Controlling of immiscible liquids fluid in a capillary reactor – from continuous to segmented flow

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Abstract. Experimental variation of the droplets form in the flow of immiscible fluids in a capillary with the inner diameter of 0.9 mm is presented. The possibility of the transition from continuous to segmented flow by varying the velocity of precursors and carrier liquids is demonstrated. It is shown that the rate of variation of one precursor in respect to other makes it possible to vary the ratio of mixing components. Simulation results for Ψ-shaped mixer in COMSOL Multiphysics software are also presented.

1. Introduction

Traditional synthesis of monodisperse nanoparticles in chemical flask has a number of shortcomings that limit the scaling of such systems for industrial applications. The solution to this problem is to turn from batch technology to flow synthesis. In comparison with traditional chemical synthesis in a flask, the flow reactor type allows increasing synthesis rate of nanoparticles. The quality improvement also occurs [1]. Apart from its obvious superiority in large scale production, flow reactor has a number of additional advantages: a) more effective heat control and mass transfer, b) the ability to control the cooling rate, b) a better synthesis reproducibility, d) lower reagents consumption.

The capillary is a central element in such reactors, where precursors are dispersed and mixed with other reagents. Fluid transfer in the channel is usually described by the Reynolds number \( \text{Re} \), which allows determining the transition from laminar to turbulent flow:

\[
\text{Re} = \frac{\rho v D}{\eta},
\]

(1)

where \( \rho \) is density, \( v \) is the characteristic flow velocity, \( D \) is the hydraulic diameter (for a circular tube it is equal to geometric diameter), \( \eta \) – dynamic viscosity of environment. Due to small diameter, microreactor channel normally corresponds to Reynolds criterion which is less than the critical value and eliminates the uncontrolled emergence of turbulent flow so that mixing occurs mainly by molecular diffusion or by means of special taps.

Mixing is achieved by the creation of strong vortex fields that are generated inside the microchannel. In paper [2] different tools and mixing mechanisms in microfluidics were presented. Of course, each design has its advantages and disadvantages, and the most appropriate mixing tool must be selected according to specific application. The authors of [3] believe that there is no single
approach when choosing mixer that meet all requirements and are suitable for all applications. However, from the productivity point of view and production cost, different technologies and mixing concepts can be described. Microfluidic mixers can be classified as active: that utilize external energy for mixing, or passive: where mixing occurs due to the microfluidic device geometry or the functional structures of a certain configuration.

The mixing degree improves the quality of synthesized particles [4]. There are various types of passive mixers (Figure 1), which are quite simple to implement.

All nanoparticles flow synthesis reactors can be divided into several groups with different types of stream creation, each of which will affect the flow shape of the reactants inside the capillary (Figure 2).

In the first reactors continuous flow was utilized but it had several disadvantages: large polydispersity of the obtained nanoparticles in consequence of precursors laminar flow as well as gradual pollution of the channel due to contact with the channel wall. The example of CdS nanoparticles synthesis [5] was demonstrated with a complete channel blockage thirty minutes from the start of the synthesis. The same paper presents another technique for reagents flow forming in a capillary using inert gas to separate the flow of liquid precursor to bullet-separated bubbles of gas. In such reactors the problem of nanoparticles polydispersity was solved but contact with the walls leading to pollution of the channel was still inevitable. In paper [6] segmented flow was formed by using a carrier fluid that does not mix with the precursor solution, but also wets the walls of the channel. In this way the problem of polydispersity of obtained nanoparticles was solved as well as the problem associated with channel pollution. The segmented flow type of reactor has been used to synthesis a wide range of materials: nanoparticles of iron oxides [7], Ag [8], CaCO$_3$ [9], BaSO$_4$ [10], zeolites [11], TiO$_2$ [12], γ-AlOOH, β-FeOOH [13], and more complex structure types like core/shell, such as SiO$_2$/Au[14] and Au/Ag/Au [15].
The present paper describes the implementation of nanoparticle synthesis in the liquid/liquid segmented flow [16]. For the binary compounds nanoparticles synthesis, one must use the upgraded Y-shape mixer (Figure 1, b). Two side capillary inlets meant for two precursors and the middle inlet for the liquid carrier altogether forms a Ψ-shaped mixer (Figure 3, a).

