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Aerosol generation and handling in microchannels

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Abstract

The application of T-shaped micromixers is demonstrated for the generation of nanoscale aerosols by the mixing of hot vapor–gas-mixtures with cold gas. The fast mixing within micromixers leads to high supersaturation of the vapor and to homogeneous nucleation. After nucleation, the particles grow to their final size until the vapor is saturated. Different mixing ratios and gas temperatures have been investigated. Special attention was paid to thermal insulation and particle deposition at the channel walls. Experimental results for particle deposition (prefabricated NaCl nanoparticles in a nitrogen carrier stream) and aerosol generation (vitamin E droplets in nitrogen) are presented. High temperature gradients up to 10^6 K/s lead to a rapid condensation and formation of nanosized droplets with a mean diameter of 20–50 nm and a narrow size distribution. First experimental results for the two-phase flow in a separation chip indicate the suitability for mixing and further improvements for phase separation.

Keywords: Microprocess engineering; Integrated processes; Particle deposition; Nano particles; Nucleation

1. Introduction

In the area of microprocess engineering particle generation and handling becomes more important due to its industrial and practical relevance. The heat and mass transfer as well as the mixing of reactants are very fast in microchannels due to their small dimensions [1]. The transport processes can be controlled in a very effective manner and lead to an effective, continuous generation of nanosized particles with a narrow size distribution. Such nanoparticles, either solid or liquid, allow for new product formulations with special properties in biological, pharmaceutical, or medical applications [2]. The production of nanoparticles in microreactors has already entered the industrial scale in specialty chemistry [3,4]. However, particle handling is difficult in microchannels due to the high surface-to-volume ratio which increases the risk of fouling and blocking of the channels [5,6]. Nevertheless, generation and handling of nanoparticles is, in principle, feasible in microchannels, as has been shown in various applications in microreaction engineering [7], and Lab-on-Chip applications [8]. The particles are generated in a liquid phase with high shear gradients [9] as well as in bubbly flow of two immiscible liquids or gas–liquid flow [10].

This contribution describes the generation of aerosols with liquid nanosized particles or droplets in gas phase either by cooling or by mixing. In both cases the state of a vapor–gas mixture is changed to exceed the saturation concentration and to form small droplets. The mixing is performed in T-shaped micromixers. Previous extensive research on liquid mixing has shown that these devices yield extremely short mixing times below 1 ms [11,12]. For aerosol generation, the flow regimes in the microchannels were numerically simulated for gas flow with different inlet temperatures in a recent study [13]. Besides the engulfment flow for nearly symmetrical inlet flow conditions, a mushroom-like vortex flow was found, which leads to an increased interface between the components and to fast mixing. In the work presented here, the particle deposition in microchannels is determined with nanoscale sodium chloride particles in a nitrogen carrier stream. For aerosol generation a gaseous vitamin E–nitrogen mixture close to saturation with 150 °C is mixed with a nitrogen stream with ambient temperature to produce a vitamin E aerosol with a droplet diameter around 20 nm. First optical investigations of two-phase water–gas flow are presented for nanoparticle separation.

2. Fabrication

Particle formation includes the process steps of nucleation and particle growth from a supersaturated mixture. The nucleation without any starting nuclei is called homogeneous and

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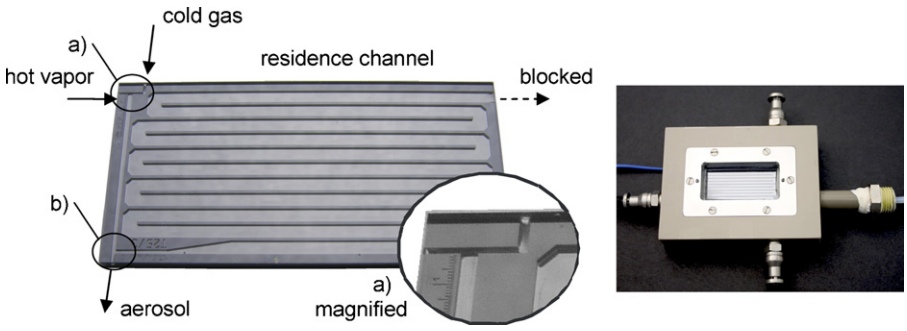

Fig. 1. Silicon chip for aerosol generation. Left side: single chip (20 mm × 40 mm area) with two mixers (a) and (b) for homogeneous and heterogeneous condensation and a meander as photo reactor for photo-polymerization. Right side: chip mount with integrated chip (180° turned) and fluidic connections.

