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ŁUKASZ MAKOWSKI*, KRZYSZTOF WOJTAS*, WOJCIECH ORCIUCH*,
JERZY BAŁDYGA*

LARGE EDDY SIMULATION OF PRECIPITATION PROCESS CARRIED OUT IN JET REACTORS

MODELOWANIE PROCESU PRECYPITACJI W REAKTORACH ZDERZENIOWYCH PRZY UŻYCIU MODELI WIELKOWIOWYCH

Abstract

The paper presents an application of large eddy simulations to predict a course of precipitation process carried out in selected types of jet reactors. In the first part of this work the simulations results were validated using PIV and PLIF techniques and also by comparing model predictions with experimental data for fast parallel chemical test reactions. In the second part of this work predictions of modeling are compared with experimental data for BaSO₄ precipitation. Precipitation model is tested in this part also by comparing predictions of the model based on LES with results obtained using the multiple-time-scale mixing model combined with the $k-\epsilon$ model.

Keywords: jet reactors, mixing, precipitation process, large eddy simulation

Streszczenie

W artykule przedstawiono zastosowanie modelowania wielkowirowego procesu precypitacji siarczanu baru przebiegającego w reaktorach zderzeniowych. W pierwszej części pracy uzyskane wyniki numeryczne zweryfikowano z wykorzystaniem technik laserowych oraz z wynikami doświadczalnymi dla przebiegu złożonych reakcji chemicznych. W drugiej części pracy rozważano przebieg procesu precypitacji siarczanu baru. Wyniki modelowania wielkowirowego dodatkowo porównano z wynikami symulacji z użyciem modelu $k-\epsilon$ oraz modelu mieszalnik burzliwego.

Słowa kluczowe: reaktory zderzeniowe, mieszanie, precypitacja, modelowanie wielkowirowe

* Ph.D. D.Sc. Eng. Łukasz Makowski, M.Sc. Krzysztof Wojtas, Ph.D. Eng. Wojciech Orciuch, Prof. Ph.D. D.Sc. Eng. Jerzy Bałdyga, Faculty of Chemical and Process Engineering, Warsaw University of Technology.

1. Introduction

Precipitation of sparingly soluble materials is an important unit operation in chemical engineering practice. The process of precipitation involves a mixing controlled chemical reaction and subsequent crystallization of the product, which includes nucleation and growth of particles [1, 2]. The solid product has often a wide crystal size distribution (CSD), which determines its quality. Another factor affecting the product quality is the morphology of precipitating particles. Both the CSD and morphology can strongly depend on the method of contacting reactants and mixing conditions during the process. This results from the fact that the elementary subprocesses forming the overall precipitation process including chemical reaction, nucleation, and growth of crystals are usually very fast, so that mixing can affect their course. Therefore, development of accurate numerical simulation methods for turbulent reacting liquid flows is necessary for design of chemical reactors. Large eddy simulation (LES) is a very attractive method for simulations of a reactive flows for wide range of Reynolds number values. The effects of the large scales are directly computed and the small subgrid scales are modelled. Small scales tend to be more isotropic than the large ones so it is easier to predict their behavior using simpler and universal subgrid (SGS) models. In this work the authors are interested in the influence of mixing on the course of precipitation of the sparingly soluble test material.

2. Experimental system

The reactors used in this study are shown in Figure 1. Considering reactors are typical T-mixers with two inlet pipes of internal diameter equal to $d = 7$ mm and one outlet pipe with internal diameter $D = 11$ mm.

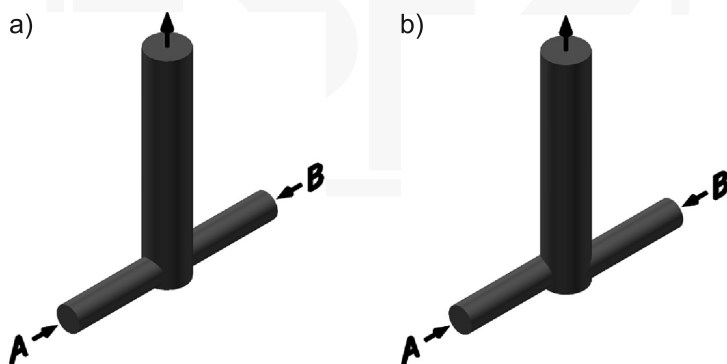


Fig. 1. Geometry of the reactors: a) symmetric T-mixer, b) vortex T-mixer

The reactors varied position of feeding pipes, in the symmetric T-mixer the inlet streams enter the mixer symmetrically from two sides of the mixer, whereas in the vortex T-mixers the feeding pipes were placed tangentially to the outlet pipes.

