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Mixing assessment by chemical probe

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ABSTRACT

Quantification of micro-mixing is a fundamental issue in industrial chemical processes. Local mixing that is not "fast enough" compared with the reaction kinetics reduces the selectivity of the reaction. Micro-mixing can be characterized by chemical probe methods based on observation of a local chemical reaction that results from the competition between turbulent mixing at micro-scales and the reaction kinetics. However, real-world experimental conditions rarely comply with the grounding assumptions of this method. Starting from physical considerations, the present study aims to establish some guidelines for obtaining quantitative information from the chemical probe and for improving the accuracy of the method by an adaptive protocol. For the first aspect, an analytical approach is proposed to define the validity domain based on analysis of the turbulent time scales. For the second purpose, a novel experimental procedure is suggested that entails targeting the concentrations of the chemical species that can provide the optimal conditions for a relevant use of the chemical probe.

1. Introduction

Characterizing micro-mixing is an important issue in the "Green Process" scheme, since it governs, in a broad class of industrial processes, byproduct effluents and consequently process efficiency. The selectivity of fast chemical reactions depends on reagent mixing at the molecular scale. In turbulent flows, the species aggregates are reduced in size by the turbulent cascade. In this process, the limiting mechanism occurs at smaller turbulence scales [1]. Thus, the sequence of micro-mixing is (i) engulfment in the energetic vortices at Kolmogorov scale, (ii) stirring in the viscous-convective subrange, where the fluid particles are subjected to laminar stretching [2], and (iii) molecular diffusion at sub-Batchelor scales that rapidly dissipates the variance in concentration. Understanding and quantifying this mechanism is essential in designing industrial processes involving fast reactions that can present characteristic reaction times smaller than the characteristic micro-mixing time.

The two final steps in the micro-mixing mechanism described above are "faster" [1–4] than engulfment at the Kolmogorov scale: as a consequence, micro-mixing depends on the turbulence energy dissipation rate, which governs the time and length scale of the smaller eddies. This fundamental property of the turbulent field can be determined by classical velocimetry methods such as laser Doppler anemometry (LDA), particle image velocimetry (PIV), or hot-wire anemometry, all of which give access, in three-dimensional space, to the nine contributions of the turbulent energy dissipation rate [5].

Alternative methods to characterize micro-mixing based on observations of a chemical system have been developed over the last few years [6–10], mostly for the cases where there is no optical access to the flow to carry out reference methods like LDA or PIV, but also for their ability to give access to the result of a chemical reaction, and thus to the straightforward result of the mass transfer. These methods were investigated especially by Bourne [11] (coupling of naphtol-1 and -2 with diazot sulfanilic acid), and Fournier et al. [12] (Villermaux–Dushman reactions or the iodide/iodate method). These techniques, called "chemical probe methods", are based on the competition between micro-mixing and well-known chemical kinetics by the straightforward observation of reaction selectivity, i.e. the secondary product concentrations. Such experiments must be performed under controlled conditions, first by ensuring that the main reaction is not fully achieved: the selectivity must be "far" from 0 and 1 to make the reaction product

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Nomenclature

c_i	concentration of species i (mol)
d	needle diameter (m)
D	reactor diameter (m)
D_t	turbulent diffusivity (m^2/s)
TKE, k	turbulence kinetic energy (m^2/s^2)
t	time (s)
t_m	micro-mixing time (s)
W	local flow velocity (m/s)
W_i	injection velocity (m/s)
$\bar{W}$	mean flow velocity (m/s)
Q	flow rate (m^3/s)
X_s	segregation index
[]	concentration (mol)
Greek symbols	
ε	turbulence energy dissipation rate (m^2/s^3)
Λ	integral length scale (m)
υ	kinematic viscosity (m^2/s)
τ	time constant (s)

sensitive to the micro-mixing. Under optimal conditions the slowest reaction time is equal to the micro-mixing time. From knowledge of the chemical reaction (mechanism, kinetics and stoichiometry), the local turbulent energy dissipation rate can readily be derived from the measured selectivity *via* phenomenological micro-mixing models [3].

