Contents lists available at ScienceDirect

Chemical Engineering Research and Design

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

Influence of mixing on particle formation of fast precipitation reactions—A new coarse graining method using CFD calculations as a "measuring" instrument

*Lukas Metzger, Matthias Kind**

Karlsruhe Institute of Technology, Institute for Thermal Process Engineering, Kaiserstr. 12, 76131 Karlsruhe, Germany

ARTICLE INFO

Article history:
Received 11 August 2015
Received in revised form 7 January 2016
Accepted 8 January 2016
Available online 15 January 2016

Keywords:
Precipitation
Population balance equation
Confined impinging jet mixer
Mixing
STAR NM approach
Coarse graining method

ABSTRACT

Methods based on Computational Fluid Dynamics (CFD) are a promising tool to gain insight into poorly accessible and swift solid formation processes such as granulation or precipitation. Unfortunately, CFD modeling of transient particle size distributions in such reactors requires enormous computational effort because complex and multi-scale interactions have to be considered. Hence, a new coarse graining approach is presented with which these complex interactions can be handled with reasonable computational effort and which enables to extract short cut methods from complex CFD simulations.

The method is exemplified for precipitation crystallization of nanoscaled solid particles from the liquid phase. This process is governed by fast primary processes, such as supersaturation build-up, nucleation and growth. Experimental access to internal parameters is very difficult or even impossible.

The new methodology which we call "Spatially and Temporally Averaged Reduced Numeric Measurement" (STAR NM) is based on a reasonable averaging and correlation of process dominating state variables or rates which are consigned to a fast 1D population balance solver. Precipitation of the sparingly soluble barium sulfate in water is used as a model process. A confined impinging jet mixer is used as a benchmark apparatus which allows for the adjustment of highly reproducible mixing conditions. Experimental results are compared to those gained with the new STAR NM approach.

1. Introduction

Precipitation crystallization is an important unit operation for the solids formation. Typical particle sizes of precipitation products range between a few nanometers and several micrometers. Supersaturation, as the driving force for the primary processes of particle synthesis, such as nucleation and growth, is a transient and local quantity that is created either by the chemical reaction of components of the reactant solutions or through the reduction of the solubility by adding a drowning-out agent. The description of the mixing step and the consecutive buildup of supersaturation are determining for the chemical reaction on a molecular level. In addition to the intrinsic kinetics, the resulting particle size distribution depends strongly on the mixing characteristics of the particular apparatus. When setting up a predictive model for precipitation processes, the consideration of such mixing influences is challenging. Several approaches to model mixing effects are proposed in the literature. Among these are the classical mixing theory, such as the engulfment model

* Corresponding author.
E-mail address: matthias.kind@kit.edu (M. Kind).
http://dx.doi.org/10.1016/j.cherd.2016.01.009

Nomenclature

A,B,a,b	fit parameter
B_{hom}	homogeneous nucleation rate (1/(m^4 s))
$\tilde{c}_i$	molar concentration of component i (mol/l)
$\tilde{c}_{i,free}$	solvated molar ion concentration i (mol/l)
D_{AB}	diffusion coefficient (m^2/s)
d_{mix}	diameter of the mixing chamber (m)
G	growth rate (m/s)
k_B	Boltzmann constant (J/k)
k_{mix}	mixing rate coefficient
K_{sp}	solubility product (mol^2/s^2)
L	particle size (m)
L_{crit}	critical nuclei size (m)
L_k	particle of size class k (m)
M_R	moment ratio of the inlet streams
N_a	Avogadro constant (1/mol)
n_k	particle number in class k
R	free lattice ion ratio
S_a	activity-based supersaturation
$S_{a,nom}$	nominal activity-based supersaturation
t	time (s)
u_{mix}	velocity in the mixing zone (m/s)
V_m	effective volume of one molecule (m^3)
$\tilde{V}_m$	molar volume (m^3/mol)
z_{mix}	mixing length (m)
γ_{SL}	interfacial energy (N/m^2)
ε	energy dissipation (W/kg)
ν_s	stoichiometric coefficient
ν	kinematic viscosity (m^2/s)
$\tilde{\rho}_i$	molar density (kg/mol)
τ_i	characteristic time i (s)
Re_{mix}	Reynolds number of the mixing zone
Sh_{min}	minimal Sherwood number (=2 for a sphere)
Da_t	turbulent Damkoehler number
St	Stokes number

introduced by Baldyga and Bourne (1990, 1999), and the Global Mixing Approach (Schwarzer, 2005; Schwarzer and Peukert, 2004). These models use various theoretical assumptions and some rate constants. They are based on the mixing scale analysis to describe the disintegration of vortices. These methods are fast in computation time, but are mostly imprecise or are restricted to single flow regimes.

