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Experimental study of reactive mixing in a mini-scale mixer by laser-induced fluorescence technique

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ABSTRACT

The liquid–liquid mixing process coupled with chemical reactions in a mini-scale jet mixer was visualized by reactive laser-induced fluorescence (reactive-LIF) technique for a deep understanding of the interplay between the mixing and the simultaneous reactions. A novel approach for implementing the reactive-LIF measurements was advanced in this work, where the principle was based on the quenching of the fluorescence signal emitted from the Rhodamine-B dye using the mechanism of Fenton reaction. The purely physical mixing and the reactive mixing processes were investigated extensively by comparing the concentration fields under different operating conditions, i.e. the different momentum ratios between the jet and the bulk flows, and the different Reynolds numbers in the mixing channel of a mini-scale mixer. The results revealed that the transient dynamics in the reactive mixing process cannot be precisely understood based on the time-averaged concentration fields from either the physical or the reactive mixing measurements. The coupled mixing and the reaction processes occurred simultaneously, unless the rapid mixing was achieved by tuning the operating conditions so that the processes can be decoupled into two isolated ones.

1. Introduction

As a principal process mixing usually has a significant effect on the performance of chemical reactors [1], because chemical reactions always occur together with the process of different reactive materials contacting each other. The relationship between mixing and reactions depends on the relative magnitude of the mixing time scale and the reaction time scale. If the former is much smaller than the latter, the reactions could be considered to start after a well-mixed state, and the perfect mixing models such as the CSTR model might be adequate. However, when the former is similar with or bigger than the latter, the mixing efficiency could greatly alter the system performances such as the reaction selectivity and the products distribution, especially in the processes where the side reactions produce undesired by-products [2,3]. Therefore, control of the mixing process is often the key technology in process engineering for a wide class of products [4]. The interaction of turbulent mixing and fast chemical reactions has been investigated in depth by a few research groups. For example, a series of articles by the group of Fox [5–10] have made unique contributions in this area. They applied particle image velocimetry (PIV) and laser-induced fluorescence (LIF) technique to reveal the simultaneous velocity and concentration fields in the turbulent mixing process, and advanced several simulation methods based on the micro-mixing models. The group of Bourne [11–13] investigated mixing and chemical reactions by experiments and discussed the interaction between reactions and mixing on various scales. Although great efforts have been made on this topic, there is still a demand for a deeper understanding on the reactive mixing.

The experimental approaches to study the mixing performance could be classified into two categories: the one by test reactions, and the other by visualization techniques.

The test reactions have been summarized into three main types, i.e. the single reaction (A + B → R), the consecutive competing reactions (A + B → R and R + B → S), and the parallel competing reactions (A + B → R and C + B → S) [14]. In the latter two schemes, yield and/or selectivity achieved for the specific reaction products can be used to quantify the mixing performance. Lots of researches were carried out by this means, such as the “Villermaux/Dushmann method” [15–19], and the “third Bourne” reactions [3,20–21]. Although the micro-mixing efficiency can be evaluated in various mixers, only the integral mixing effect is obtained by these methods because only the products at the mixer outlets are analyzed. That is to say the micro-mixing efficiency is evaluated indirectly by using the test reactions.

Laser-induced fluorescence (LIF) technique has been frequently employed for mixing research in the past few years in both macro- and micro-sized devices [8,22–27], which is a non-intrusive

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Nomenclature

$\bar{C}$	normalized concentration of species B at the complete mixing positions
C_B	normalized concentration of species B
$C_{B,phy}$	normalized concentration of species B in the physical mixing experiments
$C_{B,react}$	normalized concentration of species B in the reactive mixing experiments
d	edge length of the cross-section of the mixing channel in x–z plane (mm)
Q_A	flow rate of fluid A (mL min^{-1})
Q_B	flow rate of fluid B (mL min^{-1})
x_i	local mixing rate at each interrogation area

Greek symbols

α	flow rate ratio of two fluids
Φ	mixing extent
η	reaction extent

approach to visualize the concentration (or temperature) field with high resolution in time and in space. The principle of the LIF technique is based on the monotonic relationship between the fluorescent tracer concentration and the excited fluorescence intensity by the laser sheet through the liquids. Therefore the concentration field in the mixing zone could be visualized quantitatively, showing the dynamic mixing process of liquid streams. The predominant advantage of LIF technique over the test reactions is that it could reveal the meso- or micro-scale mixing information at each point in the mixing zone. In our previous work [28–30], LIF technique was successfully employed to assess the mixing performance in several jet mixers for fast liquid mixing design. However, all these studies focused on the physical mixing process, which is not adequate for analyzing the potential reactive mixing process where chemical reactions occur in time.

