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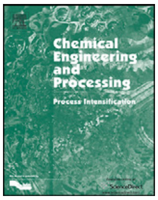

Large Eddy Simulation of mixing effects on the course of parallel chemical reactions and comparison with k–ε modeling

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ABSTRACT

The way in which reagents are mixed can have a large influence on the product distribution of chemical reactions. To model effects of mixing on various scales on the course of chemical reactions the method of Large Eddy Simulation (LES) of non-premixed, turbulent reactive flows of incompressible fluids is considered in this work. The subgrid modeling of chemical reaction is based on a beta distribution of the mixture fraction in combination with a conditional moment closure based on linear interpolation of local instantaneous reactant concentration values. The predictions obtained with LES are compared with experimental data for fast parallel chemical reactions, the fluid velocity measured using Particle Image Velocity (PIV) technique and the passive tracer concentration measured using the Planar Laser Induced Fluorescence (PLIF) technique. Predictions of the model based on LES are compared as well with results obtained using the non-equilibrium multiple-time-scale mixing model combined with a standard k–ε model and employing similar conditional moment closure as LES, applied, however, at larger scale. All comparisons show a very good performance of the model based on LES.

1. Introduction

Details of reagents flow and mixing in un-premixed reactive flows can have a large influence on the product distribution of the fast complex chemical reactions. Practical aspects of these effects are related to the fact that many chemical reactions leading to desirable intermediate and end-products (such as pharmaceutical intermediates, agrochemicals and many other fine chemicals) are accompanied by side reactions producing undesired by-products. Creation of by-products decreases the yield of desired reactions and complicates product separation. Even when the desired reaction is very fast comparing to undesired ones, its rate can be controlled by mixing, and the final selectivity can result then from competition between the desired, mixing controlled chemical reaction and the other, slower reactions. Hence, to control selectivity of complex chemical reactions one needs not only to have detailed information on kinetics and thermodynamics of chemical reactions but also understand and interpret in modeling effects of the flow and mixing on the course of chemical reactions. To predict, control and optimize mixing effects on chemical reactions one needs to apply so called micromixing models and closure methods, usually in combination with CFD. Adequate models describing reactive mixing one can find for example in Refs. [1–3]. To evaluate predictions of models describing reactive mixing one can employ specially designed mixing sensitive test reactions [1]. In this work we use the parallel reaction system that includes competitive neutralization of hydrochloric acid and alkaline hydrolysis of the ethyl chloroacetate [4–7]:

$$\underset{(A)}{\mathrm{NaOH}} + \underset{(B)}{\mathrm{HCl}} \xrightarrow{k_1} \underset{(P)}{\mathrm{NaCl}} + \mathrm{H_2O} \tag{1}$$

$$\underset{(A)}{\mathrm{NaOH}} + \underset{(C)}{\mathrm{CH_2ClCOOC_2H_5}} \xrightarrow{k_2} \underset{(S)}{\mathrm{CH_2ClCOONa}} + \mathrm{C_2H_5OH} \tag{2}$$

In this work the process of reactive mixing is modeled by using LES in combination with a simple conditional moment closure scheme based on linear interpolation of the values of the local instantaneous reactant concentration between the values characterizing instantaneous and infinitely slow reactions [1]. The same closure method was used previously in our group to interpret the course of test reactions (1) and (2) in stirred tank reactors [7,8], however, this was done in combination with a standard k–ε model and the non-equilibrium multiple-time-scale mixing model; in present work the non-equilibrium multiple-time-scale mixing model and k–ε model are replaced by LES. The method applied in present work is similar to the one applied by Michioka and Komori [9]; the main difference is in the subgrid model.

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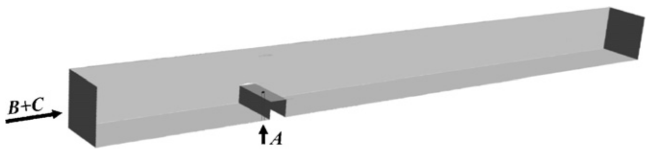

Fig. 1. Schematic diagram of the experimental system (reactor) and computational domain.

2. Experimental

Experiments were performed to investigate effects of process conditions on the course of fast parallel chemical reactions, the fluid velocity was measured using Particle Image Velocity (PIV) technique and the passive tracer concentration was measured using the Planar Laser Induced Fluorescence (PLIF) technique.

The parallel chemical reactions employed to investigate the mixing effects experimentally were the neutralisation of sodium hydroxide (A) by hydrochloric acid (B) and the alkaline hydrolysis of ethyl chloroacetate (C) as shown by Eqs. (1) and (2). The reactor applied in experiments is shown schematically in Fig. 1. It is the continuous flow channel reactor with square cross-section. The height and width of the channel are equal to 46 mm × 46 mm. Inside the reactor channel there is the flow obstacle with a feeding nozzle installed in it. The height and the width of the obstacle are equal to 15 mm. The reactor was fed by the sodium hydroxide solution (A) through feed nozzle of internal diameter equal to 1 mm, whereas the premixture of hydrochloric acid (B) and ethyl chloroacetate (C) was fed through main inlet as shown in Fig. 1. The investigations were carried out for the Reynolds number, Re, in a range between 10 000 and 40 000 and for the velocity ratio Ru in a range between 1 and 16. The Reynolds number was defined using the hydraulic diameter, and Ru is a ratio of the mean velocity in the feed pipe to the mean velocity in the channel.