The appropriate choice of operating conditions (initial reagent concentrations, injection flowrate, stoichiometry...) is not trivial and there is as yet no clear methodology for using chemical probes, especially for open-loop flows. The choice of initial concentrations is generally made by "trial and error" and sometimes is not convenient with respect to the reaction kinetics [13–15]. Accurate quantitative results can be obtained if certain conditions on the flow and the chemical system are fulfilled. The purpose of the present work is to establish guidelines for obtaining quantitative information from the chemical probe when possible and for improving the accuracy of the method by an adaptive protocol. For the first aim, an analytical approach based on analysis of the competition between the different turbulent time scales is proposed in order to assess the feasibility of chemical probe method, i.e.to answer the question if the chemical probe is able or not to give relevant information on the transfers in these peculiar conditions. For the second purpose, a novel experimental adaptive procedure is suggested, that entails targeting the optimal concentrations of the chemical species providing more accurate and more "localized" observation of the mixing time, and subsequently of the energy dissipation rate. These rules can be generalized to any chemical-probe system and can be applied in any reactor geometry.

In the present work, the mixing scales analysis and the adaptive procedure are applied to an inline heat exchanger–reactor equipped with aligned vortex generators. The iodide/iodate reaction system [12,16,17] and the micro-mixing E-model [18] employed here, are widely used in batch and continuous-flow reactors [19–22]. The chemical probe method and the micro-mixing model are succinctly reprised in Section 2. In Section 3, a scaling analysis of turbulence and of the interactions among the different scales leads to the definition of a validity domain for the chemical probe method. In Section 4, a novel experimental procedure is proposed to adapt the reagent concentrations to the turbulence level and to check the measurement volume at the injection point. Section 5 is devoted to some sample improvements that may result from the present analysis, specifically comparing a static mixer equipped with aligned vortex generators to previous experiments [23]. Concluding remarks about the application opportunities of the method are given in Section 6.

2. Chemical probe: chemical system and micro-mixing model

2.1. The iodide/iodate method

The iodide/iodate system [12,16,17] is based on competitive parallel reactions: the quasi-instantaneous borate neutralization [Eq. (1)] and the Dushman reaction [24] [Eq. (2)], which is much slower. The balanced reactions can be modeled as follows:

$$H_2BO_3^- + H^+ \leftrightarrow H_3BO_3 \tag{1}$$

$$5I^- + IO_3^- + 6H^+ \leftrightarrow 3I_2 + 3H_2O \tag{2}$$

The iodine I_2 further reacts with iodide ions I^-, yielding I_3^- ions following the quasi-instantaneous equilibrium reaction:

$$I_2 + I^- \leftrightarrow I_3^- \tag{3}$$

The kinetics of the three reactions was established by Guichardon et al. [17]. Only the characteristic time of the slowest reaction in Eq. (2) is described here, since it is used for further calculations:

$$t_{r2} = \frac{\mathrm{Min}\left(\frac{3}{5}[I^-]; 3[IO_3^-]; \frac{1}{2}[H^+]\right)}{r_2} \tag{4}$$

where the brackets denote the reagent concentration and r_2 is the rate of the second reaction:

$$r_2 = K_2[I^-]^2[H^+]^2[IO_3^-] \tag{5}$$

where the constant K_2 is a function of the ionic strength as given by Palmer et al. [25] and Guichardon et al. [17].

When the micro-mixing is limiting, a local overconcentration of H^+ can react after reaction (2) and produce iodine I_2, which itself reacts with iodide I^- and yields I_3^- ions [Eq. (3)]. The presence of I_2 and I_3^- is hence the manifestation of a mixing time smaller than the second reaction time and can be quantified by a segregation index. In continuous systems, it is defined by Fournier et al. [26] and Ferrouillat et al. [27] as:

$$X_s = 2\frac{[I_2] + [I_3^-]}{[H^+]_0}\left(1 + \frac{Q_P}{Q_{H^+}}\right)\left(1 + \frac{[H_2BO_3^-]_0}{6[IO_3^-]_0}\right) \tag{6}$$

where Q_p and Q_{H^+} are respectively the principal flow rate of the initial mixture flow and the injection flow rate of sulfuric acid. $X_S = 0$ for perfect micro-mixing and $X_S = 1$ for total segregation on the molecular scale.

In order to determine the I_2 and I_3^- concentrations in the Eq. (6), the output flow is driven to a spectrophotometer cell where the light absorption, which is proportional to the concentration of I_3^- ions, is recorded. The iodine $[I_2]$ is derived from the mass balance on iodine [26].

2.2. Micro-mixing model

The segregation index X_S provides only qualitative information on micro-mixing since it depends on the initial concentrations and on the ratio between the main and injection flows. The related quantitative parameter is the intrinsic micro-mixing time t_m,