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CFD Model of a Semi-batch Reactor for the Precipitation of Nanoparticles in the Droplets of a Microemulsion

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Abstract

Precipitation inside the droplets of a microemulsion is a promising technology for the production of nanoparticles with tailored properties, like particle size or shape [1]. In this work, a water-in-oil (w/o)-microemulsion consisting of water, cyclohexane and the non-ionic technical surfactant Marlipal O13/40 is used to synthesise $BaSO_4$ nanoparticles. The reaction is initiated by the mixing of two microemulsions, one containing the first reactant $BaCl_2$ and the other containing the second reactant K_2SO_4, in semi-batch operation mode in a standard Rushton tank (V = 300 ml). A narrow particle size distribution (Fig. 1) and particle sizes between 4 and 40 nm have been achieved by experiments [2].

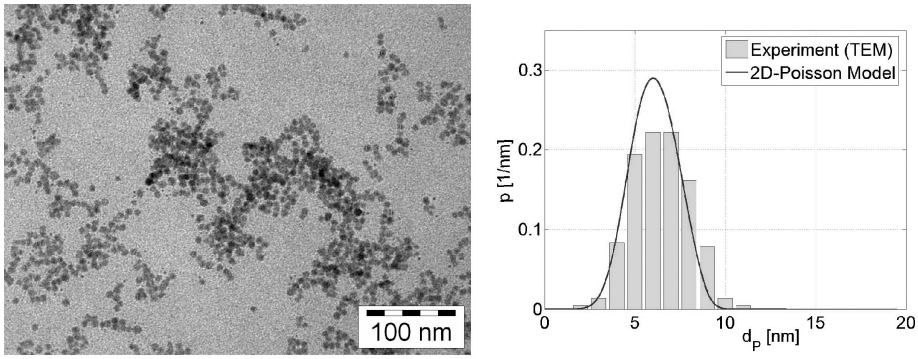

Fig. 1: TEM picture of $BaSO_4$ nanoparticles obtained by experiments with initial reactant concentrations of 0.1 mol/l (left); simulation results for an ideally mixed reactor (right) [3].

A population balance model (PBM) assuming a discrete two-dimensional Poisson distribution for the dissolved Ba^{2+} and SO_4^{2-} ions has been derived [3]. Rate constants for nucleation and growth kinetics proposed by Baldyga et al. [4] for bulk precipitation were fitted to take the slow-down effect of the droplet exchange into account. The obtained results showed a qualitatively good agreement with the experimental data (Fig. 1), but bigger deviations between the model and the experiments were observed for cases with a high concentration difference between the two microemulsions. The reason might be that the precipitation strongly depends on the supersaturation and that especially high concentration differences near the feed lead to a locally varying supersaturation profile, which is responsible for the deviations.
To analyse this behaviour the zero-dimensional (homogeneous) PBM with over 600 ODEs is reduced into a set of 4 ODEs and implemented into the Computational Fluid Dynamics (CFD) code FLUENT 6.2 via user-defined scalars and functions. Hence, it became possible to investigate the reaction process for various three-dimensional inhomogeneous hydrodynamic conditions with reasonable computation times.

Keywords: Nanoparticles, precipitation, microemulsion, PBM and CFD.

1. Numerical model and calculations

The 4 equations of the transformed ODE system are only valid in the case that only one particle can exist in one droplet. This assumption is reasonable due to the fact that the droplet size is around 5 nm and only a few dissolved ions are present inside. Taking into account droplets with several particles would make the model considerably more complex, so that this point is not considered in the present formulation.
The total number of droplets without particles (Eq. (1)) consists of a sink term for droplets in which nucleation takes place and a source term for the feeding of new droplets.

$$\frac{dn^{0}_{droplet}(t)}{dt} = -\sum_{i=n_{crit}+1}^{n_{\max}+1}\sum_{j=n_{crit}+1}^{n_{\max}+1} P_{2D}^{(i,j)}(t)\cdot r_N^{(i,j)}\cdot V_{H_2O}(t) + \dot{n}^{feed}_{droplet}(t) \tag{1}$$

The total number of molecules in solid phase (Eq. (2)) is calculated by the addition of dissolved molecules which undergo a nucleation process and the addition of dissolved molecules which contribute to particle growth.

$$\begin{aligned}\frac{dn_P(t)}{dt} = &\sum_{i=n_{crit}+1}^{n_{\max}+1}\sum_{j=n_{crit}+1}^{n_{\max}+1} N_P^{(i,j)}\cdot P_{2D}^{(i,j)}(t)\cdot r_N^{(i,j)}\cdot V_{H_2O}(t)\\ &+\sum_{i=2}^{n_{\max}+1}\sum_{j=2}^{n_{\max}+1} P_{2D}^{(i,j)}(t)\cdot r_G^{(i,j)}\cdot\frac{\pi\cdot N_A\cdot\rho_{BaSO_4}}{2\cdot M_{BaSO_4}}\cdot\bar{d}_P^{\,2}(t)\cdot\left(n^{total}_{droplet}(t)-n^{0}_{droplet}(t)\right)\end{aligned} \tag{2}$$