The fluid velocity was measured using the Particle Image Velocity (PIV) technique and the passive tracer concentration was determined using the Planar Laser Induced Fluorescence (PLIF) technique. Example of experimental data from PLIF measurements are given in next section, where they are compared with model predictions.

3. Simulations

Simulations were done using CFD code Ansys Fluent 14. The numerical grid consisted of about 1 800 000 hexahedral computational cells for each reactor. Two theoretical models were used to simulating turbulent flows: the standard k - ε model and large eddy simulation. In LES computations a dynamic stress model was employed to reflect effects of the small scale on large ones. In computations the subgrid diffusivity was calculated based on constant value of the subgrid Schmidt number [3]:

$$Sc_{sgs} = \frac{\nu_{sgs}}{D_{sgs}} \quad (1)$$

The subgrid concentration variance $\bar{\sigma}'^2$ was predicted by assuming that the small scale statistics can be inferred from the large scale statistic [4]:

$$\bar{\sigma}'^2 \approx c\bar{\sigma}'^2 = c(\tilde{f}'^2 - \tilde{f}^2) \quad (2)$$

where $\tilde{\cdot}$ denotes the test-filtered value, computed by applying the test filter (test-filter width 2Δ was used, where Δ is numeric grid size). The constant c is equal to 5 [5].

The calculations and experiments were performed for $Re_{jet} = 250 - 4\,000$, where:

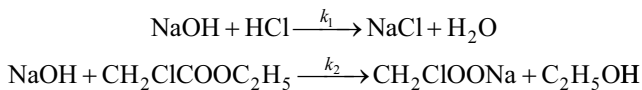
$$Re_{jet} = \frac{u_{jet} d \rho}{\mu} \quad (3)$$

and u_{jet} is mean velocity at the inlet, ρ and μ are density and dynamic viscosity respectively. Values of these parameters were taken as for water at 20°C.

4. Results and discussion

Figure 2 presents exemplary distributions of the measured and predicted values of the mixture fraction variance in the symmetric T-mixer for $Re_{jet} = 4000$. Agreement is good, which validates the models and numerical grid. Values of the numerical simulations are similar but variance calculated using LES predicted shape of distribution more similar to the experimental results for whole range of the Reynolds number values.

First the course of fast parallel chemical reactions were used to validate the LES procedure and to investigate the mixing effects on final product. In this work, common used in the literature [1, 6], the neutralization of sodium hydroxide by hydrochloric acid and the alkaline hydrolysis of ethyl chloracetate was considered:



The reactor was fed with the sodium hydroxide solution through the feed pipe, inlet *A*, whereas the premixture of hydrochloric acid and ethyl chloroacetate was fed through inlet *B* as shown in Fig.1. The concentration of the ethyl chloroacetate was measured before and after experiments chromatographically (HPLC), and the final selectivity of parallel reactions X_s was calculated from:

$$X_s = \frac{\langle c_{\text{CH}_2\text{ClCOOC}_2\text{H}_5,0} \rangle - \langle c_{\text{CH}_2\text{ClCOOC}_2\text{H}_5,\text{outlet}} \rangle}{\langle c_{\text{NaOH},0} \rangle} \quad (4)$$

The subgrid model for parallel reactions was presented by Makowski and Bałdya [6]. It was based on application of the Beta probability distribution $\Phi(f)$ of the mixture fraction f .

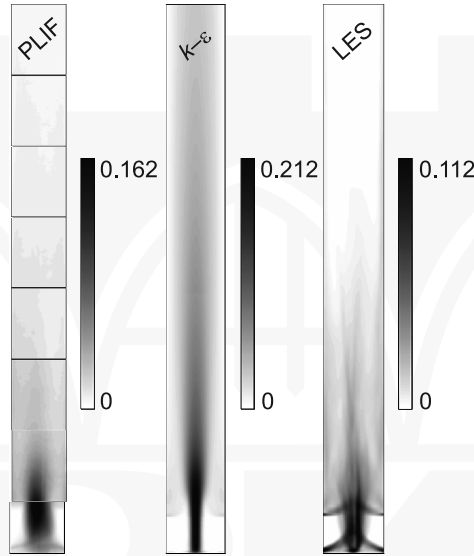


Fig. 2. Distributions of the measured and predicted values of the mixture fraction variance in the symmetric T-mixer for $Re_{jet} = 4000$

