MONODISPERSE MICROPARTICLE GENERATION FROM AQUEOUS SOLUTIONS

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ABSTRACT

We present a new approach for the generation of monodispersed droplets and tailor-made microparticles of complex liquids from a star-shaped nozzle that precisely defines the dispensed droplet sizes. From two aqueous polymer solutions: 30w% Polyvinylpyrrolidone (PVP) (viscosity $\eta \approx 105$ mPas) and 40w% PVP ($\eta \approx 490$ mPas) droplet volumes of 3.9 nl and 3.2 nl respectively were generated employing a star-shaped silicon nozzle with a diameter of 183 µm. From 1w% Mannitol ($\eta \approx 1$ mPas) droplets (100 pl) and particles (22 µm) were generated from a 59 µm nozzle. These results show for the first time particle generation with the StarJet method that could be applicable for the generation of monodispersed powders for use in healthcare, food and home care products.

KEYWORDS

Spray, monodisperse, microparticles, StarJet, Mannitol, Polyvinylpyrrolidone

INTRODUCTION

Several processing methods in the field of micro particle engineering such as milling and blending techniques, wet chemistry and phase separation processes are employed for the production of powders [1]. Amongst these some alternative techniques such as spray drying, spray freeze drying or supercritical fluid technologies have been developed and improved throughout the past seventy years. The popularity of spray drying is due to its relatively simple process, availability of large-scale equipment, the ease of operation and the ability of the production of composite materials [2]. Regarding this, spray drying technology is becoming more and more important in process engineering for the production of powders for healthcare [2], home care and food industry.

By setting the emphasis on spray drying only, the generation of powders is typically processed by atomizing liquids in spray towers, where the droplets are dried subsequently during their descent. For the atomization of liquids, several nozzles such as single fluid pressure nozzles, multi fluid nozzles or rotary atomizers are employed [3]. In this context, the generation of droplets with tailored properties, especially regarding a monodisperse droplet size distribution, is challenging. Concerning the aforementioned techniques, their relevant advance of high throughput in the range of several hundreds of liters per hour are facing disadvantages of a relatively wide droplet or particle size distribution, coalescence of droplets during descent and clogging of nozzles when dispensing high viscous liquids.

The simple and robust gas-actuated StarJet dispenser [4] - formerly developed for the dispensing of monodisperse droplets of molten metals – exhibits a great potential for the spray drying industry [3]. The generation of monodispersed particles with the StarJet method as discussed in this paper could also be employed for powder production in healthcare industry, e.g. to fabricate carrier particles of Mannitol for active pharmaceutical ingredients to be used within dry powder inhalers [5].

EXPERIMENTAL SETUP

The StarJet dispenser mainly consists of a pneumatic actuator body (Fig. 1a) and the star-shaped nozzle (Fig. 1b) fabricated from silicon by means of deep reactive ion etching (DRIE). The silicon chip with the integrated nozzle is mechanically mounted and centered under the reservoir, which is integrated in the actuator (Fig. 1a) and (Fig. 2a). For the centering a leaf-spring construction is utilized to reduce stress within the silicon chip if the whole device is heated, which is required for liquid metal dispensing, only. The connection between the star-shaped nozzle and the reservoir is established by a reservoir outlet bore hole (∅400 µm) which is referred to as the "**r**eservoir **o**utlet **t**ube" (ROT) in the following. The reservoir can either be fed with solder, which is being melted by a 100 W heater with a cylindrical shape, or with aqueous solutions at room temperature. The actuator is connected to a simple fluidic circuit for the gas pressure supply. The fluidic circuit consists of two lines that are supplied by two different pressure levels: The actuation pressure p_{act} and a lower rinsing pressure p_{rinse}. A 3/2-way valve is switching between the two pressure levels, depending on whether the system is actuated or in the rinsed mode.