2. Experiment

One of the stages in the flow reactor development for nanoparticle synthesis is the simulation of flow for certain construction of reactor. We use for such purpose COMSOL Multiphysics software with Microfluidics Module. There are two main groups of methods of flow simulations: interface tracking methods (ITM) and the dispersion methods. For large-scale problems with a large number of bubbles, drops and solid particles, a less computational resources-demanding model is required. The so-called dispersive methods which track the volume proportion attributable to each phase allows one to use less computing resources. With the help of the dispersion method, one can model for example, a circulating boiling film which is often used in food, pharmaceutical and chemical processing. The interface tracking methods is designed to simulate flow of two different immiscible fluids separated by well-defined surface. These methods are usually applied to simulate the formation of bubbles or drops; mixers, turbulators; separated oil streams, water or gas. Methods to track the interface are accurate and give a clear picture of the flow field (velocity, pressure and force of surface tension). However, they require large computational resources, making them not always preferable. These methods for interface tracking in general are better suited for microfluidic applications where monitoring a small number of drops or bubbles are essential.

Methods of interface tracking includes: level set method; phase field method; two-phase flow with moving mesh. All of these methods allow accurate tracking of the interface between two immiscible liquids. They take into account the difference in density and viscosity of the two fluids, and the influence of surface tension and gravity. Using the phase-field maps, we obtained volume fraction in the mixing of the two precursors (side capillaries) and liquid carrier (middle capillary). Figure 3 presents the simulation results using the same pressure in all three capillaries. As it can be seen, mixed precursors replace the carrier fluid both in forward and reversed direction. In the reversed flow direction, substitution occurs in a weaker manner.

![Module mixing the precursors](image)

Figure 3 – Module mixing the precursors (a) and simulation result (b) of volume fraction using the same pressure in all three capillaries inlets
In this research, we carried out experiments to find the optimal flow rates of reagents necessary for synthesis. The capillary was a flexible polytetrafluoroethylene tube having an inner diameter of 0.9 mm. Fluids rates were varied with the help of syringe pumps. For experiments water-based inks of different colours were used in the role of precursor and hexane as a liquid carrier. Figure 4 shows an image of the channel specified in the listed fluids.

Figure 4 – Flow elements in the PTFE capillary: A and B – model precursors, C – a liquid media

Figure 5 presents results of an experiment where the precursors and carrier fluid are supplied at the same rate. The smaller the feed rate of the precursors, the smaller the droplet size of the precursor mixture. But at the rate of 1.2 μl/sec mixing occurs only partially as it was evidenced by the colour of drops (yellowish tint). Based on these results, the best rate to obtain segmented flow is in the range of 10 to 20 μl/sec.

Figure 5 – Shape evolution of the segmented flow during simultaneously changing of precursors feedrate A, B and liquid media C. Numbers marked flow rate in μl/sec

Figure 6 presents the results of an experiment where the rate of one precursor was changed in relation to another. The images show that there is a complete mixing (no color alternation of droplets), but because of the relative change in the feed rate of the precursor A in relation to the B there is observed changing of color tone and the size of the output drops.
Figure 6 – Evolution of the shape of the segmented stream due to reducing the feed rate of one of the precursors ($U_A$) at constant speed of the other precursors and liquid media ($U_C = U_B =160$ μl/sec). The numbers indicate the flow rate of $U_A$ in μl/sec.

Figure 7 presents results of the change in flow rate of the fluid carrier relative to the constant feed rate of precursors, which leads to a change in droplet size of the mixed precursor solution due to the change in the fraction of carrier fluid in the capillary.

Figure 7 – The experimental results of change in flow rate of the carrier liquid at a constant flow rate of precursors ($U_A = U_B = 160$ μl/sec). The numbers indicated the flow rate of the carrier liquid in μl/sec.

After analysing the above results, it can be assumed that the optimum velocity at which there is complete mixing of the precursors and the separation of the stream into droplets with carrier fluid are rates from 10 to 50 μl/sec.

3. Results

As a result, modeling and experimental research has shown that varying the flow rate of the carrier and precursor fluids output of Ψ-shaped mixer gives additional variation of flux: 1) a transition from a continuous flow to segmented type, 2) mixing the components in different ratios, while maintaining a segmented or continuous flow form. The obtained results are used to select flow rates of the synthesis reactor nanoparticles.

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