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Quantitative Estimation of Segregation Indices in a CSTR on a Unique Parallel Competing Reaction Scheme

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Continuous-flow stirred tank reactors (CSTR) are widely employed to elucidate the kinetics and dynamics of chemical reactions. Complete information regarding the spatial heterogeneity of micromixedness over the entire tank is essential for interpreting data and identifying the mixing effects. Therefore, in this work, we quantitatively estimate the segregation indices in a CSTR on the basis of a unique parallel competing reaction scheme proposed by Villermaux and co-workers. Experimental results indicate that the segregation index is a function of stirring rate as well as of the spatial location, from which, the mixing times can be estimated. Unexpectedly, although enhancing the micromixedness over the entire tank, a higher stirring rate cannot ensure a more uniform medium.

Introduction

A mechanically stirred tank is widely adopted for homogenizing miscible liquids. Incomplete mixing can quantitatively or even qualitatively alter the complex system dynamics when the mixing time is comparable to the reaction characteristic time.[1−2] The relevance of mixing is normally discussed in terms of macromixing and micromixing. From a theoretical perspecitve, micromixing models have been employed to elucidate the role of incomplete micromixing in complicated chemical reaction systems.[3−11] However, quantitatively estimating the micromixing efficiency in a fluid system encounters the difficulty of selecting an adequate probe to record local information of fluid micromixedness.

Fournier et al.[12] thoroughly reviewed pertinent literature on available measurement methods. That survey cited three main schemes for chemical methods: single reaction ($A + B \rightarrow R$), consecutive competing reactions ($A + B \rightarrow R$; $R + B \rightarrow S$), and parallel competing reactions ($A + B \rightarrow R$; $C + B \rightarrow S$); the latter two schemes can estimate the mixing efficiency by measuring the final product distribution. In related works, Bourne and co-workers proposed several schemes on the basis of consecutive competing schemes.[13−16] Villermaux and co-workers[12,17−21] proposed a parallel competing reaction system with A, B, R, and S as $H_2BO_3^-$, H^+, H_3BO_3, and I_2, respectively, while C is the mixture of $5_I^- + IO_3^-$. That is,

$$H_2BO_3^- + H^+ \Leftrightarrow H_3BO_3 \text{ (quasi-instantaneously)} \qquad (1)$$

$$5I^- + IO_3^- + 6H^+ \Leftrightarrow 3I_2 + 3H_2O \text{ (fast)} \qquad (2)$$

According to those investigators, such a scheme allows for easy analysis (spectrophotometrically) and has acceptable sensitivity and reproducibility. Our earlier work[22] employed Villermaux's scheme for measuring micromixing efficiency in an aerated stirred tank. Our more recent work[23] conducted experiments involving a Couette flow reactor.

A continuous-flow stirred tank reactor (CSTR) is widely employed to elucidate kinetics and dynamics of a chemical reaction system. While most related studies assumed a well-mixed medium, experimental evidence reveals that, even under a rather high stirring rate, the medium in a CSTR may still be highly heterogeneous.[24,25] The fluid mechanic aspect in mixing processes has received extensive attention. Ottino[26] reviewed the frontier of current understanding. Visual observations revealed that a stirred vessel contains circulation loops. For example, the liquid stream pushed out by a turbine impeller moves radially and splits into two streams near the wall regime: one flowing upward and another downward. The hydrodynamic environment in a turbine-stirred tank is provided in refs 27 and 28. Nevertheless, as Lamberto et al.[29] and Fountain et al.[30] demonstrated, the fluid mechanics involved in a stirred tank is rather complex.

Estimating the micromixing efficiency facilitates the understanding toward the interactions between mixing and chemical reactions. Therefore, in this work, we quantitatively estimate the micromixing efficiency in a CSTR, with the assistance of the unique parallel competing reaction scheme proposed by Villermaux and co-workers. In addition, the corresponding mixing times are evaluated on the basis of the incorporation model proposed in ref 21.

Experimental Section

A standard stirred tank (1 L) was used herein as the mixing vessel, which is equipped with four baffles at 90° and a six-blade Rushton turbine impeller ($D/T = 1/3$, $Z/T = 1/3$, $B/T = 1/10$, where D, T, Z and B denote the turbine diameter, tank diameter, height of the turbine plane, and the baffle width, respectively. In addition, $D = 0.05$ m in this work). All chemicals were purchased from Merck Co., Taiwan, at their highest purity, and were used without further purification. All solutions were prepared with continuous N_2 stripping to prevent reactant oxidation. Other experimental details not mentioned herein are the same as those reported in ref 21. Figure 1 schematically illustrates the mixing vessel.