Experiments were carried out at $T = 293$ K with $k_2 = 23\,\mathrm{dm}^3\,(\mathrm{mol\,s})^{-1}$. The first reaction can be interpreted as instantaneous with $k_1 \to \infty$. Initial concentrations of reactants were equal to $c_{A0} = 450\,\mathrm{mol\,m}^{-3}$, $c_{B0} = c_{C0} = 9\,\mathrm{mol\,m}^{-3}$.

In order to calculate the final selectivity of parallel reactions, X_S

$$X_S = \frac{\langle c_{C0}\rangle - \langle c_C\rangle}{\langle c_{A0}\rangle} \tag{3}$$

the concentration of the ethyl chloroacetate was measured before and after experiments chromatographically (HPLC). It is important to note that X_S represents a relative amount of the substrate A converted into the byproduct S. Results of experiments are shown together with model predictions in Section 4 of this paper.

Local, instantaneous values of fluid velocity and passive tracer concentration were measured using two techniques: Particle Image Velocimetry (PIV) and Planar Laser Induced Fluorescence (PLIF). Double-cavity Nd-YAG laser 532 nm with energy equal to 50 mJ per pulse was applied. The laser beam was transformed to a collimated laser sheet of thickness $\delta \cong 300\,\mu\mathrm{m}$. The sheet crossed the experimental system vertically through the axis of the tracer injection nozzle and the channel symmetry plane.

The solutions were seeded with the spherical particles of polyamide of average diameter equal to 20 μm to enable the PIV measurements. The concentration of particles was the same in both solutions fed to the reactor. Rhodamine B was used as a fluorescent tracer; its concentration in the solution fed through the nozzle was equal to $200\,\mu\mathrm{g\,dm}^{-3}$. Spatial resolution of the PLIF measurements is related to the resolution of digital images and thickness of the laser sheet. In present case this is represented by 18 × 18 × 300 μm. Spatial resolution of the PIV measurements depends also on the size of a sampling window, which in present work is equal to 264 × 264 × 300 μm.

From the PIV measurements one gets two components of the velocity vector, and therefore, when comparing model predictions with experimental data the velocity magnitude will be calculated using these two components as well. The PLIF results collected during long enough time period to remove fluctuations of the mean mixture fraction can be used to obtain the mean mixture fraction from Eq. (4):

$$\langle f\rangle = \frac{average\ \ volume\ \ of\ \ the\ \ tracer\ \ solution}{volume\ \ of\ \ mixture} = \frac{average\ \ tracer\ \ concentration\ \ in\ \ a\ \ mixture}{tracer\ \ concentration\ \ in\ \ the\ \ nozzle\ \ feeding\ \ stream} \tag{4}$$

Again results of experiments are shown together with model predictions in Section 4 of this paper.

3. Modeling

Computations with the Large Eddy Simulation (LES) model were carried out using the commercial CFD code Fluent-Ansys with the Smagorinsky closure for the subgrid turbulence, and for the system geometry presented in Fig. 1. The commercial CFD code was supplemented with the user defined functions to model mixing and reactive mixing. The grid employed for the simulation consisted of about 3 000 000 computational hexahedral computational cells, and it was checked that the results of computations were not sensitive to a further increase of the number of cells. Computations were regarded as satisfactory converged when the total normalized residuals were smaller than 10^{-6}. In LES computations a dynamic stress model was employed to reflect the effects of subgrid-scale eddies on larger ones. The mean values of flow parameters were obtained using a time-averaging procedure. The time interval employed for averaging was taken as $10\,\tau$, where τ represents the mean residence time in the reactor presented in Fig. 1, whereas the time step was equal to $1/100\,\tau$. The time step was fulfilling a Courant–Friedrichs–Lewy (CFL) stability criterion modified to include the effect of reaction.

Typical contours of instantaneous and mean velocity magnitude are shown in Fig. 2. In the case of instantaneous values one can see that the stricter similar to the von Kármán vortex street is predicted.

The distributions of the filtered mixture fraction $\langle f\rangle$ are described using the gradient diffusion approximation:

$$\frac{\partial\langle f\rangle}{\partial t} + \langle u_j\rangle\frac{\partial\langle f\rangle}{\partial x_j} = \frac{\partial}{\partial x_j}\left[(D_m + D_{SGS})\frac{\partial\langle f\rangle}{\partial x_j}\right] \tag{5}$$

where the residual scalar filter flux was closed with a gradient-diffusion model, where $D_{SGS} = \nu_{SGS}/Sc_{SGS}$. The value for the subgrid turbulent Schmidt number was taken as equal to $Sc_{SGS} = 0.4$ based on Ref. [10]. To compare the new LES results with results obtained with the (k–ε) RANS model supplemented with the non-equilibrium multiple-time-scale mixing model and the conditional moment closure [7,8] the k–ε model based computations were carried out as well. As can be seen in Fig. 2 the most important and most difficult to model effects of mixing and the same time most spectacular effects are expected in the vicinity of the A solution feeding point. For this reason in what follows we will investigate the velocity and concentration distributions close to the point of feeding with the A solution.