IMPROVING CRYSTAL SIZE DISTRIBUTION USING MICROREACTOR MIXING UNITS

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ABSTRACT
In this work, we investigated the effect of microreactor mixing units on crystal sizes and crystal size distribution (CSD) during barium sulfate crystallization. A cheap and mass production compatible fabrication scheme was developed for PMMA micromixing devices, using a milling robot capable of generating features down to 200 μm. A drastic improvement in CSD was observed for a number of flow distributors and a scheme to tailor crystal sizes with a narrow CSD was developed.

KEYWORDS: Crystallization, CSD, Mixing Units, PMMA

INTRODUCTION

During the last decade, microreactors have silently moved from academia to some industrial applications [1]. It has become clear that, despite the claimed benefits of microreactors, practical hurdles and an often doubtful reliability have prevented a real industrial breakthrough of this promising format. The benefits in the specific application areas of viscous liquids and crystallization can be expected to be truly dramatic. A flat rectangular shallow channel format can provide a combination of reasonable throughput on the one hand and tight and uniform temperature and plug-flow control on the other hand.

THEORY

Mixing in microreactors has been investigated most thoroughly for dimensions below a typical critical dimension of 100 μm, mostly conceived in Si devices by dry etching techniques, but also by e.g. LIGA. In contrast with turbulent flow mixing in continuous processes, and active mixing in batch reactors, these small dimensions allow mixing at the molecular level. In this work, we have studied the mixing efficiency of several milled mixing units in PMMA. This low cost fabrication method is ideally suited to study applications that have a high probability of producing irreversible damage to the microreactor, where the use of expensive metal devices is prohibited.

EXPERIMENTAL

The channels were milled and sealed by thermal bonding on a PMMA cover sheet (170°C, 30 min). The microreactors were connected to a syringe pump with equal concentrations of $BaCl_2$ and Na_2SO_4 as substrates. It is due to the low solubility (K_{sp} = 1.0842 10^{-10}) of $BaSO_4$ that crystals are formed. At the outlet of the microreactor, the product is instantly diluted and filtered to halt further crystal growth. The analysis of the crystals was performed with SEM. Four types of reactors containing different mixers were applied: an impinging jet (T) mixer and three mixers with varying obstacles (Fig. 1). Different substrate concentrations (0.04 M and 0.01 M) were used for the reactive crystallization, favoring either nucleation or growth [2].

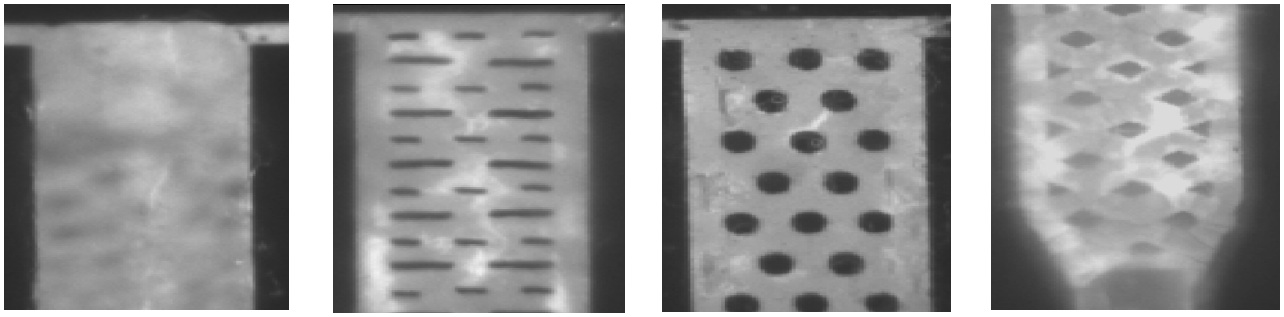


Figure 1: Mixing units. From left to right: T-shaped mixer, stretched pillars (S), circles (P), diamonds (R). The mixing units were visualized by 7-amino-4-methylcoumarin fluorescence detection. The slight deviations in fluorescence not caused by the pillars, are due to the limited milling precision. The width of the inlet channels is 200 μm, the width of the main channels is 1200 μm. The aspect ratios (AR) of the stretched pillars are 4 and 8, the AR of the full diamonds 1.5.

It was shown earlier that a simple impinging jet mixer can deliver a narrow CSD for nanosized crystals [3]. Part of this work consisted of examining the distribution of larger crystals (5-10 μm) to define the effect of mixing on both nucleation and growth. First, the effect of the concentration and the channel length (flowrate 0.1 ml/min) was studied in a T-shaped mixer. This was done for a 1 cm mixing unit and an outlet capillary of different lengths (1, 2 and 5 cm). Second, the experiment was repeated for the mixing units with the flow distributors to define the mixing efficiency.