The total number of droplets (Eq. (3)) is only changed by the feeding of new droplets due to the fact that microemulsions are thermodynamically stable and the fusion of two droplets directly leads to the fission into two equally sized droplets.

$$\frac{dn_{droplet}^{total}(t)}{dt} = \dot{n}_{droplet}^{feed}(t) \tag{3}$$

Due to mass conservation, new Ba^{2+} can only enter the reactor by the feeding and therefore the total number of Ba^{2+} in the reactor can be calculated by

$$\frac{dn_{Ba^{2+}}^{total}(t)}{dt} = \overline{n}_{Ba^{2+}}^{feed} \cdot \dot{n}_{droplet}^{feed}(t) \; . \tag{4}$$

Further necessary variables, e.g. the mean numbers of reactant ions in one droplet needed for the determination of the Poisson distribution, are calculated by a few algebraic equations. A quite similar PBM has been recently developed by Singh & Kumar [5] and validated by the results of exact Monte-Carlo computations.

The mean particle diameter is calculated by

$$\overline{d}_P(t) = \sqrt[3]{\frac{6 \cdot M_{BaSO_4}}{\pi \cdot N_A \cdot \rho_{BaSO_4}} \cdot \frac{n_P(t)}{n_{droplet}^{total}(t) - n_{droplet}^{0}(t)}} \tag{5}$$

and the kinetic rate approaches depend on the individual supersaturation, S, of each possible ion combination inside one droplet are represented by

$$r_m^{(i,j)} = k_m^{eff} \cdot \left(S^{(i,j)} - 1\right)^{\alpha_m} \quad , m = N, G. \tag{6}$$

This simplified model has been first applied for the homogeneous reaction process (zero-dimensional analysis) by MATLAB 7.0 before performing the inhomogeneous computations (three-dimensional analysis) in FLUENT. The results obtained from this time-dependent calculation are later compared with those obtained by CFD. The computation takes only a few seconds for the zero-dimensional case.

As explained previously, a Rushton tank has been used with a 6-bladed impeller rotating at 300 rpm in the clockwise direction (Re = 4,500) and with 18 baffles. The geometry and the grid of the reactor are shown in Fig. 2. There exists a total number of 79,776 volume elements in the whole domain.

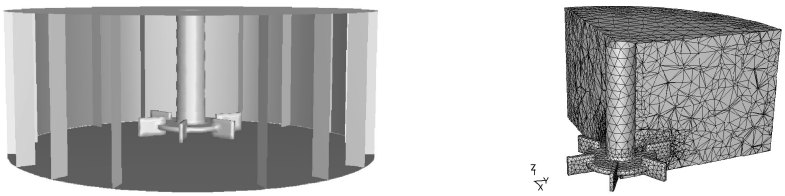

Fig. 2: Geometry (left) and computational grid of the reactor (right) (the full dimensions are given in [2]).

The droplets containing Ba^{2+} ions are fed into the reactor (where the SO_4^{2-} ion containing droplets are already exist) during a period of 257.14 s with a constant feed rate. The three-dimensional simulations in the reactor have been performed in two stages by assuming a batch system (i.e. the liquid volume is not changing): Firstly the flow field has been simulated without the reaction process until homogeneous hydrodynamic conditions are achieved and secondly the whole reaction process has been simulated by switching off the flow and the turbulence model (i.e. using frozen-flow condition) while activating chemical reactions. By this way, the computations have been considerably accelerated. The computing times are respectively 24 h and 3 h for the first and the second stage employing a single Pentium-IV Linux PC (2.7 GHz/2 GB memory).
In order to simulate the motion of the impeller, the multiple reference frames (MRF) model has initially been applied yielding an approximate flow estimation in a steady state and thereafter the obtained solution has been used as an initial guess for the further unsteady state simulation applying the sliding mesh model (SMM). Unlike the MRF model, the SMM is capable of reflecting the impeller-baffle effects taking the time-dependent location of the impeller into consideration. Therefore the SMM delivers much more accurate results for an unsteady state calculation [6]. During these flow field simulations 2^{nd}-order discretization has been used in space and a 2^{nd}-order implicit time formulation has been chosen for the unsteady solution of the SMM.
The standard *k*-ε approach has been used for the turbulence model since this model should supply a reasonable accuracy and short computing times for such baffled tanks in which no strong, swirling flow occurs [7].

2. Results

Time-periodic flow conditions have been achieved after 100 full rotations of the impeller (i.e. 20 s real time) during the unsteady simulation employing the SMM. The velocity vectors on the middle cross-sectional surface of the reactor and the turbulent kinetic energy contours around the impeller with respect to the final results of the first-stage simulations are shown in Fig. 3.