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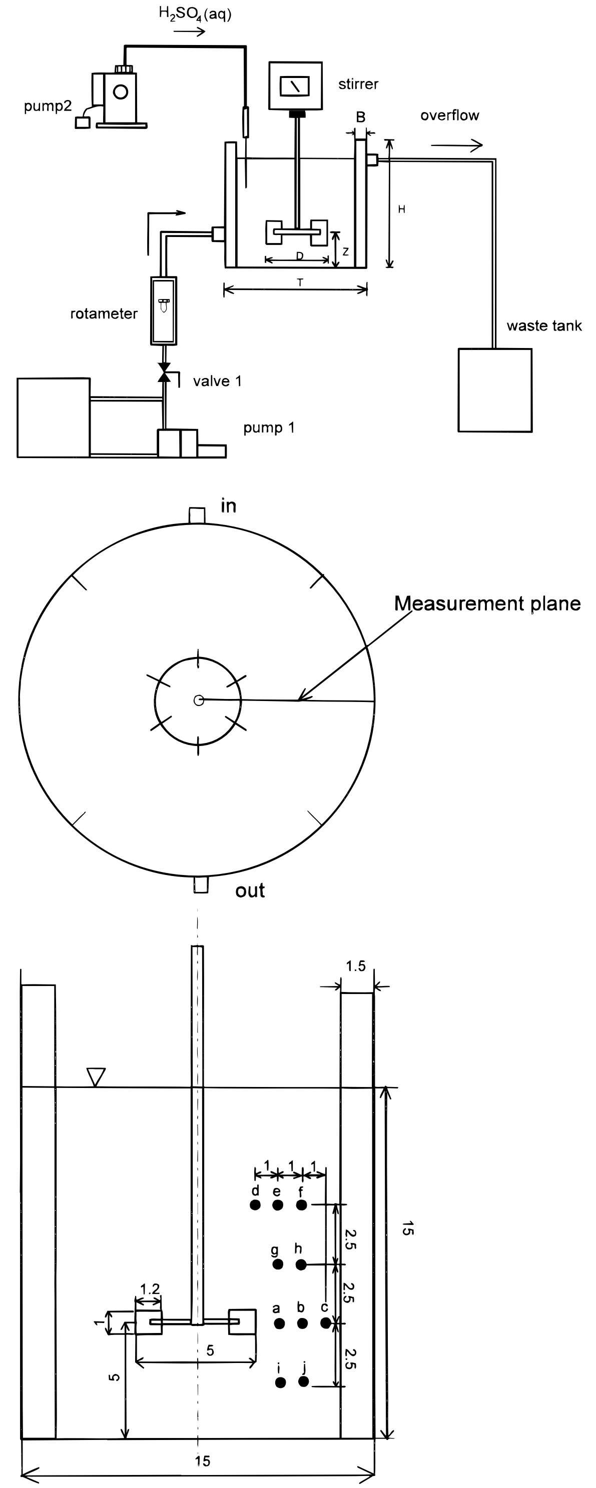

Figure 1. Schematic of the stirred tank.

The boric acid and sodium hydroxide were initially added into deionized water to produce a solution at pH 10. The concentrated solutions of potassium iodate and potassium iodide were then introduced into the tank. The flow rate of solution was 1.5 L/min, whose initial boric acid concentration was 0.0121 M; while for iodate, 0.00233 M; and for iodide, 0.0116 M. These feed concentrations allow us to estimate the maximum limit for iodine production. The stirring rate ranged from 200 to 500 rpm, corresponding to a Reynolds number on the basis of impeller diameter ranging from 52,000 to 130,000. Such a high Reynolds number together with the help of four baffles in the vessel, extensive turbulent can be achieved, particularly for the regimes near the impeller tip. Micromixing tests proceeded by slowly injecting a small amount of sulfuric acid (2.34 mol/min) into the tank at either one of the 10 feed positions on a vertical plane locating at 45° to two baffles (depicted as position (a)−(j) in Figure 1). Position (a) corresponds to the near-tip regime, while positions (d)−(h) and (i)−(j) belong to the upper loop and the lower loop, respectively. The sulfuric acid was slowly injected to prevent possible incorporation of macromixing. Herein, we neglect the possible role of the solution's density difference caused by adding sulfuric acid. The outflow stream was continuously sampled to trace the amount of iodine formed.

