INFLUENCE OF MICROMIXING ON THE COURSE OF HOMOGENOUS CHEMICAL REACTIONS IN SUSPENSIONS

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Abstract. The size and concentration of suspended particles affect turbulent flows of suspensions as well as mixing phenomena. Presented analysis shows how particles affect concentration spectra and micromixing parameters. Such effects are identified experimentally with reactive tracers (parallel competitive reactions) and predicted using modified micromixing parameters in E-model and two CFD models: the one based on simulation of turbulence modulation and the Mixture Model.

Keywords: chemical reaction, micromixing, modulation of turbulence, stirred tank, suspension flow.

1. INTRODUCTION

Theoretical studies and experimental results show that the size and concentration of suspended particles affect turbulent flows of suspensions as well as mixing phenomena [1,2,3]. Effects of particles on turbulence itself are referred to as modulation of turbulence. Modulation of turbulence is related to microscale fluid flows and related mixing phenomena including effects of such flows on micromixing. In Section 2 we perform theoretical analysis to show how presence of particles affects modulation as well as concentration spectra and micromixing parameters, and check how these effects depend on relation between particle size and the eddy scale. In Section 3 we use the parallel chemical test reactions (test system based on neutralization of sodium hydroxide with strong acid and ethyl chloroacetate hydrolysis) to identify these effects experimentally. Finally in Section 4 we use three models employing micromixing parameters derived in section 3 to interpret experimental data and simulate the process: the modified [4] E-model and two different CFD based models. The first one assumes suspension homogeneity and accounts for turbulence modulation, while the second model, the Mixture Model available in the Fluent-ANSYS package, accounts additionally for particles segregation in agitated suspensions.

2. MODELLING OF TURBULENCE AND TURBULENT MIXING

Modulation of turbulence results from complex unsteady motions of the particles that may result as well in non-uniform spatial distribution of the particles and, possibly, particle segregation. Experimental observations suggest that small particles tend to attenuate the carrier phase turbulence while large particles tend to augment it [1]. Furthermore, the magnitude of these effects has been shown to scale with the particle concentration [2]. This is explained by the fact that large particles generate wakes that are responsible for the additional production of turbulence while the particle-eddy interactions are responsible for the additional dissipation of turbulent energy. For dense flows particle-particle collisions participate as well in modulation. Mando et al., [3] proposed the phenomenological model that accounts for both attenuation and augmentation effects. This model describes averaged effects and can be used...
as a first step for determination of modulation effects on the structure of turbulence and effects observed on microscale.

Let us start from parametric sensitivity of this model. Figure 1 shows how predicted intensity of turbulence, $\sigma$, is modified by presence of particles; on this figure $(\sigma-\sigma_0)/\sigma_0$ is presented versus the ratio of particle size to the integral scale of turbulence, $\sigma_0$ and $\sigma$ represent the turbulence intensities for clear flow and particle–laden flow respectively, and

$$\sigma = \left( \frac{2}{3} k \right)^{\frac{1}{2}} \langle u \rangle$$  \hspace{1cm} (1)

Simulations were carried out using the standard $k\varepsilon$ model, Fluent, ANSYS. Computations were performed for water as a continuous phase with $\rho=998.2$ kg/m$^3$, $\mu=1.003 \cdot 10^{-3}$ kg/(ms).

![Figure 1. Turbulence modulation at the centerline of a vertical pipe of diameter $D=0.04$ m and length $L=8$ m; effect of particles mass fraction, $C$.](image)

One can conclude that augmentation can be expected only for very large particles; comparing results presented in Figure 1 with results presented in [3] for a gas as a continuous phase, we see that the particle density must be much higher than fluid density to see effect of augmentation.

Let us consider now in detail interaction at small scales. The local values of particle and fluid velocity and turbulent diffusivity can differ significantly. The relative fluid-particle velocities, $\Delta u$, and scales of particle movements, $l$, were calculated using either an approach based on the Tchen’s theory in the form extended by Hinze [5] for very small particles, or Levich method [6] for larger scale phenomena in the inertial subrange of turbulence.