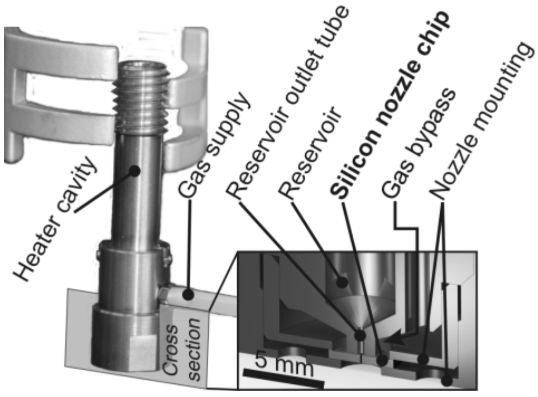
In the rinsing (non-actuated) state the pressure is too low and thus, liquid is prevented from entering the ROT due to capillary forces caused by an appropriate non-wetting surface of the ROT. Once a constant and continuous nitrogen gas pressure p_{act} is applied on top of the reservoir a gas flow through the bypass bore holes (included in the actuator) and bypass channels (included on the silicon chip) is established. Thus, a reduction of the static pressure occurs at the end of the ROT. Therefore, the liquid can overcome the capillary pressure and flows into the ROT and the star-shaped nozzle (Fig. 2b).

When the liquid continues to flow into the star-shaped nozzle, it is being centered due to capillary forces within the nozzle as described in detail in [4] and [6]. Due to interaction of the liquid and the flowing gas in the bypass channels, a periodic droplet break-off occurs within the nozzle (Fig. 2c). Finally, the droplets are transported out of the nozzle supported by the sheath-gas flow.

EXPERIMENTAL RESULTS

Metal Particles

The ability to dispense monodisperse micro droplets of molten metal with the StarJet method was demonstrated by continuous dispensing of a lead- and flux-free solder (Sn95Ag4Cu1) at liquid temperatures of T=230°C.



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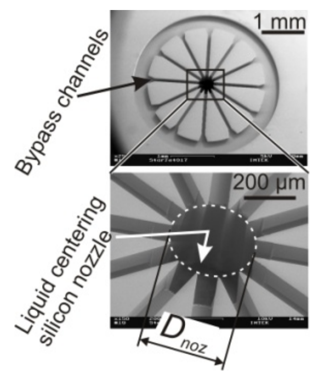


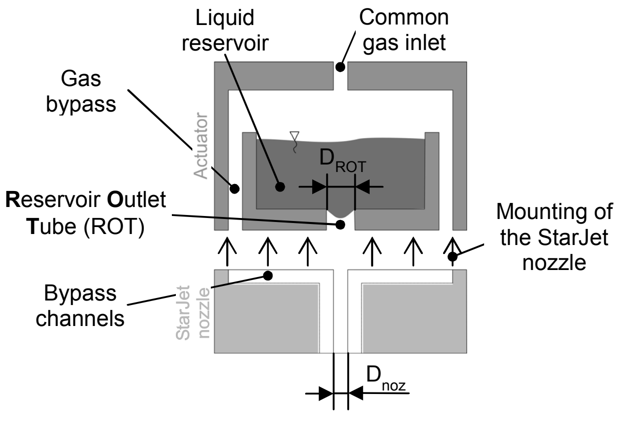
b)

*Figure 1: **a)** StarJet dispenser manufactured of brass and silicon. The cross section shows the assembly of the main parts. **b)** StarJet's star-shaped silicon nozzle. The liquid is centered within the nozzle due to repellent capillary forces.*

With a nozzle diameter of D_{noz} = 144 µm spherical and monodispersed metal particles with a volume mean diameter of $d_{v,50}$ = 149 µm were produced (Fig. 3). The StarJet utilizes the original high surface tension (σ> 0.45 Nm^{-1}) of the dispensed liquid metal and its high contact angles towards a silicon surface (Θ> 150°). Due to the repellent capillary forces the liquid is centered within the star-shaped silicon nozzle (Fig. 1b). Shadowgraphy measurements of the generated particles have shown that the StarJet method delivers an extremely monodisperse particle distribution. Regarding the $d_{max}/d_{v,50}$ ratio that is often used in spray drying to express monodispersity, the produced metal particles showed a ratio of $d_{max}/d_{v,50}$ = 1.07. In comparison, conventional nozzles such as turbulence nozzles and pneumatic atomizers deliver values of $d_{max}/d_{v,50}$ = 1.5 to 3.5. Rotary atomizers establish drop size distributions in the range of $d_{max}/d_{v,50}$ = 1.4 to 3.0. For naturally disintegrated laminar jets the $d_{max}/d_{v,50}$ ratio is about 1.4 [7]. Considering the relative span (RS) (Eq. 1),