While the test solution contained excess iodide, the subsequently formed iodine molecules according to eq 2 would largely react with iodide ions and transform into triiodide ions with the reaction equilibrium constant of $K = 736$ L/mole. Fournier et al.[12] employed a spectrophotometric technique to estimate the concentration of triiodide ion at a wavelength of 353 nm. The UV spectra for a solution under equilibrium with iodide, iodine, and triiodide ions would exhibit two absorption maximum peaks at 288 and 353 nm. Herein, we used the absorption intensity at 353 nm as the index, from which the segregation index (X_s) can be subsequently obtained via calibration. Notably, X_s is defined as the ratio of the amount of iodine formed in a test to the theoretically upper limit for iodine amount generated under complete segregation. Fournier et al.[12] gave detailed calculation procedures of segregation index. By definition, $X_s = 1$ denotes complete segregation; or $X_s = 0$ for perfect micromixing. The UV measurement was made within 20 s after sampling. Mass balance calculations revealed a negligible iodine loss.

Results and Discussion

Visually observing the vessel reveals an upper and a lower circulation loop. Although increasing the stirring rate does not alter the flow pattern, it enhances the global circulation rate. Herein, the possible structures in the fluid system are not explored as vividly demonstrated in ref 30. The present flow pattern appears to correlate well with previous literature.

Figure 2 depicts the segregation indices under various rotational rates. According to this figure, the spatial distribution of X_s correlates well with the global flow pattern. A low X_s regime is noted near the stirrer-tip regime. More specifically, at 200 rpm, X_s is 0.32 at position (a), 0.55 at position (b), and becomes 0.65 at position (c). At a stirring rate of 500 rpm, on the other hand, the corresponding X_s becomes 0.20, 0.27 and 0.31, respectively. The micromixing is thereby rather efficient near the tip regime. However, the micromixing efficiency decays rather rapidly when moving apart from the tip regime, particularly in the loop regimes. At the outer layer of the upper and lower loops, the segregation index is around 0.52−0.70 at 200 rpm, and 0.34−0.56 at 500 rpm. Of particular mention is the central regime (position (f) and (j)) of the loops, where the segregation remains at a high level (0.56−0.66) and is relatively insensitive to stirring rate. Consequently, the spatial distribution of X_s becomes more *heterogeneous* rather than more *homogeneous* at a greater stirring rate. Take the variance of the X_s data as an index. At 200 rpm, the variance is 0.105; it increases to 0.123 at 500 rpm. Restated, although enhancing the micromixing efficiency over the entire tank, the increase in stirring rate does not ensure a more uniform medium. This finding is somewhat unexpected.

Fournier et al.[21] employed an incorporation model for estimating the micromixing time by assuming a simple dilution−

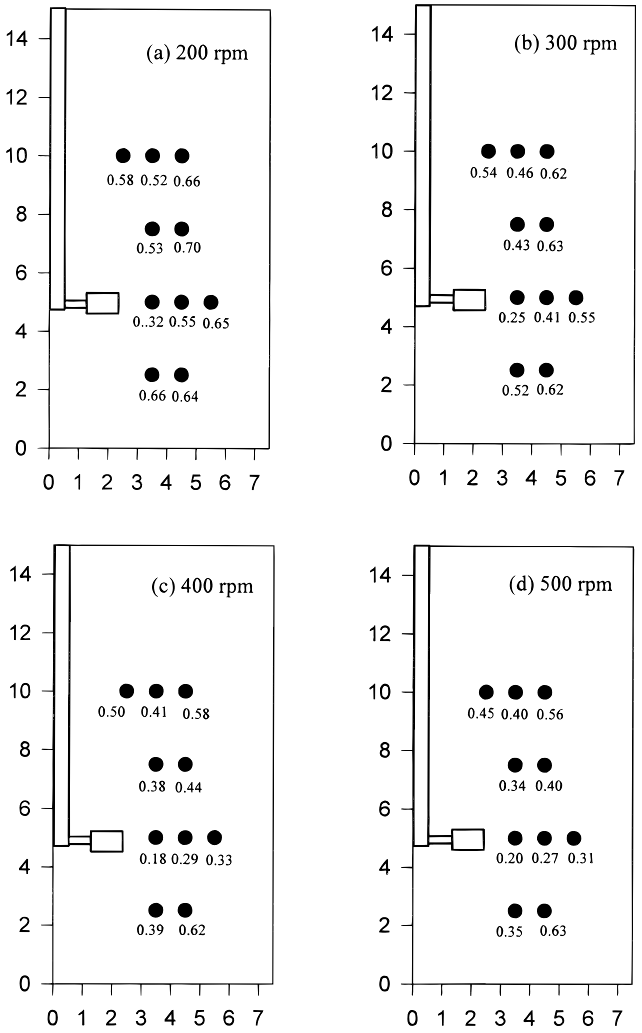

Figure 2. Spatial distribution of segregation index. (a) 200 rpm; (b) 300 rpm; (c) 400 rpm; (d) 500 rpm.

reaction scheme as stated in the following:

$$\frac{\mathrm{d}C_j}{\mathrm{d}t} = (C_{j10} - C_j)\frac{1}{g}\frac{\mathrm{d}g}{\mathrm{d}t} + R_j, \qquad (3)$$

where C_j denotes the concentration of reactant j; C_{j10}, that for the surrounding liquid; R_j, the reaction term; and g, a function controlling the mass exchange rate between the fluid parcels and the surrounding liquid. Herein, we employ the same scheme in ref 17, but using different kinetic parameters.

