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Multi-scale modeling of a mixing-precipitation process in a semibatch stirred tank

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Abstract

In this work the influence of turbulent mixing on the course of barium sulfate precipitation is investigated for a process carried out in a semibatch stirred tank reactor. A time-scale analysis for the controlling process mechanisms is presented to highlight the multi-scale nature of the process. A detailed CFD based process model is presented which accounts for all relevant phenomena from the micro- to the macro-scale and interactions between mechanisms on different scales. Computational results of the models for various operating conditions, i.e., different agitation rates, reactant concentrations and feed addition modes, are compared with experimental data and simulation results obtained using a simpler mechanistic model, thus highlighting the strengths of the complex model.

Keywords: CFD; Mixing; Precipitation; Turbulence; Barium sulfate

1. Introduction

Semibatch stirred tank precipitation is a widely used process in the fine chemicals and pharmaceutical industry. However, up to now no standard design procedures could be established for such a process, which allow for a rational process development leading to a product of desired properties. Commonly the process design is based on empirical methods and is usually rather time consuming.

This is in particular the case, when the precipitation is fast and turbulent mixing is influencing its course. Under such conditions the model-based process design seems to be most promising to account for the complex interactions between all the mechanisms involved.

In the literature different types of models have been proposed to describe such processes (Podgorska, 1993; Wei et al., 2001; Jaworski and Nienow, 2003; Vicum et al., 2003; Kresta et al., 2005). In most cases small-scale mixing mechanisms are characterized with simplified mechanistic models such as the E-model (Bałdyga and Bourne, 1989; Phillips et al., 1999), whereas macro-mixing is described by simplified models. Mixing-precipitation models, which use a detailed characterization of the macro-mixing, have also been used (Wei et al., 2001; Jaworski and Nienow, 2003), but in these cases small-scale mixing effects are neglected, thus the multi-scale nature of the process is not modeled in all details. However, it has been shown that accounting for such effects can be crucial to capture correctly the system behavior (Bałdyga and Orciuch, 2001).

In this work the mixing-precipitation process in a stirred tank is analyzed in detail, where the process is operated in semibatch mode, thus increasing its complexity because of its time-dependent character. The comparison of all relevant time- and length-scales in the system highlights the need for a multi-scale modeling approach. A computational fluid dynamics (CFD)-based multi-scale model is presented and applied to predict how a change in the operating conditions affects the properties of the product particles. Furthermore, a classical mixing model is used for the characterization of this process. Simulation

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results of both models are compared with experimental data, thus highlighting their relative strengths.

2. Time-scale analysis

In this work the influence of turbulent mixing on the course of a precipitation process is studied for the semibatch process shown in Fig. 1. Barium sulfate is frequently used as a model system to investigate the interaction between turbulent mixing and precipitation (Podgorska, 1993; Wei et al., 2001; Jaworski and Nienow, 2003; Vicum et al., 2003):

$$\underset{(A)}{BaCl_{2(aq)}} + \underset{(B)}{Na_2SO_{4(aq)}} \rightarrow \underset{(C)}{BaSO_{4(s)}} \downarrow + 2NaCl_{(aq)}. \tag{1}$$

Barium chloride aqueous solution (A) and sodium sulfate aqueous solution (B) are mixed in the stirred tank reactor and solid barium sulfate (C) is formed by precipitation. When the process is operated in the single feed semibatch mode sodium sulfate aqueous solution is fed into the vessel where barium chloride aqueous solution is initially loaded. For the double feed operation both barium chloride and sodium sulfate aqueous solutions are fed through separate feed inlets into the reactor, which is filled initially with water. Since the contacting of barium and sulfate ions for the formation of solid barium sulfate occurs on a molecular level, small-scale turbulent mixing directly affects the particle formation. Large-scale mixing indirectly influences the particle formation by defining the environment for the small-scale mixing effects. To characterize how mixing affects the precipitation and thereby to identify the relevant mechanisms to be considered in the model of the process, time-scales of the particle formation and of the mixing mechanisms are compared in the following.