To validate the improved mixing efficiency of the mixing units, fluorescence measurements were performed. Methanol was mixed with 7-amino-4-methylcoumarin (diluted in methanol) and the fluorescence profile was detected by means of a CCD camera.

The growth of relatively large crystals without an increased residence time was investigated. The nucleation step and the growth step were both stimulated. At the inlet of the mixer the substrates (0.04 M) were added and 0.5 cm downstream the mixing unit more substrate (0.01 M) was added. The outlet capillary was 5 cm long and the analysis was performed with SEM.

RESULTS AND DISCUSSION

It is found that for a given dimension (width, height), the distribution in an impinging jet mixer depends on concentration and channel length (Fig. 2). A high concentration leads to a high amount of crystals with similar (small) sizes. This is probably due to a fast depletion of material caused by the high nucleation rate. A lower concentration leads to a broader distribution, because of the diffusion based mixing and slower depletion of material (less nucleation). The distribution for the used flow rates is narrower for the distributor mixers (Fig. 3).

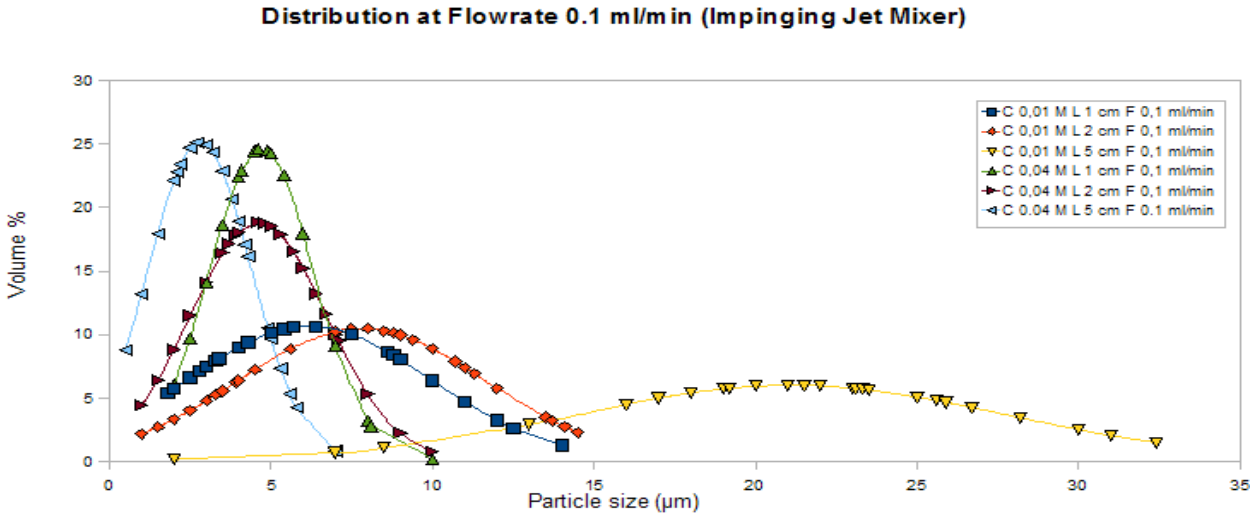


Figure 2: CSD using Impinging Jet Mixer (T). The distribution is dependent on the channel length and concentration. In this laminar flow regime, diffusion acts over a long distance. The dimensions of the mixing unit are slightly different than in the pictures shown in figure 1.

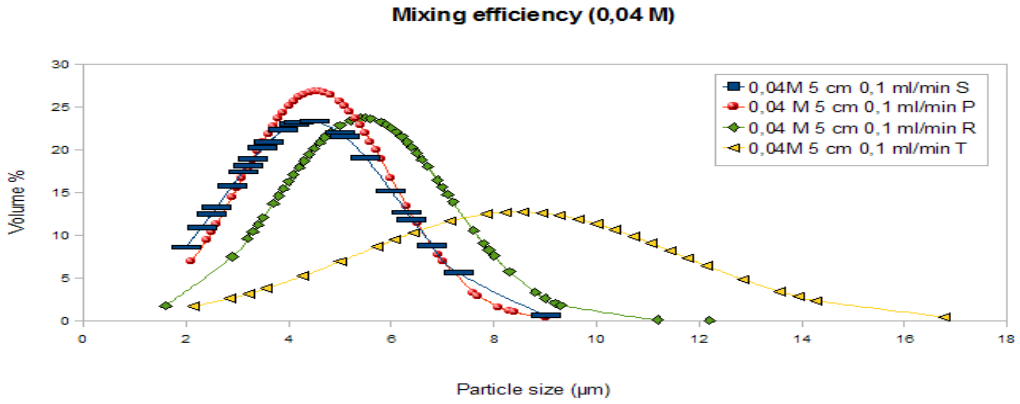
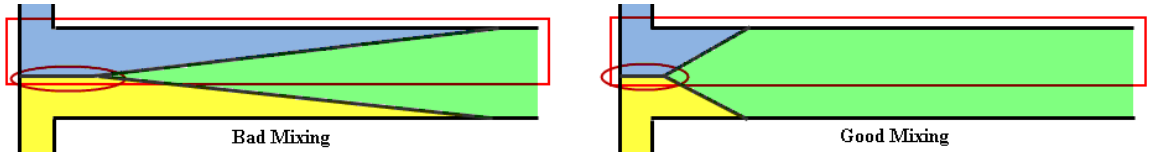