The particles are classified depending on the scale of particle motion $l$ and the inertia of the particles (expressed by relaxation time). In order classify particle motions in the viscous regime they need to satisfy the condition $\tau_p/\tau_k \ll 1$, where $\tau_k$ is the Kolmogorov time microscale $\tau_k = (\nu/\varepsilon)^{\frac{1}{2}}$ and $\tau_p$ represents relaxation time. Among the particle moving in the viscous regime one can distinguish small particle movements, $l \approx \lambda_k$, and very small particle movements, $l << \lambda_k$. For particle movements in the inertial regime, $l >> \lambda_k$ (large particles) we assume no direct viscous effects on particle motions. Notice that this classification depends on several characteristics including particle size, particle density, liquid properties and process conditions. For liquid suspensions particles in viscous regime are represented in most cases by micro- and nanoparticles of the size equal or smaller than Komogorov microscale but in the case of vigorous turbulence and heavy particles the scale $l$ of movements particles of $d_p < \lambda_k$ can be much larger than the Kolmogorov microscale $l >> \lambda_k$.

Presence of particles affects the rate of energy dissipation and microscale flows, so should affect micromixing as well. Figure 2 shows how particle affect the concentration...
spectrum. This spectrum was derived using the method presented in ref.[4] from energy spectrum for kinetic energy of turbulence derived using the Tchen-Hinze-Levich approach [5,6]. Fig. 2 shows that at higher volume fraction of particles the concentration fluctuations of a passive tracer present in the continuous phase are smaller at high wave numbers (small scales) and larger at low wave numbers (large scales). This should affect the rate of meso- and micromixing as well, and influence this way the course of mixing sensitive test reactions.

![Figure 2. The concentration spectrum of passive scalar for $\varepsilon = 1 m^2/s^3$, $d_p = 100\mu m$; effect of particle volume fraction, $X_V$.](image)

For the clear flow one has [4] for the engulfment micromixing parameter

$$E = 0.058\left(\frac{\varepsilon}{\nu}\right)^{1/2} \quad (2)$$

When effects of particles are included, the prefactor 0.058 becomes a function of process conditions and suspension structure (in our case between 0.041 and 0.046). Similarly effect is observed in the case of prefactor $A$ in the time constant for the inertial-convective mixing

$$\tau_s = A \cdot \Lambda_C^2 / \varepsilon^{1/3} \quad (A=1.2 \text{ for clear flow}),$$

where $\Lambda_C$ is the integral scale of turbulence. Of course there is modulation effect of particles on the rate of energy dissipation, $\varepsilon$.

3. EXPERIMENTAL METHODS AND EXPERIMENTAL RESULTS

To investigate effects of particle presence on micromixing, the system of two parallel, irreversible, second order test reactions was used [4]. Reactions between sodium hydroxide and either hydrochloric acid or ethyl ester of monochloroacetic acid were used as test reactions. First reaction was assumed to be mixing controlled and concentrations of reactants of the second reaction were chosen so that the rate of second was similar to the rate of mixing.

$$\text{NaOH}(A) + \text{HCl}(B) \rightarrow \text{NaCl} + \text{H}_2\text{O}$$

$$\text{NaOH} (A) + \text{CH}_2\text{ClCOOC}_2\text{H}_5 (C) \rightarrow \text{CH}_2\text{ClCOONa} + \text{C}_2\text{H}_5\text{OH}$$

