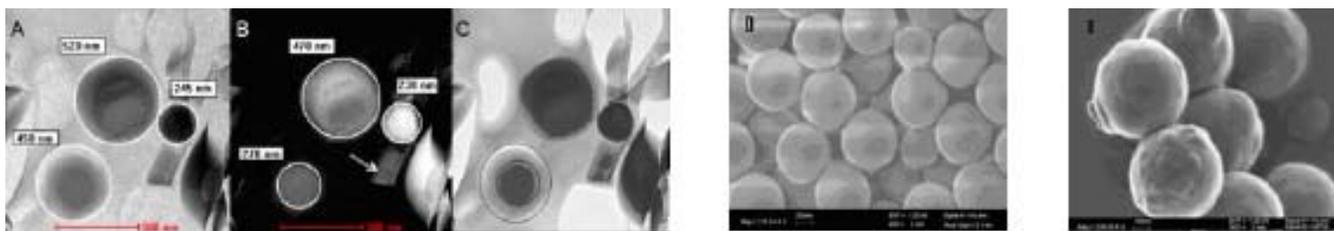


Figure 4: Silica particles coated with EUDRAGIT. TEM-EELS images of EUDRAGIT encapsulated particles: (A) Zero loss; (B) Si-distribution; (C) superimposition of A and B; (D) Original silica particles; (E) SEM image of the particles coated with EUDRAGIT. The operating conditions are 80 bar, 35°C, and the solution flow rate is 4 ml/min. The ratio of host particles to guest particles is used as 9:1 wt/wt% for above coating experiment.