Figure 3: The improved distributions of the mixers with flow distribution (S, P, R) compared to the impinging jet mixer (T). The features give rise to smaller diffusion distances and thus better mixing. This effect is observed for both higher and lower concentrations (results for the lower concentration not shown in graph). Due to the better mixing, there is more nucleation and hence more and smaller particles with a narrower distribution. The mixing units shown in figure 1 were used for this experiment.

The fluorescence analysis of the mixers confirmed that mixing is enhanced by the flow distributors The mixing starts faster due to a disruption of the flow profile and the slope of the fluorescence increase (on the methanol side – decrease on the coumarin side) is larger (Fig. 4).



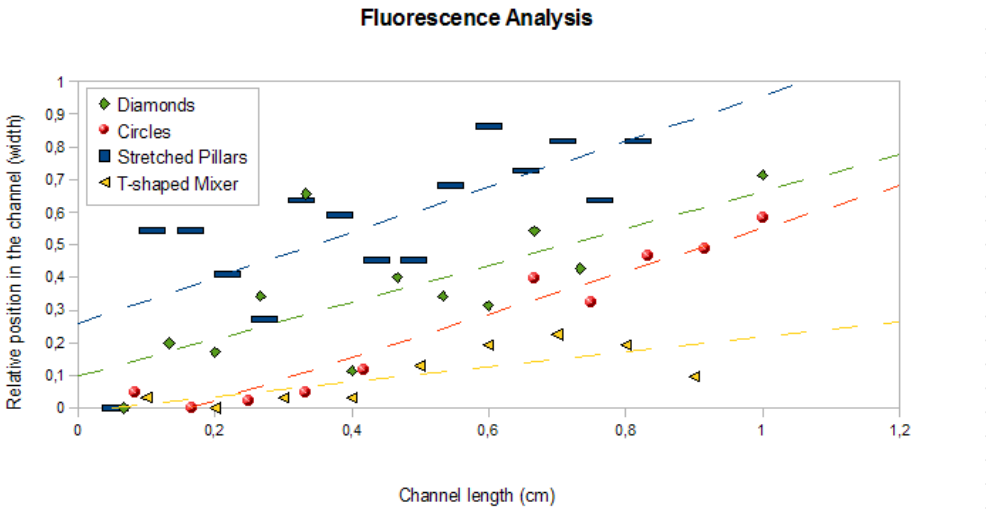


Figure 4: Top: Schematic fluorescence profile depicting bad and good mixing. If the slope of the 'mixing line' is larger, the mixing is faster. In red encircled is the distance in the channel before mixing can be visualized. The red square is the section visualized in the graph. Bottom: The experimental result of the fluorescence visualization of the mixer, the intensity cut-off I was 20 % of the maximum intensity I_0. The Y-axis gives the relative distance between the position of the initial cut-off value and the channel wall. The slopes of the flow distributing mixing units are steeper and the distance before mixing can be visualized is shorter (S, R) due to the disruption of the flow pattern by the flow distributors. The fluctuation between the experimental results and the expected linear profile is possibly due to the limited milling precision (as visualized in figure 1).

A nucleation stimulating step followed by a growth stimulating step by adding substrates at respectively higher and lower concentrations in the mixer enabled us to produce larger crystals. Crystals were up to 23% larger for the flow distributing mixers (diamonds). No growth effect was detected in the impinging jet mixer.

CONCLUSION

The results confirm that PMMA microreactors are a valid and cheap alternative for batch reactors. The distribution depends on both channel length and concentration. The results indicate that mixing benefits from flow distributors as seen by fluorescence measurements. A better mixing leads to smaller crystals and a narrower distribution. Size tailoring of crystals is possible as shown by the preliminary results obtained in the growth experiment. Further investigation (longer growth time, more growth phases) will be performed to quantify the growth rate .

The fabrication scheme enables fast and cheap screening, improvement and production of applications for any process that requires tight control of reaction steps.

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