$$RS = \frac{d_{v,90} - d_{v,10}}{d_{v,50}} \qquad (1)$$

the StarJet method produces a RS = 0.08. Compared to the mentioned atomization techniques and the natural laminar jets, which often exhibit relative spans of 0.5 - 4.0 [7], the performance of the StarJet method in the production of monodisperse droplets and particles, as demonstrated in this experiment, is significantly better.



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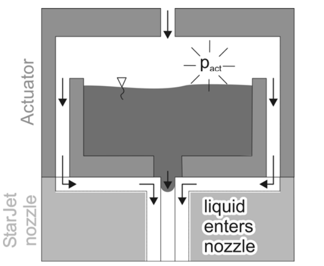

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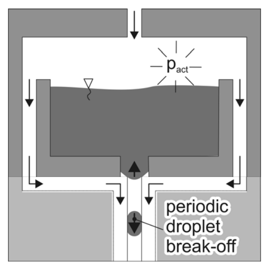


c)

*Figure 2: **a)** Sketch of the assembly. The star-shaped nozzle is mechanically mounted under the actuator, which includes the liquid reservoir and pneumatic connections. **b)** & **c)** Sketch of the working principle: After applying a gas pressure at the common gas inlet a pressure drop along the bypass channels occurs; liquid is forced to enter the nozzle. Due to the gas-liquid interaction within the nozzle and the reservoir outlet tube the liquid column is constricted and a droplet breaks off.*

Aqueous Liquids

In order to be able to use the StarJet dispenser with aqueous liquids, a high contact angle towards these liquids is required on the silicon nozzle chips to achieve sufficient centering of the liquid column within the star-shaped nozzle. Numerical simulations have shown that the meniscus retraction into the ROT after droplet break-off as well as the backward flow of liquid inside the ROT are crucial to establish the periodic droplet break-off. To ensure the meniscus retraction, not only the silicon nozzle has to exhibit a superhydrophobic layer, but also the ROT.

The necessary coating was created by a composition of Teflon and Carbon-Black resulting in contact angles above 157° for water towards the coated surface [6].

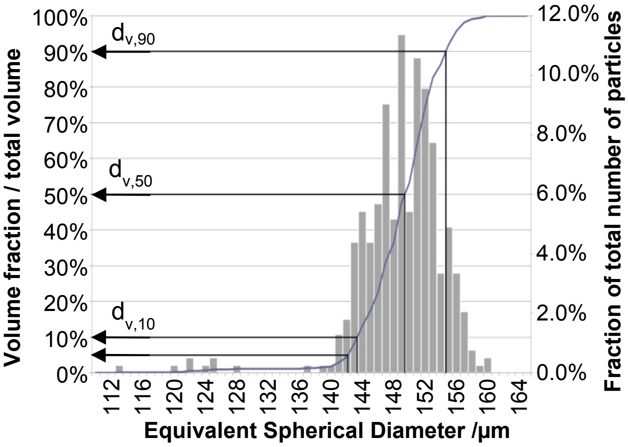


Figure 3: The particle diameter of dispensed and solidified liquid metal droplets. The particle diameter remains nearly constant at d_{50} = 149 µm and is restricted by the nozzle diameter D_{noz} = 144 µm.

Three types of aqueous solutions have been prepared for dispensing with the superhydrophobically coated StarJet: 1) Solution of 1w% Mannitol in water. 2) Solution of 30w% and 3) Solution of 40w% of Polyvinylpyrrolidone (PVP) K30 in water, respectively. Viscosities and surface tensions for the highly viscous PVP/water solution were measured. The viscosity measurements were done with the plate-cone configuration rheometer TruGap Physica MCR from Anton Paar and the CP50-1 cone. The surface tensions were measured with the DataPhysics OCA15plus device employing the pendant drop method. Results are given in the text below.

