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Operation of microfluidic liquid slug formation and slug design for kinetics measurement

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Abstract

This paper reports experimental investigation of mixing performances inside microfluidic liquid slugs using the Villermaux–Dushman reaction. Slug-based microfluidics offers rapid mixing by internal circulation and transport with narrow residence time distribution, making it suitable for precise reaction and mixing operations. The experimental investigation presents operation methods to form microfluidic liquid slugs having the reactant arrangements. Mixing performances of flows with and without internal circulation are compared and mixing rates for the axial and radial arrangements of reactants are also compared. Moreover, for the radial arrangement, mixing performances can be evaluated using a dimensionless number irrespective of flow rate and slug length, based on the novel method discussed in our previous paper, which proposes the modified Peclet number Pe^* to estimate mixing rates and design liquid slugs to obtain desired mixing rates. These results give support to the suggestions by the previous simulation results.

Keywords: Multiphase flow; Laminar flow; Microfluidic liquid slug; Mixing; Modified Peclet number

1. Introduction

Use of liquid slugs in microfluidic systems simultaneously allows rapid mixing and narrow residence time distribution under laminar flow regime (Song and Ismagilov, 2003; Tice et al., 2003). Slug mixing is generally developed for immiscible liquid–liquid systems. Mixing in a slug traveling through a microchannel is enhanced by internal circulating flow that reduces striation length, and residence time distribution is narrowed as a result of confined dispersion. Nanoparticle synthesis (Shestopalov et al., 2004) and reaction kinetic measurement (Song et al., 2003) are applications of microfluidic liquid slugs. Methods to determine the slug length, diameter, and velocity are crucial to achieve desired mixing rates because mixing rates need to be adjusted according to the diffusivity of solution and reaction kinetics in order to achieve efficient reaction operations and accurate reaction rate measurements.

In our previous paper, phenomena related to mixing by internal circulating flow and effects of operating parameters (such as slug cross-sectional shape, slug diameter and length, slug velocity, and initial arrangement of reactants inside a slug) on mixing rates inside a slug were quantitatively investigated using the computational fluid dynamics (CFD) simulation (Tanthapanichakoon et al., 2006a). The initial arrangement of reactants inside a slug is the most important parameter determining mixing rate at a constant slug velocity and slug diameter. Axial reactant arrangement gives much faster mixing rate than radial reactant arrangement. The modified Peclet number $Pe^* = U_s d_s^2/lD$, where U_s is slug velocity, d_s is slug diameter equal to the cross-sectional dimension of the channel, l is slug length, and D is diffusivity of the reagents in water, is defined to determine whether mixing is diffusion-dominated or convection-dominated. The relation between dimensionless mixing rates and Pe^* offers a novel method to estimate mixing rates in slugs for both reactant arrangements. The method is also applied to designing new slug mixing operations for specific purposes such as mixing enhancement by channel contraction simulation (Tanthapanichakoon et al., 2006b).

In this paper, mixing performances inside microfluidic liquid slugs having the reactant arrangements are experimentally investigated using the Villermaux–Dushman reaction, a known

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competitive parallel reaction system (Fournier et al., 1996; Ehrfeld et al., 1999). The effects of mixing enhancement by internal circulation flow and the influences of the reactant arrangements are confirmed. Moreover, validation of applying Pe^* to estimating mixing rate is discussed.

2. Experimental

We evaluated mixing performance by the Villermaux–Dushman reaction (Fournier et al., 1996; Ehrfeld et al., 1999). The reaction system consists of instantaneous neutralization and rapid redox reactions:

$$CH_3COO^- + H^+ \rightleftarrows CH_3COOH, \quad (1)$$

$$5I^- + IO_3^- + 6H^+ \rightleftarrows 3I_2 + 3H_2O. \quad (2)$$

The reactions occur when mixing an HCl aqueous solution with an aqueous solution mixture of CH_3COONa, KI, and KIO_3. When the two solutions mix rapidly enough to produce a reaction-controlled condition, H^+ will be consumed only by reaction (1). However, when mixing is slow, reaction (2) also proceeds, resulting in I_2. Iodine then reacts with I^- to form I_3^-. Since I_3^- has a maximum UV absorption peak at 352 nm, the absorbance (ABS) at 352 nm increases with decreasing mixing rate. Therefore, mixing performance can be evaluated by measuring ABS. However, ABS has to be measured as soon as possible since an iodine generation after the end of the mixing is unavoidable in this reaction system. In the following experiments, a linear ABS increase of about 0.006 a minute has been observed. Meanwhile, improved reaction processes avoiding the iodine generation have been reported (Panic et al., 2004; Kockmann et al., 2006).

