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Experimental investigation of reagent feeding point location in a semi-batch precipitation process

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HIGHLIGHTS

- Study of the effect of reagent feeding point location in STR on $BaSO_4$ crystallization.
- Visualization of temporal history of $BaSO_4$ precipitation by EIT.
- CFD model of the crystallization hydrodynamics in a batch STR.
- Validation of Rasmuson's TR-number.
- The effect of macro and mesomixing on d_{90}, CSD and morphology of $BaSO_4$ crystals.

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ABSTRACT

This research is dedicated to a study of $BaSO_4$ crystallization process in a batch stirred reactor. The temporal development of the precipitation process is measured by conductivity at global and local levels. The effect of the macromixing on temporal evolution of local conductivity is shown in the experimental results obtained by EIT. The effects of the mixing intensity and the $BaCl_2$ feed location on the CSD and morphology are considered. Morphology of the crystals was found to be independent from mixing intensity in the studied range. The CFD simulations of the mixing hydrodynamics were used to estimate the influence of turbulent dispersion on crystal size. The correlation of mean crystal size and TR number proposed by (Torbacke and Rasmuson, 2001) has been checked against d_{90} in the range of 10^3–10^5 and showed reasonable agreement. The scatter of the results plotted can be explained by the macromixing scale and critical time of the crystallization not included into TR number. The combined effect of mixing at meso and macro scales onto crystal size is proposed.

1. Introduction

Precipitation plays an important role in chemical and pharmaceutical industry. Crystallization process of reaction products facilitates solid liquid separation, characteristics of which affect quality of final product. Batch wise crystallization has lower production capacity compared to continuous one. Nevertheless, it was actively studied by numerous researchers due to Stirred Tank Reactor (STR) simplicity, isolation from upstream process and transient manner.

Main parameters, controlling crystallization process, have been the objects of intensive research. The mechanism of crystallization is described comprehensively by Mullin (2001). Influence of mixing speed onto Crystal Size Distribution (CSD) has been studied earlier (Kim and Tarbell, 1999, Torbacke and Rasmuson, 2004, Wang et al., 2009, Steyer et al., 2012). Precipitation of barium sulphate was used as a typical crystallization process to investigate influence of mixing at all scales by Torbacke and Rasmuson (2001). They proposed a dimensionless number (TR-number Eq. (1)) evaluating ratio of reagent feeding time and specific spatial mesomixing time scale. This dimensionless number correlates well with mean weight particle size within the studied range 10^4 to 10^6. However, there is a scatter of particle sizes at close TR values, which tells that the number proposed is useful but doesn't take into account some parameters affecting crystallization.

$$TR = \frac{t_{feed}}{t_{meso}} = \frac{U_{bulk}}{d} t_{feed}, \quad (1)$$

where t_{feed} is the time of reagent feed, s; t_{meso} is the mesomixing time scale, s; U_{res} is the bulk velocity, m/s; d is the hydraulic

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Notation

Symbols	meaning, units
A	signal amplitude, –
d	hydraulic diameter of injection pipe, m
D_t	turbulent dispersion, m^2/s
n	number of samples, –
N	mixing speed, rps
N_{el}	number of electrodes, –
N_i	number of grid cells in ith grid, –
N_q	dimensionless pumping number of impeller, –
p^*	order of discretization, –
P	mixing power, W
St	Stoke's number, –
t_{feed}	time of reactant injection, s
t_{macro}	macromixing time scale, s
t_{meso}	mesomixing time scale, s
t_D	turbulence dispersion time scale, s
TR	TR-number, –
U_{bulk}	velocity of local bulk flow, m/s
V	volume of reactor, m^3

Greek letters	Meaning, units
ε	turbulence energy dissipation rate, m^2/s^3
k	turbulence kinetic energy, m^2/s^2
σ_1	conductivity distribution of homogeneous mixing, Sm/m
σ_2	conductivity distribution of non-homogeneous mixing, Sm/m
$\Delta\sigma$	resulting conductivity distribution of gas-liquid mixing, Sm/m
τ	torque, N·m
$v(i)$	voltage at i-th electrode, V
v_{image}	imaginary part of measured voltage, V
v_{real}	real part of measured voltage, V
φ	signal phase, V
φ_1	CFD simulation results on coarse grid, –
φ_2	CFD simulation results on fine grid, –