Utilizing a star-shaped nozzle with D_{noz} = 59 µm for the continuous dispensing of the 1w% Mannitol/water solution (dynamic viscosity $\eta \approx 1$ mPas) first droplet break-offs were observed at $p_{act} \approx 50$ hPa. When the actuation pressure was increased to approximately 55 hPa, the droplet ejection changed from an irregular ejection to a regular and periodic ejection with droplets that were aligned in a row. When p_{act} was increased to 65 hPa, the distance between single droplets decreased, indicating an increase of the droplet ejection frequency. At actuation pressures above 65 hPa irregular break-off and coalescence of droplets was observed. From stroboscopic pictures droplet volumes of approximately 100 pl (Fig. 4) were measured. After the deposition and the subsequent drying of the droplets on a hydrophobic surface, particles with diameters of 22-25 µm were found (Fig. 5).

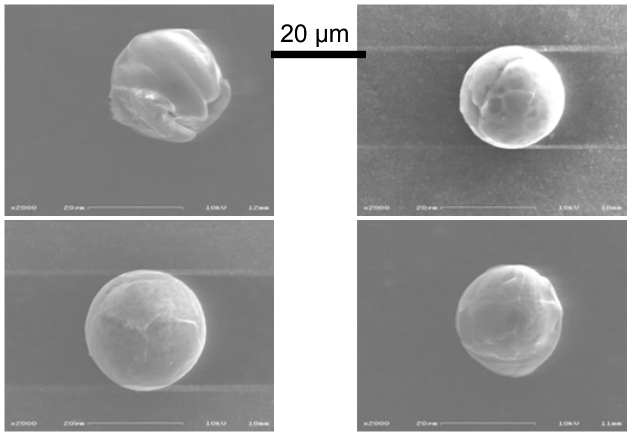


Figure 4: Each picture shows dried particles from a 1w% Mannitol/water solution. The particles have sizes of about 22-25 µm.

The stroboscopic pictures show that the Mannitol/water solution leaves the nozzle as a formed droplet. No disintegration of a liquid jet outside the nozzle could

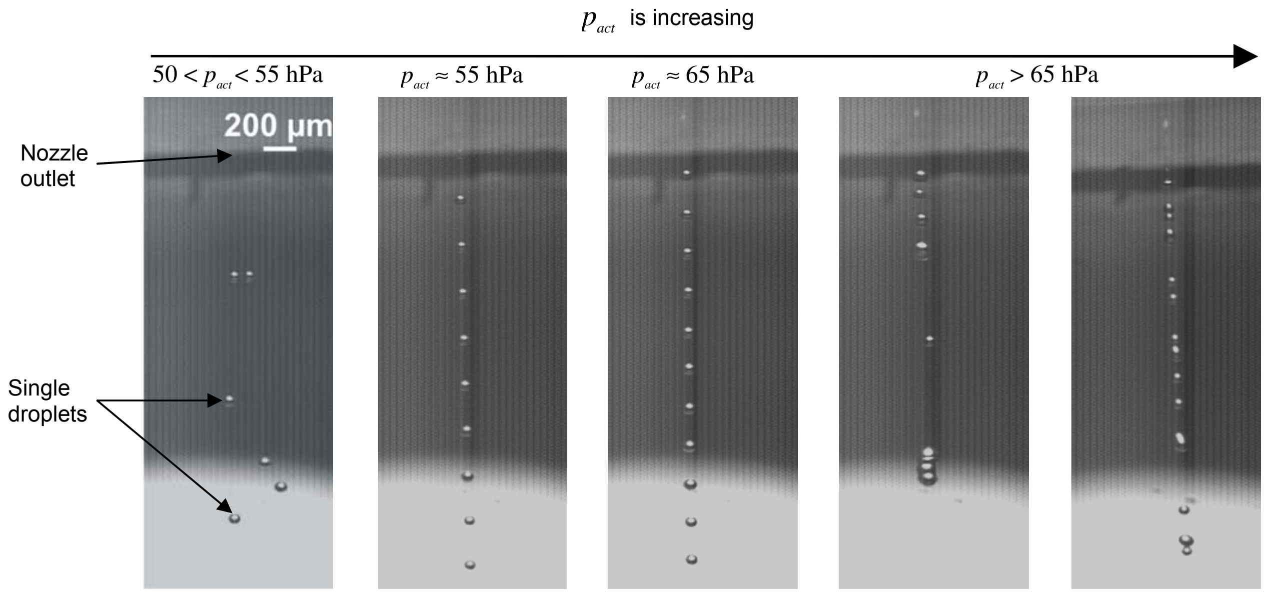
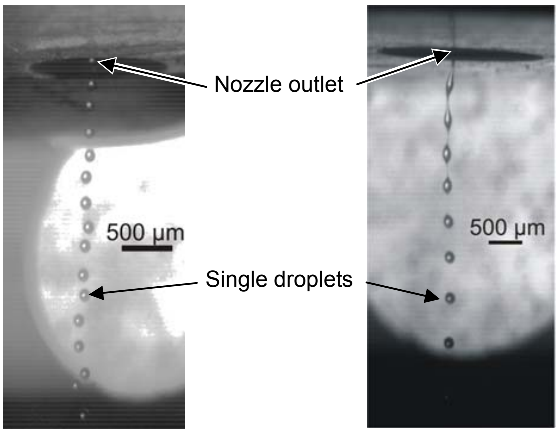