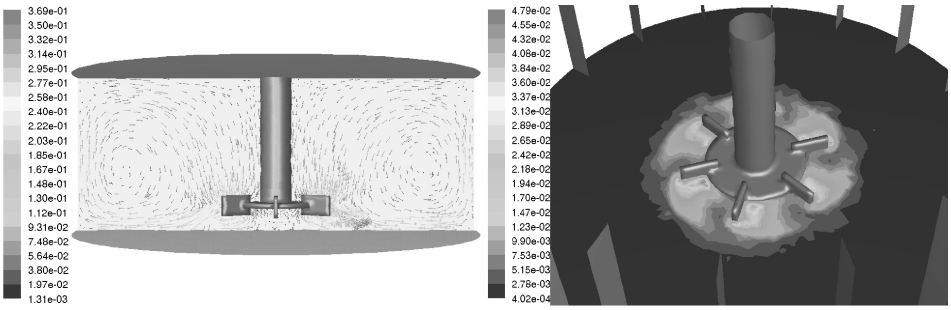

Fig. 3: The velocity vectors in m/s (left) and the turbulent kinetic energy contours in m^2/s^2 (right).

The evolution of the mean number of dissolved Ba^{2+} and SO_4^{2-} ions per droplet and the mean particle diameter with respect to time according to the second-stage simulation (including only the inhomogeneous precipitation on top of the frozen flow) are represented in Fig. 4 for both zero- and three-dimensional analysis. Referring to this comparison, it can be concluded that an almost homogeneous reaction process is observed in the reactor. This proves that the mixing conditions inside the reactor are almost perfect so that three-dimensional effects are quite negligible in this configuration.

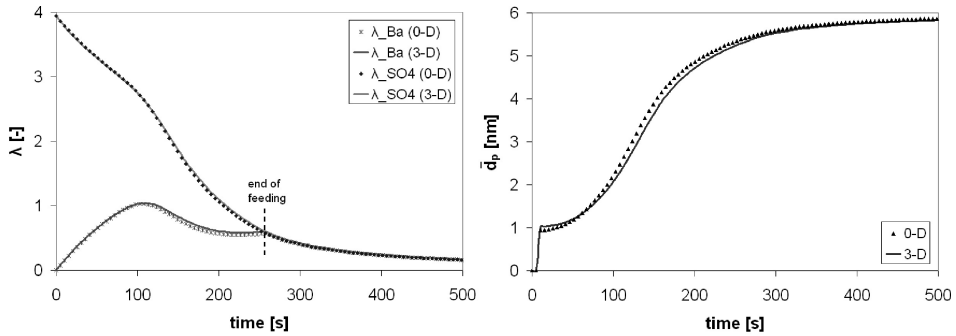

Fig. 4: Profiles of the mean number of dissolved Ba^{2+} and SO_4^{2-} ions per droplet (left) and the mean particle diameter (right). Zero- and three-dimensional analysis in comparison.

3. Conclusions and outlook

The aim of this work was to develop a simplified model describing the precipitation of $BaSO_4$ in a microemulsion droplet population and to implement this model for the three-dimensional, real case analysis of the reaction process in a semi-batch reactor. The initial numerical calculations demonstrate that the inhomogeneous case results agree with the homogeneous case results, which leads to the conclusion that the mixing conditions are almost perfect. The embedding of the PBM formulation within the CFD code allows numerically efficient unsteady flow computations.
Next, non-stoichiometric processes will be simulated for various feeding rates and hydrodynamic conditions in order to analyse the influence of different inhomogeneous conditions.

Acknowledgement

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Nomenclature

$\bar{d}_P$	mean particle diameter [m]
k^{eff}	effective kinetic rate constant
M_{BaSO_4}	molecular weight of $BaSO_4$ [g/mol]
N_A	Avogadro number [1/mol]
N_P	ion number matrix: securing of an equal amount of both ions for 1 nucleus ($n_{max} \times n_{max}$)
$n_{Ba^{2+}}^{total}$	total number of Ba^{2+} ions in the reactor (in solid phase and as dissolved ions)
$\bar{n}_{Ba^{2+}}^{feed}$	mean number of Ba^{2+} ions inside one droplet of the feed
n_{crit}	critical number of molecules needed to form a stable nucleus
$n_{droplet}^{0}$	number of droplets without a particle
$n_{droplet}^{total}$	total number of droplets
$\dot{n}_{droplet}^{feed}$	feeding flux of droplets [1/s]
$n_{\max}$	maximum number of dissolved ions of one kind per droplet
n_P	total number of $BaSO_4$ molecules in solid phase
$\bar{n}_P$	mean number of $BaSO_4$ molecules in solid phase per droplet
P_{2D}	2-dimensional Poisson distribution for dissolved Ba^{2+} and SO_4^{2-} ions ($n_{max} \times n_{max}$)
Re	Reynolds number
r_G	growth rate matrix ($n_{max} \times n_{max}$) [m/s]
r_N	nucleation rate matrix ($n_{max} \times n_{max}$) [1/(m^3 s)]
S	supersaturation ratio
V_{H_2O}	total volume of the water inside the droplets [m^3]
λ	mean number of dissolved Ba^{2+} and SO_4^{2-} ions per droplet
ρ_{BaSO_4}	density of $BaSO_4$ [g/m^3]