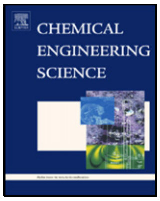
Chemical Engineering Science 64 (2009) 709 – 720

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces



Simultaneous 3D observation of different kinetic subprocesses for precipitation in a T-mixer

Johannes Gradl, Wolfgang Peukert*

Institute of Particle Technology, Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

ARTICLE INFO

Article history:
Received 23 November 2007
Received in revised form 4 June 2008
Accepted 20 August 2008
Available online 6 September 2008

Keywords:
Nanoparticle precipitation
Population balance
Nucleation
Growth
Aggregation
Electrostatic stabilization
DLVO theory

ABSTRACT

A coupled direct numerical simulation (DNS)—population balance equation (PBE)–DLVO approach is presented to calculate the product properties of particles originating from precipitation in a T-mixer. A special focus is given to the coupling of different subprocesses such as mixing, nucleation, growth, stabilization and aggregation for a rapid precipitation process. Based on the predictive computation of the resulting particle size distributions (PSD) full 3D-field information of all transient parameters are accessible, e.g., supersaturations, nucleation rates, particle sizes and stabilities. By interpolating the kinetic data, relevant subprocesses can be visualized and studied separately in the mixer. The resulting PSDs are predicted for different conditions where aggregation can be neglected. For unstable conditions aggregation and transient stabilization effects are determined by the DLVO theory. The size of the particles, their surface potential and the ionic strength of the solution vary extensively during the solid formation process. The dynamic evolution of the particle stability leads to a better description of the PSD based on the DNS–PBE–DLVO approach for unstable conditions and allows to develop strategies how to better stabilize particles. This approach is verified for barium sulphate precipitation but can be transferred to any other ionic system for which the relevant material specific data are known.

1. Introduction

Nanoparticles offer interesting application spectra since many of their product properties are determined not only by the materials' bulk properties but also by their particles size, their structure and their morphology. Precipitation is a widely used industrial process to generate such particles. To control the synthesis of nanoparticles and to handle the resulting product for subsequent applications, molecular aspects at the particulate interface have to be considered and understood (Peukert et al., 2003).

In precipitation, the product properties result from the competing kinetics of the various interacting steps involved, such as mixing, nucleation, growth, ripening and aggregation. It is difficult to study these subprocesses separately as they may occur in parallel on the same time scale (Kind, 2002). One major question is if these subprocesses have to be considered simultaneously in a model or whether a sequential approach is sufficient. Up to now, it is not clear, how the individual subprocesses influence each other and in which parts of the reactor critical regions can be expected. There are many publications about the influence of mixing on precipitation (e.g., Falk and Schaer, 2001; Marchisio et al., 2002; Schwarzer and Peukert, 2002, 2004; Judat et al., 2004; Paschedag, 2004; Baldyga and Jasinska, 2005; Schwarzer et al., 2006), which show the complexity of modeling rapid precipitation processes including mixing effects. Schwarzer et al. (2006) showed that mixing significantly influences the shape and the size of the resulting particle size distribution (PSD) and gave an approach for coupling fluid dynamics with primary solid formation kinetics by Lagrangian particle tracking. This approach is a baseline for the applied model in the present work.

Besides mixing, aggregation plays an essential role in precipitation processes (Bramley et al., 1997; Hounslow et al., 1998, 2001; Marchisio et al., 2002). When and to what extent aggregation takes place under the influence of other ongoing subprocesses as mixing, nucleation and growth is an open question. In order to answer this question, the electro-physical conditions of the suspension during precipitation have to be considered. The particle–particle interactions in an electrolyte have to be obtained based on the DLVO theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948) which describes the forces between charged surfaces interacting through a liquid medium.

In this work, a 3D parameter field of all characteristic kinetic subprocesses in the mixer is calculated based on the DNS–PBE approach. The focus thereby lies on the correlation between local

---

* Corresponding author. Tel.: +49 9131 85 29400; fax: +49 9131 85 29402.
E-mail address: W.Peukert@lfg.uni-erlangen.de (W. Peukert).

0009-2509/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2008.08.023

supersaturation and nucleation rate, the detection of critical regions, where e.g., a high particle concentration occur and the influence of different initial conditions on the spatial distribution of the solid formation kinetics. In addition to enabling the monitoring of single subprocesses, simulated final PSDs are compared with measurements. Our approach can predict the resulting PSD correctly if aggregation is prevented in the experiment. To what extent aggregation influences the ongoing solid formation process is determined by the DLVO theory. By implementing the electro-physical calculations in the DNS–PBE approach and by considering aggregation, the resulting PSD is also predicted for unstable conditions.

2. Experimental procedure

Barium sulfate precipitation experiments using aqueous solutions of barium chloride and sulfuric acid were carried out as continuous experiments at 25 °C in a T-mixer. The T-mixer consisted of two feed tubes of 0.5 mm diameter positioned centrically opposite each other and a main tube with a quadratic cross-section of $1{\times}1\,\mathrm{mm}^2$ and a length of 10 mm. The small geometric sizes of the mixer were chosen to provide intense mixing, necessary for nanoparticle precipitation. Nevertheless, the capacity of the mixer is about 80 kg of nanoscaled $BaSO_4$ per day.