Some researchers have implemented the LIF technique for reactive mixing measurement by using reaction-sensitive fluorescents instead of the ordinary LIF tracers. The measured fluorescence intensity changes with the development of the chemical reaction(s). Thus, the extent of the reaction procedure can be characterized by the spatial distribution of the dynamically changed species concentration in terms of the fluorescence variation. Ito and Komori [31] utilized 'Rhodamine-2' ($C_{40}H_{43}ClN_4O_{11}$) as the reactive-LIF tracer, for it does not emit fluorescence unless chelating with Ca^{2+} ion. Hence, the solutions with 'Rhodamine-2' and calcium chloride were used as the two reactive streams, respectively. Shinohara et al. [32] visualized reacting flows based on the pH-dependent fluorescence dye (i.e. 'quinine'), where the fluorescence intensity is correlated with the pH value of the solution. In their experiments, acetic acid solution and ammonia hydroxide solution were employed as the two reactive streams. Therefore a neutralization reaction took place together with the mixing process, and the reaction progress was revealed by the dynamic signals of the fluorescence intensity.

Although the reactive-LIF technique could visualize the competitive relationship between mixing and chemical reactions, the prices for the laser apparatus and the fluorescence tracer become the limiting factors for the reactive-LIF experiments. The specific tracer can only be excited by a laser with a certain wavelength, e.g. 'quinine' by 355 nm and 'Rhodamine-2' by 532 nm. These reaction-sensitive tracers usually bear a prohibitive price, for example, 'Rhodamine-2' for more than 200 dollars per milligram.

In this work, we advanced a novel approach to realize the reactive-LIF measurement in liquid phase based on an ordinary laser apparatus at 532 nm and the low price fluorescence tracer of Rhodamine-B. The reactive mixing process in a mini-scale jet mixer was measured and the relationship between the reaction and the mixing in the mixing zone were analyzed.

2. Experimental

2.1. Reactive-LIF technique

Different from a general LIF technique, reactive-LIF measurement must be able to capture the variation of a species concentration in time due to the joint effect of mixing and reaction. And it should be able to visualize and quantify the interplay between the physical mixing and the simultaneous chemical reactions. The basic idea of the proposed reactive-LIF technique is to use a reaction to quench the fluorescence signal, so that the reactive mixing process can be recorded quantitatively. In this approach, a fluorescence tracer is dissolved in one of the two streams to be mixed. When the two streams mix, the tracer concentration field, which also represents the species concentration from one stream, could be visualized due to the difference of the fluorescence intensity in the mixing zone. A chemical reaction for quenching the fluorescence signal is introduced by adding another liquid stream, which takes place simultaneously with the mixing process. With a certain consumption rate of the fluorescence tracer, this model reaction can be applied to mimic an interested kinetics to identify the effect of mixing on the reaction performance. To be noted, the reaction should be powerful enough to oxidize the tracer added in fluids for quenching the fluorescence signals. Among many oxidation reactions, the *Fenton reaction* was chosen for its effectiveness for a wide variety of organic substances. The kinetics and mechanism are discussed as follows.

Fenton reaction, named as its finder [33], reveals that the ferrous ion could strongly promote the hydrogen peroxide to oxidize the malic acid. Subsequent studies had shown that the combination of H_2O_2 and a ferrous salt, i.e. the Fenton's reagents, is an effective oxidant. The mechanism of the Fenton reaction was explained by Haber and Weiss [34] as a hydroxyl radical reaction, where the reaction of Fe^{2+} with H_2O_2 in an aqueous solution leads to the formation of a hydroxyl radical ($OH^\bullet$) (reaction (1)). Barb et al. [35] investigated further the mechanism of Fenton reaction and proposed a second-order kinetic model. The reaction rate constant of reaction (1) was reported on the magnitude of 10^2 L mol^{-1} s^{-1}. Once the $OH^\bullet$ is formed, it will rapidly oxidize the organic substance in the solution, including the fluorescence tracer, with a reaction rate constant of 10^7 to 10^{10} L mol^{-1} s^{-1} [36]. Although there exist some arguments on the mechanism of Fenton reaction [37], the approach can be well adopted in the reactive-LIF measurement. That is, when Rhodamine-B (absorption spectrum: 460–590 nm, max = 550 nm; emission spectrum 550–680 nm, max = 590 nm) is oxidized, the fluorescence signal will disappear. And, the model reaction to quench the fluorescence signals can be considered as a fast reaction with a reaction rate constant on the magnitude of 10^2 L mol^{-1} s^{-1}:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + HO^- \qquad (1)$$

The novelty of the proposed reactive-LIF technique lies in the two aspects. Firstly, the inexpensive dye, i.e. Rhodamine-B, was employed in the measurements, instead of very expensive dyes such as Rhodamine-2 or Rhodamine-WT. As a result, LIF measurements on the liquid mixing processes with large flow rates can be feasible. Secondly, the reactive-LIF approach employed the oxidation reaction mechanism to make the fluorescence from Rhodamine-B quenched so that the reactive mixing process can be measured in time and in space. As a contrast, the principle of reactive-LIF experiments using Rhodamine-2 was based on the combination reaction, as described above.