Figure 5: Stroboscopic records of dispensed Mannitol/water droplets (100 pl).

be observed. This indicates the typical StarJet droplet generation in contrast to the well-known Rayleigh breakup.

For the 30w% PVP/water solution ($\eta \approx 105$ mPas, $\sigma = 64.5 \pm 0.5$ mN/m at 23°C) a periodic droplet break-off was achieved with a nozzle of $D_{noz} = 183$ µm at actuation pressures of $p_{act} = 200$ hPa (Fig. 6a). The single droplet volume is estimated to be 3.9 nl. Again, a typical StarJet-type droplet break-off is observed, because the liquid is leaving the nozzle as single droplets.

Dispensing of a 40w% PVP/water solution ($\eta \approx 490$ mPa·s) with a $D_{noz} = 183$ µm nozzle at 200 hPa resulted in a continuous droplet generation, with a droplet break-off *outside* the silicon nozzle. This suggests that the droplet breakup in this case could be of a Rayleigh-type or of mixed type (Fig. 6b). Further investigations are required to study the type of droplet breakup mode in dependence of the relevant parameters (Weber number, Ohnesorge number etc.) The droplet volume in this experiment was measured to be 3.2 nl.



a) *b)*

Figure 6: Stroboscopic records of a PVP/water solution. ***a)*** *Continuously dispensed droplets (3.9 nl) of 30w% PVP in water ($\eta \approx 105$ mPa·s).* ***b)*** *Continuously dispensed droplets (3.2 nl) of 40w% PVP in water ($\eta \approx 490$ mPa·s).*

CONCLUSION

The excellent monodisperse particle distribution achieved by the StarJet method for liquid metal droplets suggests the application of the method for the generation of micro particles from aqueous solutions. This work has experimentally proven that the method indeed can be applied to different water based polymer solutions to generate polymer particles at high frequencies, as long as a proper hydrophobic coating of the microfluidic channels and nozzle is performed.

Future work will be dedicated to an increase of the liquid material throughput by the parallelization of the nozzles. In this context also the dependency of the breakup mode as well as the droplet size and frequency as a function of Weber number and Ohnesorge number have to be studied.

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ACKNOWLEDGEMENTS

We gratefully acknowledge financial support from Deutsche Forschungsgemeinschaft for the project ZI/1201/3-1 within the priority program Prozess-Spray 1423. We also gratefully acknowledge Inspire IRPD for the particle distribution measurements.