Experiments were carried out at $T = 298$ K ($k_2 = 33$ dm$^3$mol/s) in the baffled, semibatch stirred tank reactor shown schematically on Figure 3. There was initially the premixture of HCl (40 mol/m$^3$) and CH$_2$ClCOOC$_2$H$_5$ (123.8 mol/m$^3$) in the vessel, as well as an adequate amount of particles represented by their size $d_p$ and the volume fraction, $X_v$. The solution of NaOH (2000 mol/m$^3$) was fed during the process in the semibatch mode. Experiments were carried out for different feed time and different feed tube positions. The influence of particle size and volume fraction was investigated. Measurements were carried out for the stirrer speed from the range between 700 and 850 rpm in order to keep the solid particles fully suspended as predicted by the Zwietering [7] criterion. In order to calculate the final selectivity of parallel reactions the concentration of ethyl chloroacetate was measured chromatographically (HPLC) before and after experiments.
The final selectivity was calculated from the following expression:

\[ X_s = \frac{\bar{c}_{c0} - \bar{c}_C}{c_{40}} \]  

(3)

where \( \bar{c}_{c0} \) are the average feed concentrations. Notice that lower \( X_s \) means better mixing.

Effects of operating conditions, e.g. the feed position, feed time and size of particles on the reaction yield are presented in Figure 4 for \( X_f = 0.041 \) and \( N = 700 \text{ rpm} \). Clearly, presence of particles affects micromixing. This results from effects of turbulent microflows generated by particles on the kinetic energy of turbulence, the rate of dissipation of kinetic energy and mixing. Experimental results show that both presence of particles and increase of their size decrease the rate of mixing. Such behavior is observed for feeding below and above the impeller. Notice that feeding points differ significantly in the local rate of energy dissipation and local flow structure.

![Figure 4. Effect of particle size on selectivity, feeding above (left) and below (right) the stirrer, \( X_f = 0.041 \), \( N = 700 \text{ rpm} \).](image)

4. RESULTS OF MODELLING AND COMPARISON WITH EXPERIMENTAL DATA

Three models were applied to simulate the process. In each model the same method was used to predict effects of presence of particles on micromixing parameters. The first one was the multiple-scale model combining the viscous-convective mixing (E-model) with inertial-convective mixing [8], with presumed map of the rate of energy dissipation on circulation in the tank [4]. In this case it was assumed that the particles are uniformly distributed in the tank.
Results of application of this model are presented in Figure 5. The model predicts well effect of feeding time but underestimates an effect of particle size.

CFD simulations were based on the multiple-time-scale turbulent mixer model and the conditional moment closure based on beta distribution [4]. In the first case the flow was at first calculated assuming uniform distribution of particles, afterwards the effects of modulation, mixing and chemical reaction were simulated. Figure 6 shows results of simulations. Effect of feeding time is predicted better than by the E-model but effect of particle size is wrongly predicted in the case of modulation model (see opposite trend).

Figure 6. Influence of feeding time and particle size on selectivity, $X_1=0.041$, $N=700$ rpm, feeding above the stirrer. Comparison of experimental data with predictions of modulation-model.

Figure 7. Influence of feeding time and particle size on selectivity, $X_1=0.041$, $N=700$ rpm, feeding above the stirrer. Comparison of experimental data with predictions of the Mixture-model.
The second CFD approach is based on application of the multiphase flow model (Mixture model) by Fluent Ansys, and includes effects of particle segregation, see Figure 7. This model predicts very well effects of feeding time and particle size.

![Image](image1.png)

Figure 8. The particles phase distribution presented as the particles volume fraction for particle size 100µm, 500 µm and 2000 µm respectively. \( X_v=0.041 \), \( N=700 \text{ rpm} \), feeding above the stirrer. Mixture model.

5. CONCLUSIONS

One can conclude that the distribution of particle concentration has the most significant effect on the product distribution of test reactions. Figure 8 shows that the distribution of particles in the stirred tank depends indeed strongly on the particle size. Of course one needs to apply such mesomixing and micromixing models that properly predict effects of particle size, particle and fluid density and volume fraction of particles on the meso- and micro-mixing parameters. Comparison of predictions of E-model (without modulation) and modulation-model shows that including modulation effects alone is not enough to improve predictions.

Acknowledgement

This work has been supported by the European Union in the framework of European Social Fund through the Warsaw University of Technology Development Programme, realized by Center for Advanced Studies.

6. REFERENCES