<87e> Manipulation and control of the particle size distribution of nanoparticles during their formation in microemulsion droplets by a suitable feed strategy

Björn Niemann[1] and Kai Sundmacher[1,2]

[1]*Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany*
[2]*Otto-von-Guericke University Magdeburg, Process Systems Engineering, Germany*

The properties of nanoparticles and the performance of products made with nano-sized precursors significantly depend on the shape of the particle size distribution (PSD) or more precisely the broadness of the PSD, the modality and of course the specific particle sizes covered by the PSD. Especially the controlled adjustment of particle size is of interest due to the size-dependent physical and chemical properties of nanoparticles below 100 nm [1]. The precipitation of particles inside the droplets of a microemulsion is a process, which allows the control of the particle size e. g. by the variation of initial concentrations of the reactants. Adityawarman et al. [2] showed that it is possible to precipitate narrowly distributed (variance: +/- 2-6 nm) barium sulfate nanoparticles in a range between 6 and 40 nm in a standard semi-batch operated stirred tank reactor by the microemulsion technique. Initially one reactant (potassium sulfate) was dissolved in the droplets inside the reactor with a certain concentration and the other reactant (barium chloride) was dissolved inside the feed droplets with a second concentration. The feeding time and the feed volume were kept constant for all these experiments. Feed strategies like a pulsed feed or a change of the feeding rate during the process, which could both have a significant influence on the resulting PSD, were not investigated so far.

Due to expensive and time consuming experiments an extensive experimental study for a broad range of parameters concerning the feed strategy is inefficient and unreasonable. Therefore a discrete-continuous population balance model with three internal coordinates [3], namely the two concentrations of the dissolved reactants and the particle size, is used to analyze a number of different feed strategies. The model consists of a two-dimensional discrete probability distribution for the dissolved reactants and the one-dimensional discrete-continuous number density function for the PSD. Both equations are coupled due to the dependence between the particle formation mechanisms (nucleation and particle growth rates) and the amount of the dissolved reactants. The kinetic parameters of the nucleation and particle growth rate approaches are estimated by a least square minimization algorithm concerning the experimentally obtained PSDs [2] and the simulated PSDs.

In this work we present results for a pulsed feed. This means that simulations were performed for the following feed schedule: 1. an arbitrary part of the feed volume is added to the reactor with a certain feed rate (influence of feed volume and feed rate on the final PSD), 2. feeding is stopped and the reactor is operated in batch mode (influence of duration time of the batch operation on the final PSD), 3. adding of the remaining feed volume to the reactor with a second not necessarily equal feed rate (influence of the second feed rate on the final PSD). The obtained results show a high potential for the synthesis of nanoparticles with a tailored PSD and therefore a precise product design.

Example: The influence of the duration time between the two semi-batch periods is investigated. The same feed rate for both semi-batch periods and the same feed volume

for the first semi-batch period are used for the simulations. By this simple variation it is already possible to produce nanoparticles with a bimodal PSD, where the location of the two maxima and the height can be precisely adjusted (see figure 1). Bimodal PSDs were not observed in the experiments of [2], where only the influence of the initial concentrations was investigated.

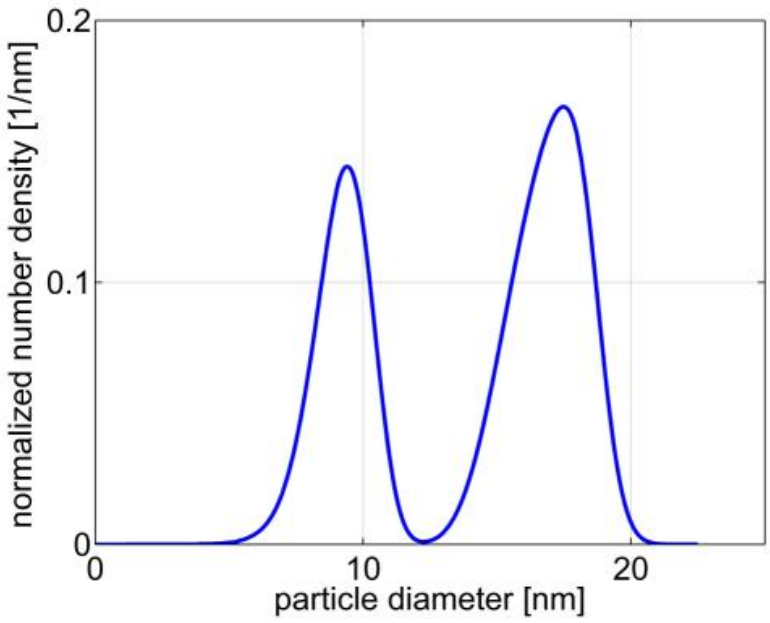

Figure 1: Bimodal PSD obtained from the applied feed strategy.

Further simulations showed that the shape of the PSD can be predicted by the knowledge of the interaction between the nucleation and growth kinetics and with this knowledge it will be possible to adjust conditions, where e. g. further nucleation of new nuclei or only growth of the existing particles is preferred. Therefore a fundamental understanding of the nucleation and particle growth mechanisms in the microemulsion process will lead to a controlled adjustment of the broadness, the location and the modality of the PSD. To validate the model and its parameters further selected experiments will be performed and analyzed.

[1] Luther, W.: Industrial Application of Nanomaterials-Chances and Risks, Vol. 54, Technological Analysis of Future Technologies, Future Technologies Division of VDI Technologiezentrum GmbH, Düsseldorf, 2004.

[2] Adityawarman, D.; Voigt, A.; Veit, P.; Sundmacher, K.: Precipitation of barium sulfate nanoparticles in a non-ionic microemulsion: Identification of suitable control parameters. In: Chem. Eng. Sci. 60 (2005), 12, p. 3373-3381

[3] Niemann, B.; Sundmacher, K.: A discrete-continuous population balance approach for the nanoparticle precipitation in microemulsion. 5$^{th.}$ World Congress on Particle Technology, Orlando, USA, 2006