Constant pulsation-free flow rates for the (continuous) experiments were provided by two pistons that were moved by a stepping motor and gear reduction in two feeding tubes. Equi-volumetric flow rates of the feeds were chosen and the total flow rate was varied between 0.2 and 12 ml/s, i.e., *Re* numbers between 250 and 15 000 calculated based on the mixer main duct diameter, which corresponds to $10\text{–}2{\times}10^7$ W/kg (of suspension produced). Samples were collected for analysis after precipitation to obtain the PSD based on quasi-elastic light scattering using a commercial device (UPA 150 by *Microtrac*).

3. Numerical approach

The challenge for modeling a fast process such as precipitation under mixing–controlled operating conditions is to couple the fluid dynamics with the primary (nucleation and growth) and secondary solid formation processes (aggregation). The fluid flow in the T-mixer is calculated by direct numerical simulation (DNS). The synthesis of the polydisperse phase is simulated based on a 1D population balance equation (PBE) including nucleation, growth and aggregation, which is solved by a commercial package PARSIVAL (from *CIT*).

3.1. Mixing

To implement mixing influences into the model, the fluid flow in a T-mixer is calculated by DNS for two different *Re* numbers 500 and 1100. The code of the DNS uses a finite-volume discretization of the Navier–Stokes equation and a scalar transport equation for incompressible flow. The flow field is computed on a Cartesian grid with about $16{\times}10^6$ cells and can be resolved down to the smallest vortex length (Kolmogoroff length), which is estimated as 4.5 µm for $Re = 500$ and 3 µm for $Re = 1100$. The simulation is validated by particle-image velocimetry and laser-induced fluorescence (LIF). Fig. 1 shows the temporal concentration fluctuations, characterized by the rms values, averaged over the cross-section along the main duct of the mixer (*x* direction). The rms values are calculated according to

$$\mathrm{RMS} = \frac{1}{A}\int_A \sqrt{\left|\bar{c}^2 - \frac{1}{k}\sum_1^k c_i^2\right|}\,\mathrm{d}A \tag{1}$$

where *A* is the area of the cross-section, *c* the measured concentration and *k* the number of measurements conducted. As can be seen in Fig. 1 the rms value decreases for both investigated *Re* numbers in the region above the inlet tubes (0.5–1 mm) indicating high mixing intensities. In this region convective mixing plays an essential role. Subsequently, diffusion becomes dominant indicated by a slow decrease of concentration fluctuations. In general, the rms values of the concentration values obtained from LIF measurements are predicted quite well. Deviations at the inlet region are caused by an insufficient spatial resolution of the experiment over the cross-section. Especially in regions with turbulent flow field structures small concentration gradients could not be fully resolved. Further details on the flow field simulation are given by Schwertfirm et al. (2007).

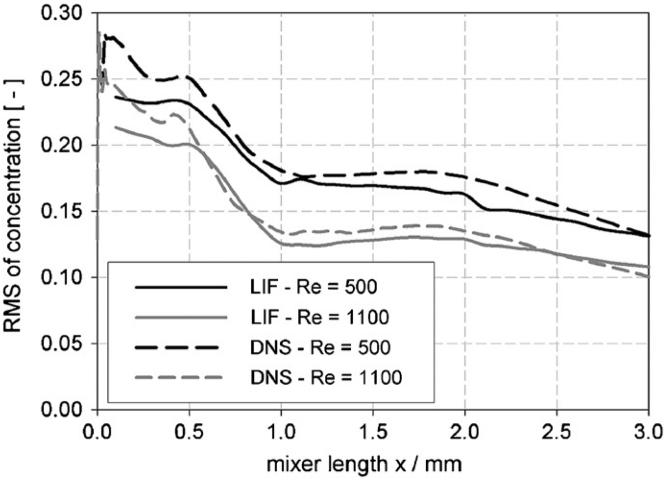


Fig. 1. Comparison between calculated (DNS) and measured (LIF) concentration fluctuations over the cross-section along the main duct.

Lagrangian particle tracking couples the flow field simulation by DNS with the micromixing model and the kinetics of the solid formation. The information provided from the DNS (local specific power input and local instant concentration) along the paths of finite volumes through the mixer enters into a micromixing model. The engulfment model of Baldyga and Bourne (1999) is extended by considering the aspect of micromixing at length scales smaller than the Kolmogoroff length as well as the influence of slow macromixing. Further details on the Lagrangian approach and the applied micromixing model are given in Schwarzer (2005), Gradl et al. (2006) and Schwarzer et al. (2006).

3.2. Nucleation

Under the investigated operating conditions homogeneous nucleation is the dominant mechanism for phase transfer (Mersmann, 2000). The nucleation rate is given by

$$B_{\mathrm{hom}} = 1.5 \cdot D\left(\sqrt{K_{SP}} \cdot S \cdot N_A\right)^{7/3} \cdot V_m\sqrt{\frac{\gamma_{PF}}{k_B T}} \times \exp\left(-\frac{16\pi}{3}\left(\frac{\gamma_{PF}}{k_B T}\right)^3 \frac{V_m^2}{(\nu\,\ln(S))^2}\right) \tag{2}$$

where *D* is the diffusion coefficient, which can be calculated by the Stokes–Einstein equation, K_{SP} is the solubility product for barium sulphate in aqueous media, taken from Monnin (1999), V_m is the molar volume of a barium sulphate molecule, k_B is the Boltzmann constant, *T* is the temperature and ν is the stochiometric factor. Two variables have a crucial impact on the nucleation rate: supersaturation *S*, which is the driving force for the solid formation process