requires a high supersaturation of the precipitating component. There are two possible routes to produce a high supersaturation of a hot gas–vapor mixture: rapid cooling of the mixture alone below the saturation line or, as anticipated here, fast mixing with a second stream of cold gas. In a micromixer, rapid cooling may happen as an adverse side effect due to the high temperature gradients present at the fluidic inlets. This undesired cooling of the vapor–gas mixture generates an early nucleation at the channel entrance and particle growth during further cooling resulting in relatively large particles with a wide size distribution. Additionally, a major part of the condensing vapor adheres to the cold wall and is lost for the particle precipitation. Contrary to that, fast mixing produces an instantaneous high supersaturation with many nuclei. The result is an aerosol with a narrow particle size distribution and small mean diameter which is often desired in particle processing.

To investigate the different precipitation processes, silicon mixer chips with T-shaped mixing elements are designed and fabricated, see Fig. 1. The first mixing element has 200 μm × 300 μm inlet channels and a 500 μm × 300 μm mixing channel. To avoid particle generation by cooling, the inlet channels leading to the T-shaped mixer are kept very short (1 mm) for the hot vapor–gas mixture. The inlet channel for the cold gas stream includes a 90° bend for topological reasons. The entire chip contains the first mixer for particle generation, a second T-mixer for an additional process step and a residence time channel for chemical reaction purposes. In the last two parts of the chip, only particle losses are determined in this study, not the process steps for which they were designed. A short overview about the entire studied process is given by Kockmann et al. [14] with particle generation, handling, and separation.

The channels are fabricated by photolithography and silicon DRIE etching resulting in a rectangular cross section and comparably smooth walls ($R_{RMS} < 1$ μm). The chips are covered with Pyrex glass for optical observation. Photo masks made from printed polymer transparencies with 8000 dpi resolution were used for a very fast and flexible design and data transfer to the photolithographic processes. Due to the in-plane channel design, one photo mask is sufficient for the DRIE process. The channels are connected from the chip side via a molded silicone sealing. For more details on this see [15].

The integration of the mixer chip into the fluidic mount is illustrated in Fig. 1, right side. The connection for the hot vapor–gas mixture is thermally insulated to provide a saturation state of the mixture at the mixer chip inlet.

3. Experimental investigation of particle deposition

First experimental investigations of the deposition of polydisperse NaCl particles indicate the critical, fouling-prone points of the T-shaped micromixer. These experiments were conducted in cooperation with the University of Karlsruhe. The experimental conditions are described by Heim et al. in [5], which clearly indicates, that curves and bends of the microchannels lead to increased particle deposition, see Fig. 2. The swirling flow in the mixing element of the T-shaped mixer generates an enhanced wall contact of the particles which adhere and agglomerate, see Fig. 2 left side. The wide bends in the serpentines of the residence time channel are less prone to particle deposition, as visible in Fig. 2, right.

In the further experimental investigations, a vitamin E vapor and nitrogen gas mixture is used to produce nanoparticles by partial condensation. The liquefied vitamin E flows as nanoparticles with the gas stream, but also adheres as a thin film at the wall. Optical observations through the glass lid and experimental experience lead to the conclusion, that this process is negligible for the investigated process conditions.

4. Vapor phase particle generation

In a contact evaporator the vapor–gas mixture is generated from vitamin E and nitrogen with a saturation temperature of 130 °C and is superheated to 150 °C to avoid condensation in the connecting tubes. The temperatures of the vapor in the evaporator and the overheated zone and of the chip are measured with thermocouples. After entering the chip the mixture flow is inevitably cooled down by the cold walls and the first particle nuclei are formed by homogeneous condensation. Until entering the mixing element, the particles grow due to further cooling. Due to the high thermal conductivity of silicon, the wall temperature can be estimated by the chip temperature, which is at 23 °C at the beginning of the experiments and slowly increases to about 30 °C within several hours of measurements. By mixing the vapor–gas mixture with a cold nitrogen stream, a supersaturation is formed and leads to further nucleation. The nucleation processes and the particle growth can be seen in the particle size