Acronyms	Transcript
CFD	computational fluid dynamics
STR	stirred-tank reactor
CSD	crystal size distribution
EIT	electric impedance tomography
NRMSE	normalized root mean square error
PIV	particle image velocimetry
SEM	scanning electronic microscopy

diameter of the feeding pipe, m. This formulation does not take into account several important factors such as bulk flow direction relative to the feed flow, feed velocity magnitude, global flow pattern in reactor, and cumulative time of chemical reaction and crystallization, which is critical.

Overall flow pattern of agitated Newtonian liquid in STR has been simulated accurately using Computational Fluid Dynamics (CFD) modelling (Yeoh et al., 2004; Bakker and Oshinowo, 2004; Joshi et al., 2011; Gradov et al., 2016, Lane, 2017). Barrett et al. (2011) performed CFD simulations to assess the influence of meso and micromixing onto premature nucleation of benzoic acid in a batch reactor. In their research, different time scales were estimated and compared in order to define effect of mixing scales. The macromixing (Eq. (2)) as well as turbulent dispersion (Eq. (4)) time scales were found to have major influence on the crystallization process while the effect of micromixing and mesomixing due to internal convection is negligible.

$$t_{macro} = \frac{V}{N_q N D^3} \tag{2}$$

$$D_t = 0.1\frac{k^2}{\varepsilon} \tag{3}$$

$$t_D = \frac{Q_{feed}}{U_{bulk} D_t}, \tag{4}$$

where V is the reactor volume, m^3, N_q is the impeller pumping number (0.72 for Rushton turbine), N is the mixing speed, rps, D is the impeller diameter, m, k is the turbulence kinetic energy, m^2/s^2, ε is the energy dissipation rate, m^2/s^3, Q_{feed} is the volumetric flow rate of fed reagent, m^3/s.

Visualization of crystallization process can be done with a help of non-intrusive technique Electrical Impedance Tomography (EIT). Research group from The University of Manchester described successful applications of EIT technique for stirred tanks to visualize precipitation process (Wabo et al., 2004, Kagoshima and Mann, 2005, Stanley et al., 2005, Mann, 2009). They demonstrated that EIT is a suitable technique to study conductive fluid systems that are opaque. Reaction visualization pattern as well as local conductivity readings were in reasonable agreement with independent measurements.

The purpose of this research is to consider effect of macro and mesomixing on crystal size and morphology by studying an example of classical precipitation process of barium sulphate in a batch STR at lab scale. EIT instrument is applied to measure temporal local conductivities in the batch STR to reveal the spreading pattern of chemical reaction and precipitation of $BaSO_4$. Numerical simulation is used to estimate local mesomixing via fluid flow hydrodynamics modelling. The effect of turbulent mesomixing is considered and discussed.

2. Materials and methods

2.1. Batch crystallization set-up

A lab-scale baffled stirred reactor, made of plexiglass, with standard six-blade Rushton turbine was investigated in the current research. A schematic representation of the vessel geometry and its dimensional parameters are presented in Fig. 1a. The impeller clearance was set at the distance equal to its diameter from the bottom of the tank. Power draw was measured by on-shaft torque meter.

Barium sulphate precipitation was arranged as a batch process where barium chloride (0.1 M) is injected into predissolved water solution of sodium sulphate (0.1 M) at a constant flow rate in several spatial points as it is illustrated in Fig. 1b. A peristaltic pump Masterflex L/S was used to maintain stable 2 mL/s flowrate of the reagent through a glass pipet ($d = 1$ mm) during 50 s. The experimental time line is presented in Fig. 2. The batch process has been performed at different volumetric power inputs: 19, 63 and 500 W/m^3 that correspond to 2.5, 5 and 7.5 rps of the stirring speed. The global conductivity has been tracked during each