A set of filtered differential balance equations for any reacting species is then solved:

$$\frac{\partial \bar{c}_j}{\partial t} + \bar{u}_i \frac{\partial \bar{c}_j}{\partial x_i} = \frac{\partial}{\partial x_i} \left[(D_m + D_{sgs}) \frac{\partial \bar{c}_j}{\partial x_i} \right] + \bar{r}_j \quad (5)$$

where \bar{c} denotes filtered value. The first reaction is assumed to be instantaneous. The rate of the second reaction is given by:

$$\bar{r}_2 = k_2 \bar{c}_{\text{NaOH}} \bar{c}_{\text{CH}_2\text{ClCOOC}_2\text{H}_5} = k_2 \int_0^1 c_{\text{NaOH}}(f) c_{\text{CH}_2\text{ClCOOC}_2\text{H}_5}(f) \Phi(f) df \quad (6)$$

where $k_2 = 0,023 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and reactant concentration c_j for a mixture defined by f is predicted by linear interpolation:

$$c_j(f) = c_j^\infty(f) + \frac{\bar{c}_j - \bar{c}_j^\infty}{\bar{c}_j^0 - \bar{c}_j^\infty} [c_j^0(f) - c_j^\infty(f)] \quad (7)$$

The RANS model was completed with the non-equilibrium multiple-time-diffusion model – turbulent mixer model (TMM) [7] and the conditional moment closure [1, 8]. Comparison of the predictions of both models, LES and RANS with experimental data is presented in Fig.3.

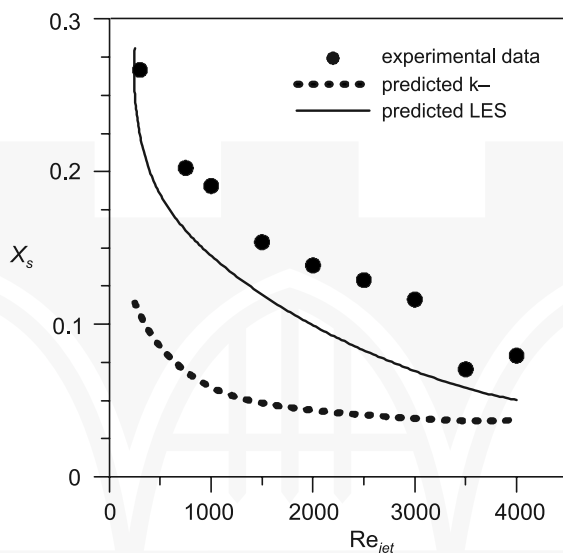
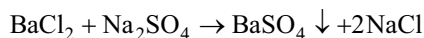


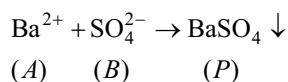
Fig. 3. Effects of Re_{jet} on final selectivity X_s , symmetric T-mixer, inlet reactant concentrations: $c_{j0} = 0.1M$

One can see that predictions of both models give tendencies observed in experiments, with better agreement with experimental data of LES results. For high Re_{jet} both models predict similar results which can be explained by two reasons: the first one is that the $k-\epsilon$ model is valid for high Re_{jet} only, the second one is that very fast reactions characterized by very small time constants are considered here, and such reactions are very sensitive to details of micromixing.

In the case of crystallization process the precipitation of barium sulphate from two water solutions of sodium sulphate and barium chloride was considered:



This is a classical test system for precipitation of sparingly soluble product P from liquid ionic solutions A and B [9–12]:



The driving force for nucleation and growth was defined by Ba^{2+} (A) and SO_4^{2-} (B) ions concentrations:

$$\Delta c = \sqrt{c_A c_B} - \sqrt{K_S} \quad (8)$$

where K_S is the concentration solubility product for BaSO_4 . The local instantaneous rates of nucleation and crystal growth depended on two local instantaneous values of the ions concentrations c_A and c_B . Other parameters, like temperature or solvent composition, were constant in our considerations.