Having available an ever-increasing computational power, coupled computational fluid dynamics (CFD)-population balance equations (PBE) simulations have been attempted to describe the particle formation process at the same local resolution as that of the flow field. Obviously, computing of particle size distribution within CFD leads to high computational load. Therefore, reducing methods for describing and computing the development of the particle population were developed. Such methods are the standard method of moment (SMOM) or improved methods, such as the quadrature method of moments (QMOM) or the direct quadrature method of moments (DQMOM). Some important work in this field using the SMOM approach is reported in Baldyga et al. (2007), Marchisio et al. (2002), Öncül et al. (2005) and Vicum and Mazotti (2007). Marchisio et al. (2003) and Gavi et al. (2007) improved the SMOM procedure toward handling of size-dependent growth rates or aggregation (QMOM approach). They showed that CFD-PBE coupling is a promising tool, which, however, needs long multicore computation time and which leads to certain difficulties, such as the reconstruction of a particle size distribution from its characteristic nodes.

This contribution presents a new approach which we call "Spatially and Temporally Averaged Reduced Numeric Measurement"—STAR NM. This coarse graining approach uses fast single phase CFD simulations and certain "measurement" routines to provide necessary data regarding the influence of mixing on the timely development of the supersaturation, as it is needed for population balance calculations. This is in contrast to complex CFD-PBE couplings, where mostly three external (the spatial coordinates x,y,z) and at least one internal coordinate (for instance, particle size L) have to be solved.

The STAR NM procedure is explained in the following. Simulation results using this new CFD coarse graining method are compared to experimental data of barium sulfate ($BaSO_4$) precipitation in a Confined Impinging Jet Mixer (CIJM).

2. Experimental Section

Barium Sulfate is used as a mixing-sensitive precipitating model system. In earlier works we showed that $BaSO_4$ is definitely mixing-controlled for values below $\bar{\varepsilon} = 10^4$ W/kg (Kucher, 2009; Kucher et al. (2006); Metzger and Kind, 2015a). This mean energy dissipation correlates to $Re_{mix} < 1000$ in the T-mixer presented. The resulting particle size serves as an important indicator for the prevailing mixing quality. Either two gear pumps (*Ismatec MCP-Z-Process* with *Z 130* piston head) or two different syringe pumps, each with two pistons, were used. A commercially available syringe pump (*Chemics Nexus 6000*, total liquid capacity = 120 ml) was used to provide for the reactant volume flow for low flow rates. Additionally, a self-constructed piston pump (total liquid capacity = 300 ml) integrated into a universal testing machine (*Zwick Roell*) was used for high flow rates ($Re_{mix} \geq 3000$). Experimental data is achieved as proposed by Kucher (2009); Kucher et al. (2006) and Schwarzer (2005), for an activity-based supersaturation $S_{a,nom} = 1000$ $\left(\tilde{c}_{Na_2SO_4} = 0.0723\,\text{mol/l},\ \tilde{c}_{BaCl_2} = 0.2902\,\text{mol/l}\right)$ and a free lattice ion ratio of $R = 5$ with a syringe pump setup at 298 K and ambient pressure. The activity coefficient $\gamma_\pm$ is calculated with the modified Debye–Hückel approach after Pitzer (1973). The formation of ion pair complexes (Vicum et al., 2003) is included into activity coefficient calculations. K_{sp} is the solubility product of $BaSO_4$ ($K_{sp,BaSO_4} = 9.91 \cdot 10^{-11}$ mol^2/l^2, Monnin, 1999).

$$S_a = \gamma_\pm \cdot \sqrt{\frac{\tilde{c}_{Ba^{2+},free} \cdot \tilde{c}_{SO_4^{2-},free}}{K_{sp}}} \tag{1}$$

$$R = \frac{\tilde{c}_{Ba^{2+},free}}{\tilde{c}_{SO_4^{2-},free}}. \tag{2}$$

Molar reactant concentrations $\tilde{c}_i$ as well as initial parameters were kept constant, while the flow rate (moment ratio: $M_R = 1$) was varied. Particle size is measured using static and dynamic light scattering techniques (*Malvern Zetasizer Nano ZS*).

3. CFD settings

The commercial solver *ANSYS Fluent 15.0* was used for the numerical investigation. Turbulence is modeled with a DES