Experiments were performed using syringe pumps (Harvard Technology and KD Scientific) to feed reaction solutions and Multispec-1500 (UV–VIS Spectrometry, Shimadzu) to measure the ABS at 352 nm. Reagents (HCl, KI, KIO_3, and CH_3COONa) were purchased from WAKO Chemicals. The concentration of the HCl solution was 0.138 mol/L. The mixture of KI, KIO_3, and CH_3COONa was prepared by mixing an equal volume of a solution of KI and CH_3COONa and a solution of KIO_3 and CH_3COONa soon before each experiment. The concentration of the KI–CH_3COONa solution was [KI] = 0.032 mol/L and [CH_3COONa] = 1.33 mol/L. The concentration of the KIO_3–CH_3COONa solution was [KIO_3] = 0.0064 mol/L and [CH_3COONa] = 1.33 mol/L.

A poly(dimethylsiloxane) (PDMS) microcross-mixer (I.D. 500 μm × 500 μm, Fluidware Technologies) was used in the experiments. A schematic of the cross-mixer channel is shown in Fig. 1. Dimethicone (dimethyl silicone fluid, KF-96A-6cs, Shinetsu Chemicals) was used as the continuous phase and the prepared aqueous solutions as the dispersed phase (slug phase). Viscosity of Dimethicone is 5.6 mPa s. Dimethicone including surfactant (0.1 wt% of PEG-3 dimethyl silicone fluid, KF-6015, Shinetsu Chemicals) was flowed through the cross-mixer for 15 min before each experiment to prevent the slug phase from leaving a trace on the channel wall when passing through the channel. The flow was observed using an optical microscope

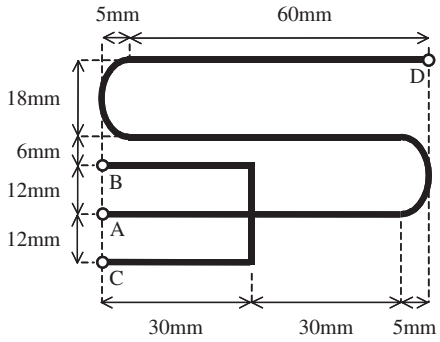

Fig. 1. A schematic of the cross-mixer channel (rectangular channel, 500 μm × 500 μm). A is the inlet of Dimethicone, B is the inlet of the aqueous solution mixture of CH_3COONa, KI, and KIO_3, C is the inlet of the HCl aqueous solution, D is the outlet.

(Carton CBM-15) of 40 times magnification. Slug lengths were determined from a photograph of the slugs taken by a digital camera (Olympus Camedia C-755). Total flow rate V_t and water fraction wf were varied in the experiments. V_t and wf were defined by

$$V_t = V_{w1} + V_{w2} + V_o, \quad (3)$$

$$wf = (V_{w1} + V_{w2})/V_t, \quad (4)$$

where V_{w1}, V_{w2}, and V_o are flow rates of the aqueous solution of HCl, the aqueous solution mixture of CH_3COONa, KI, and KIO_3, and Dimethicone, respectively. V_{w1} and V_{w2} were fixed in the same value. The flow was allowed to reach the steady state before the Dimethicone and aqueous phases were sampled together in a UV cell (optical length = 4 mm). The Dimethicone and aqueous phases then separate from one another, with the Dimethicone phase above the aqueous phase. ABS values at 352 nm of the aqueous phase were then measured.

Fig. 2 shows the schemes to form the flows with and without internal circulation. The radial arrangement was formed by flowing Dimethicone while merging the two aqueous streams at the cross junction and letting the merged aqueous streams snap off into a droplet as shown in Fig. 2a. Values of wf larger than 0.6 allow stable merging of the two aqueous streams at the junction. Lengths of slugs increase with wf when V_t is fixed. The axial arrangement was formed by generating two kinds of slugs flowing alternately in a microchannel and then forcing these two kinds of slugs to merge as shown in Fig. 2b. Alternately flowing slugs merge on spots where the channel temporarily and locally enlarges, particularly the channel curves in the experiment. Since the fluid of continuous phase expands to the whole width of the channel on those spots, the fluid between two slugs is swept out and then the slugs merge. A low wf value is also needed to form alternately flowing slugs (Zheng et al., 2004). The parallel flow without internal circulation was formed by merging the two aqueous streams at the cross junction without flowing Dimethicone ($V_o = 0$) as shown in Fig. 2c. Values of the absorbance at 352 nm of the three flows were then measured.