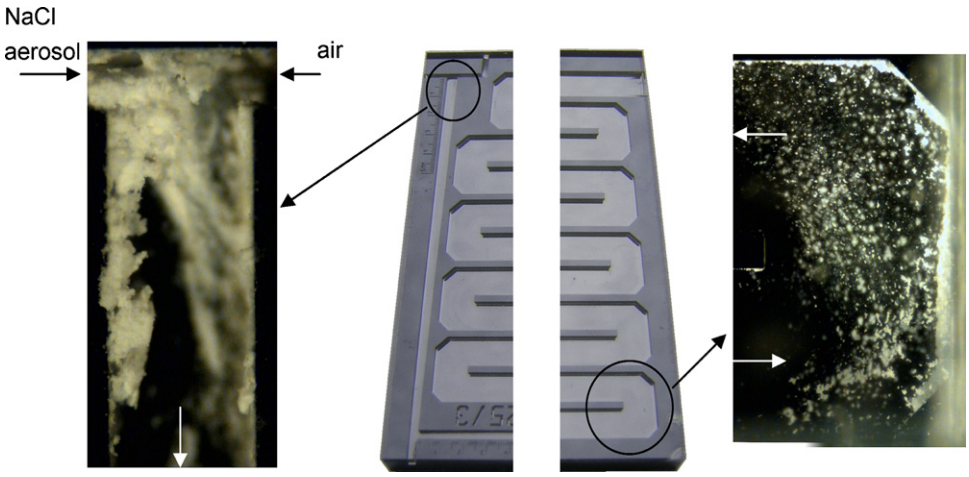

Fig. 2. Silicon chip for aerosol generation: particle deposition of a polydisperse NaCl aerosol (up to ~1 μm diameter) in the first micromixer (left side) and in a bend of the meandering channel (right side).

distribution, see Fig. 3, measured by a scanning mobility particle sizer SMPS [5]. Particles with a mean diameter of about 20 nm are formed by fast mixing below 50 ns. With increasing chip temperature from 23 °C to about 30 °C, fewer particles are formed by cooling the mixture at the inlet, i.e. the number of larger particles decreases.

With the typical inlet flow velocity of about 28 m/s (Reynolds number $Re = 340$) and an inlet length of 1 mm, a temporal temperature gradient of about $\Delta T_t = -0.7 \times 106$ K/s is induced leading to high supersaturation. For this estimation, a simulated temperature difference of 25 K along the inlet channel was used. Resulting from prior investigations [13] for *Re* numbers higher than 350, the mixing length in the channel is constant with about four times the hydraulic diameter d_h. The cold gas stream enters the chip with a temperature of 25 °C. During mixing the hot vapor is cooled to about 85 °C of the aerosol. This means a further temporal temperature gradient of -0.87×10^6 K/s for the hot gas cooling with a velocity of about 22 m/s in the mixing channel ($Re = 440$). For the cold gas stream, the mixing ratio leads to a temperature gradient of about 1.3×10^6 K/s. These extremely high temperature gradients are responsible for the small droplet diameter and narrow droplet size distribution, see Fig. 3. The generated nanoparticles grow further when flowing through the mixing channel, until the supersaturation is consumed.

One of the future steps will be the fabrication of the microchips in polymers by molding to avoid the high cooling of the hot mixture at the chip entrance.

5. Separation of two-phase flow

Once generated nanosized particles have to be formulated in a proper way to transport, store, and apply the particles as a suspension or emulsion. A special silicon chip with channels for aerosol–water contacting in a spray nozzle and gas–liquid separation in an impactor is shown in Fig. 3, right side. The aerosol enters from the left side parallel to a water stream to be contacted. In a spray nozzle (Fig. 3 right side) or in a Venturi nozzle (Fig. 4 left side) the water is mixed with the aerosol–gas stream. The following channel widenings with posts and bends enforce the contact between liquid and aerosol to wash out the nanoparticles, see Fig. 4 middle.

The T-shaped impactor, which fills almost the lower half of the chip (20 mm × 20 mm footprint), should separate the liquid from the gas stream by momentum and capillary forces. The gas–liquid mixture is sprayed onto a perforated wall consisting of 30 μm diameter pillars with a distance of 30 μm, visible as a