Nucleation kinetics for BaSO_4 was described by the following empirical equations for nucleation rate R_N :

$$\begin{aligned} \text{for } \Delta c < 0.01\text{M: } R_N &= 6.00 \times 10^{12} \Delta c^{1.775} \\ \text{for } \Delta c \geq 0.01\text{M: } R_N &= 2.53 \times 10^{39} \Delta c^{15} \end{aligned} \quad (9)$$

Constants in eq.(9) were determined using experimental data by Nielsen [13] for heterogeneous and homogeneous nucleation respectively. This kinetics was applied before for example by Bałdyga et al. [9] during the study of the test process in a tank reactor and by Bałdyga and Orciuch [10] for the simulations of the BaSO_4 precipitation in a T-mixer.

In this work we assumed that the crystal growth results mainly from two processes: the transport of the ions through the solution to the crystal surface and the process of the ions integration into the crystal structure. The integration step is assumed to be a second-order process. Therefore, the rate of the crystal growth G depended on the ions concentrations in the solution, c_A and c_B , and on the ions concentrations at the crystal surface, c_{Ai} and c_{Bi} :

$$G = k_r (\sqrt{c_{Ai} c_{Bi}} - \sqrt{K_S})^2 = k_D (c_A - c_{Ai}) = k_D (c_B - c_{Bi}) \quad (10)$$

The rate constant for the surface integration step $k_r = 0.058 \text{ [(m s}^{-1}\text{)(m}^6 \text{ kmol}^{-2}\text{)]}$ was given by Nielsen [13] and the coefficient k_D was equal to $10^{-4} \text{ [(m s}^{-1}\text{)(m}^3 \text{ kmol}^{-1}\text{)]}$ [10].

Microphotographs of the product showed no aggregates in the samples. That is way the nucleation and crystal growth only were considered in the population balance of dispersed phase and aggregation and breakage were neglected. The balance was solved using the standard method of moments [14] and the closure procedure proposed for RANS simulations by Bałdyga and Orciuch [10, 15]:

$$\begin{aligned} \frac{\partial \langle m_j \rangle}{\partial t} + \langle u_{pi} \rangle \frac{\partial \langle m_j \rangle}{\partial x_i} &= \frac{\partial}{\partial x_i} \left(D_p \frac{\partial \langle m_j \rangle}{\partial x_i} \right) + 0^j \int_0^1 R_N(f) \Phi(f) df + \\ &+ j \frac{\langle m_{j-1} \rangle}{\langle c_P \rangle} \int_0^1 G(f) c_P(f) \Phi(f) df \quad \text{for } j = 0, 1, 2, \dots, 5 \end{aligned} \quad (11)$$

where $\langle \rangle$ denotes local mean value, m_j is the j -th moment of number distribution of characteristic particle size L , u_{pi} is component of particle velocity and D_p is particle diffusivity. In the closure procedure [10, 15] the concept of the mixture fraction f is used. The local instantaneous value of the nucleation rate reads:

$$R_N(f) = k_n \Delta c^n = k_n (\sqrt{c_A(f) c_B(f)} - \sqrt{K_S})^n \quad (12)$$

where coefficients k_n and n take values from eqs (9). The local value of the crystal growth rate is calculated from eqs (10):

$$G(f) = k_r \left[\sqrt{\left(c_A(f) - \frac{G(f)}{k_D} \right) \left(c_B(f) - \frac{G(f)}{k_D} \right)} - \sqrt{K_S} \right]^2 \quad (13)$$

Population balance must be completed with the mass balance for the dissolved reactants:

$$\begin{aligned} \frac{\partial \langle c_j \rangle}{\partial t} + \langle u_i \rangle \frac{\partial \langle c_j \rangle}{\partial x_i} &= \frac{\partial}{\partial x_i} \left(D_j \frac{\partial \langle c_j \rangle}{\partial x_i} \right) + \\ &+ \frac{k_a \rho_p \langle m_2 \rangle^1}{2M_p \langle c_p \rangle} \int_0^1 G(f) c_p(f) \Phi(f) df \quad \text{for } j = A, B \end{aligned} \quad (14)$$

where ρ_p and M_p are density and molar mass of precipitating product (BaSO_4) and k_a is surface shape factor of crystals.

In the case of large eddy simulation of precipitation process the subgrid fluctuations were neglected. Based on the time constant analysis Makowski et al. [16] have shown, that if the time constant for inertial-convective process and characteristic time constant for nucleation process are comparable, and the subgrid mixing time is smaller than the nucleation time, one is just on the limit when subgrid closure will be necessary.