2.1. Precipitation

The controlling mechanisms for barium sulfate particle formation are nucleation and growth under the operating conditions considered in this work. Secondary particle formation effects such as agglomeration and particle breakage are of negligible influence in this case (Podgorska, 1993; Vicum et al., 2003).

The characteristic time of barium sulfate nucleation τ_N can be defined by the induction time, which is the time period from the creation of supersaturation to the experimental detection of first particles. The experimental induction time data for barium sulfate (Nielsen, 1961) have been employed to derive a correlation for the induction time as a function of supersaturation:

$$\ln(\tau_{N,i}) = A_i + \frac{B_i}{\ln^2 S_a} \quad (i = \text{hom}, \text{het}), \tag{2}$$

where $A_{\text{hom}} = -15$ and $B_{\text{hom}} = 100$ for homogeneous nucleation, and $A_{\text{het}} = 0.5$ and $B_{\text{het}} = 3$ for heterogeneous nucleation, with S_a being the supersaturation ratio calculated based on a Pitzer activity model. The characteristic time of particle growth τ_{Gr} can be defined by

$$\tau_{\text{Gr}} = \frac{M_{\text{BaSO}_4}}{G\rho_{\text{BaSO}_4}} a_{\text{surf}} c_c, \tag{3}$$

where M_{BaSO_4} is the molar mass of barium sulfate, G is the particle growth rate, ρ_{BaSO_4} is the solid density of barium sulfate, a_{surf} is the specific surface area of barium sulfate particles and c_c is a characteristic concentration of barium sulfate in solution, which can be approximated by the local minimum value of barium and sulfate ion concentrations (Bałdyga et al., 1995).

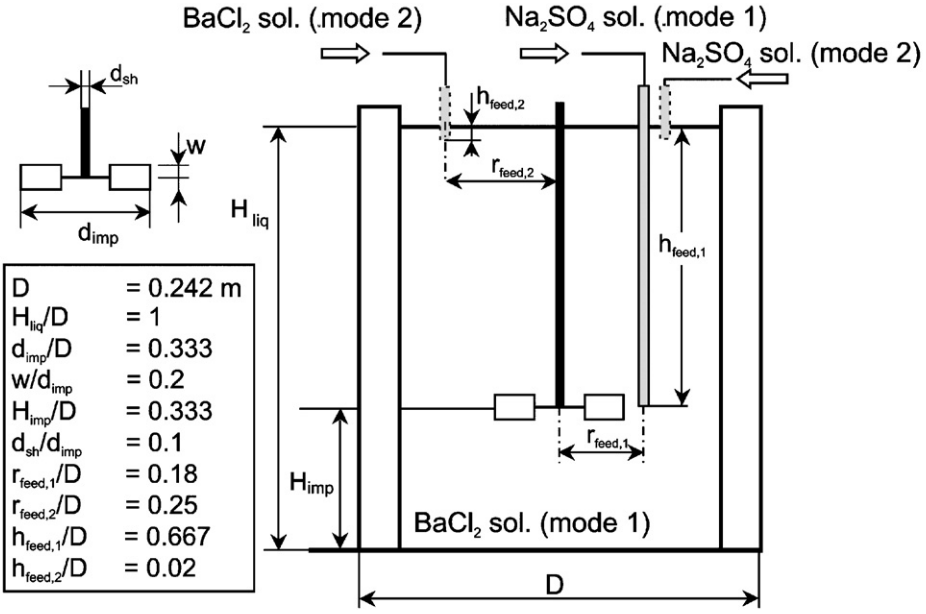

Fig. 1. Schematic of the semibatch stirred tank reactor, Mode 1: single feed addition, Mode 2: double feed addition in to the reactor initially containing water, the two inlets are symmetric with respect to the axis of the reactor and of the same length.