Two models: linear ($g(t) = 1 + t/t_m$) and exponential ($g(t) = \exp(t/t_m)$), are employed for $g(t)$, where t_m denotes the mixing time. The mixing time data in CSTR can be subsequently estimated and illustrated in Figure 3. The incorporation model is of an empirical nature. Therefore, commenting on the superiority of the employed $g(t)$ is unnecessary. The obtained values from both models, however, could be taken as an order-of-magnitude estimate of the micromixing efficiency.

The t_m data depicted in Figure 3 reveal a highly heterogeneous nature, which correlates well the flow patterns. The t_m can differ by 1−2 orders of magnitude in the present lab-scale stirred tank. At tip regime, t_m changes from 0.15 to 0.028 s (linear) or from 6.9 to 0.99 s (exponential) for a stirring rate at 200 to 500 rpm. The t_m's of central regimes of loops exceed 10−100 s, i.e., too high for a 1 L stirring tank. Such an occurrence may be attributed to the inherent limitation of incorporation model.[31]

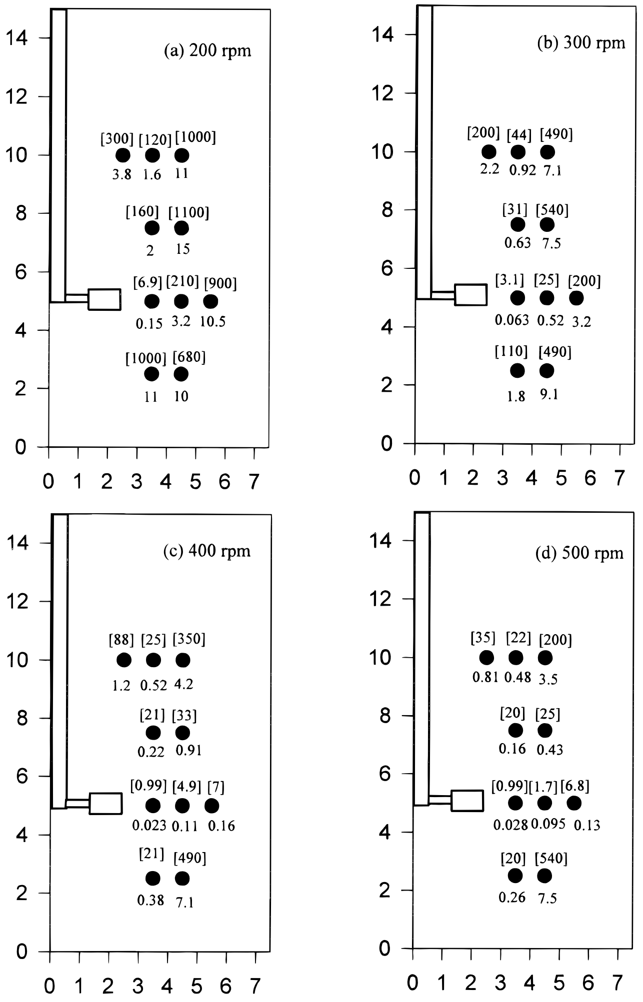

Figure 3. Spatial distribution of estimated t_m. (a) 200 rpm; (b) 300 rpm; (c) 400 rpm; (d) 500 rpm. The values in brackets are for the exponential model; while the others are for the linear model.

The above-mentioned t_m values could, however, serve as an initial estimate for designing a stirred reactor to meet a specific requirement. A marked difference is expected for the product distribution if the reactants are fed at different positions and the characteristic time of chemical kinetics is comparable to the local mixing time.

Furthermore, previous literature largely confers that the mixing time data for a lab-scale fluid-stirring system range from 1 to 10^{-3} s. In this regard, the linear model more reasonably estimates those regimes close to the turbine tip than does the exponential model. However, the exponential model more aptly describes the micromixing process when moving to the rim regime of the vessel. The dilution characteristics of fluid parcels likely change when subject to various hydrodynamic environments.

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