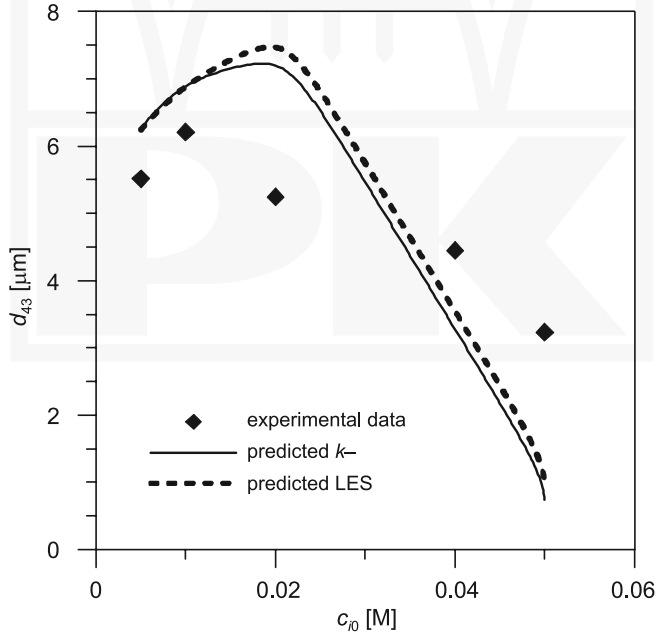


Fig. 4. Effects of inlet concentrations $c_{A0}=c_{B0}$ on mean particle diameter d_{43} , the symmetric T-mixer, $\text{Re}_{jet} = 3000$

Mean characteristic particle size L can be calculated from the moments. Figures 4 and 5 present the diameter d of sphere of the same volume as the volume of particle of characteristic size L . Particle volume v reads:

$$v = k_v L^3 = \frac{\pi}{6} d^3 \quad (15)$$

where k_v is volume shape factor of particles. So, volume weighted mean diameter d_{43} can be calculated from the moments:

$$d_{43} = \left(\frac{6k_v}{\pi} \right)^{1/3} L_{43} = \left(\frac{6k_v}{\pi} \right)^{1/3} \frac{m_4}{m_3} \quad (16)$$

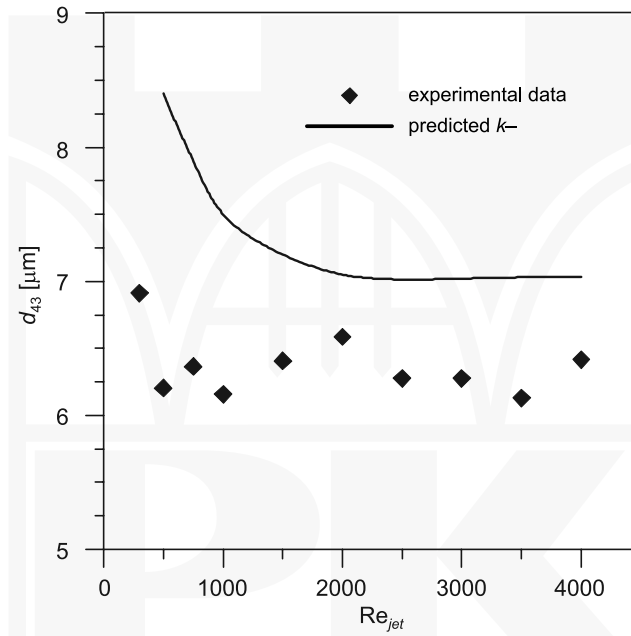


Fig. 5. Effects of Re_{jet} on mean particle diameter d_{43} , the vortex T-mixer, inlet reactant concentrations: $c_{A0} = c_{B0} = 0.01M$

One can see that predictions for both models are very similar (Fig. 4), and there is no effects of the Reynolds number above $Re_{jet} > 3000$ (Fig. 5). That means that mixing is faster than precipitation.

5. Conclusions

The LES and k - ϵ models were applied to simulate two complex processes (parallel chemical reactions and precipitation) in two T-mixers. The PIV and PLIF techniques were applied to validate numerical results. Presented here and earlier [16] results show that LES modelling gives better results especially for low Reynolds numbers. This illustrates importance of effect of large scale inhomogeneities that are predicted by LES and neglected by RANS. The second explanation for these differences results from theory of the k - ϵ model that was developed for fully turbulent flow. For higher Re_{jet} both models predict similar results.

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