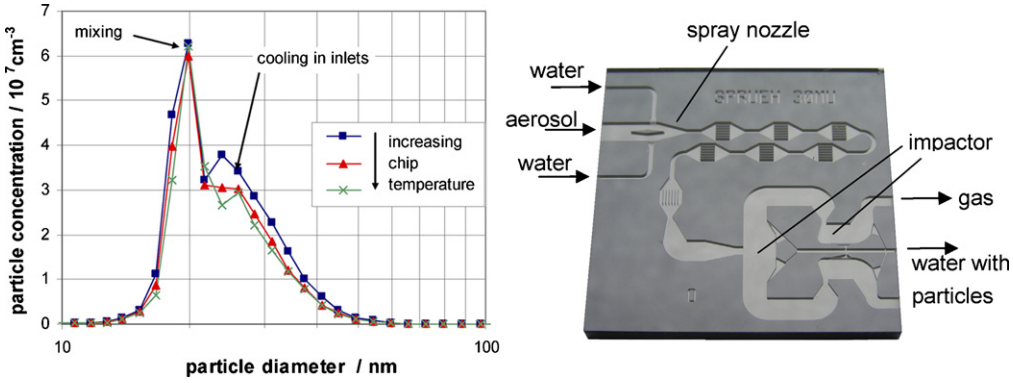

Fig. 3. Left side: particle size distribution of vitamin E aerosol generated in the micromixer. Right side: single separator chip (20 mm × 20 mm area).

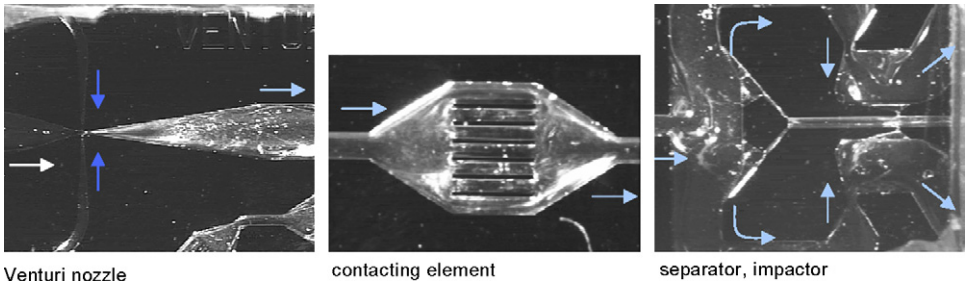

Fig. 4. Gas–liquid two-phase flow in the separator chip. Left: Venturi nozzle with gas flow entering from the left side, water entering from top and bottom into the nozzle. A two-phase flow exits the nozzle and is lead through the mixing elements. Middle: Mixing element with gas–liquid two-phase flow from left to right. Right: two-stage impactor for separation of gas–liquid flow.

line in Fig. 3 right. A second impactor is following the first one, treating only one half of the mass flow. Therefore, the second impactor is shaped like a 90° bend. Here, two pillar lines are used to separate the liquid from the gas flow by capillary forces. The liquid is collected in a channel network along the center line of the two-stage impactor.

The forced convection two-phase flow in microchannels is difficult to describe, hence first optical investigations of the gas–liquid flow are presented here. The Venturi nozzle provides for a good mixing and contacting of the components, see Fig. 4 left. The fast fluid velocity can be seen directly after the nozzle as well as the formation of annular-slug flow in the straight wide channel. Each mixing element with channel widening and contact grid leads to a good mixing and contacting of both phases. The small channels between the grid pillars show some characteristics of bubbly, slug, and annular flow, see Fig. 4 middle. The two-stage impactor with the gas–liquid flow is shown in Fig. 4 right. The liquid is collected in the flow dead zones behind the corner of the jet flow and forms a rotating adhering droplet. Some liquid is entrained and flows to the perforated side. Due to the capillary force, the liquid is sucked into the pillar row, but due to the high velocity and impact pressure, also gas enters the pillar row and the collecting channel. The bubble formation in the collecting channel is clearly visible and leads to an incomplete gas–liquid separation. Different flow rates and channel velocities exhibit a similar behavior of the two-phase flow separation.

In the future work, each contacting and separation element will be investigated separately to control effectively and independently the flow parameters. Also, the pressure loss and the fluid distribution in the elements have to be improved in the future design.

6. Conclusion

This work presents experimental investigations of precipitation processes and succeeding particle separation steps. The deposition of solid particles happens primarily in bent and disturbed flow, which has to be considered in the channel design. The homogeneous condensation of vitamin E vapor with temporal temperature gradients up to 1.3×10^6 K/s produces nanoparticles with a mean diameter of about 20 nm. The temperature control of the mixer chip is crucial for the production of small particles with narrow size distribution. To separate the nanoparticles from the gas flow, an impactor chip was designed and tested with gas–liquid two-phase flow. The mixing of the two-phase flow works excellently, but the separation of the liquid from the gas flow has to be improved.

Further investigations are planned for the encapsulation of nanosized particles by heterogeneous condensation of a monomer and consecutive photo-polymerization and particle formulation in an aqueous dispersion.

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