

Effect of droplet size distribution on reaction heat in a liquid–liquid heterogeneous reaction process

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Abstract

In heterogeneous liquid–liquid reaction processes, explosions have been reported. An aim of this study is to simulate the accident stories, which might be caused by inappropriate mixing conditions in the heterogeneous reaction process. The reaction of water-insoluble anhydride and water was selected as a model process. The experimental trend data of droplet size with agitation in a batch reactor were fitted to an empirical equation. The good fittings show the applicability of the equation in our reaction conditions.

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1. Introduction

Some explosions, which occurred in heterogeneous liquid–liquid reaction processes, have been reported. For such reactions to progress smoothly, reactants need to be mixed well by mechanical agitation. It is the failure to control the mixing that causes unusual reaction and sometimes leads a runaway situation.

A better explanation of the heat release behaviour under some condition of mixing would lead to better understanding of the explosion stories. It could be quite useful to reduce the occurrence of same type of explosion.

An aim of this study is to simulate accident stories, which might be caused by inappropriate mixing conditions in the reaction process. The typical example is a liquid–liquid two-phase heterogeneous reaction whose rate is controlled by only agitation speed for mixing. That is, the faster speed, the faster reaction rate, and the slower, the slower. In this case, we guessed that the accident was brought on a runaway reaction triggered by the faster agitation speed than one in the latest successful batch. The reason of the modification of the control sequence of the agitation was to improve productivity by the faster reaction. As the result, the reaction temperature might finally achieve to the boiling point and the bubbling might start. After that, the slower agitation could

not make the reaction rate smaller any more because the bubbling would stir up the reactants instead of the mechanical stirrer.

To simulate it, the heat release rate in the heterogeneous reaction must be estimated under any agitating speed.

There were some trial of reaction heat prediction in heterogeneous liquid–liquid reaction. For the prediction of maximum overall heat release rate [1,2], the equation has been proposed with the assumption that the rate is in proportion to the contact area of the two liquid phases and the reaction rate per unit of area.

Furthermore, the simulation also was tried [3]. On the induction process of the equation for the simulation model, the equation of the particle size for the steady state was expanded. However, the time to achieve the steady state would be usually some hours and the size would be gradually decreasing.

In the previous work [4], in order to predict the heat release rate on any time, the method which could lead the equation to predict, is proposed using an empirical equation of time versus particle size [5] with the experimental results from a reaction calorimeter RC1. The hydrolysis of anhydride is selected as a model reaction, which reaction rate is suitable.

In this paper, some experiments to evaluate change of particle size distribution over reaction time are shown with FBRM system, a laser reflection type in situ probe. And

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one of the experiments is visualized with an in situ fibre-probe.

The maximum heat rate $Q_{r_{\max}}$ is empirically expressed with the modified Weber number [3].

$$Q_{r_{\max}} - Q_0 = kWe'^{\gamma} \quad (1)$$

where, $Q_{r_{\max}}$ means the heat rate [W], Q_0 means the heat release rate on slower agitation speed than the critical agitation speed [W], We' means the modified Weber number defined as below [-].

$$We' = \frac{\rho(N - N_c)^2 L^3}{\sigma} \quad (2)$$

where ρ means the specific density of continuous phase [kg/m^3], N means agitation speed [s^{-1}], N_c means the critical agitation speed of mixing of two phase [s^{-1}], σ means the interfacial tension of two phases [N/m], L means the diameter of the stirrer [m].

1.1. Changing of heat rate over time

The change of heat rate over time could be expressed with the simple assumption that the overall reaction rate is equal to the multiplication of the contact area of the two liquid phases.

The area per unit volume is expressed as below.

$$A = \frac{6\phi}{d_{32}} \quad (3)$$

where ϕ means the volumetric fraction of the dispersed phase [-], d_{32} means the Sauter Diameter of particle [m]. d_{32} is also expressed [5],

$$d_{32_{\text{eq}}} = k_1(1 + k_2\phi_{\text{eq}})We_{\text{eq}}^{-\gamma}L \quad (4)$$

$$d_{32}(t) = d_{32_{\text{eq}}}(1 + k_3(Nt)^{k_4}) \quad (5)$$

where $d_{32_{\text{eq}}}$ means the particle size in the equilibrium state, $d_{32}(t)$ means the particle size on the any time (t) from the start of the agitation, L means the diameter of stirrer [m]. ϕ_{eq} and We_{eq} means the volumetric fraction of the dispersed phase and the Weber number in the equilibrium state.

These empirical Eqs. (4) and (5), were derived for very small ϕ factor, which is approximately under 0.03.

The Eqs. (3) and (4) could lead to the equation of the heat rate in the equilibrium state.

$$Q_{r_{\text{eq}}} = KA_{\text{eq}}V = \frac{K6\phi_{\text{eq}}V}{k_1(1 + k_2\phi_{\text{eq}})L}We_{\text{eq}}^{\gamma} \quad (6)$$

Then, the equation of the rate before the equilibrium state could be also led with Eqs. (3) and (5). Furthermore, it was applied the modified agitation speed $N - N_c$ instead of N .

$$\frac{Qr(t)}{\phi(t)} = \frac{Q_{r_{\text{eq}}}}{\phi_{\text{eq}}} \frac{1}{1 + k_3((N - N_c)t)^{k_4}} \quad (7)$$

The Eq. (7) was applied to the experimental results with the nonlinear least-squares Marquardt–Levenberg algorithm.

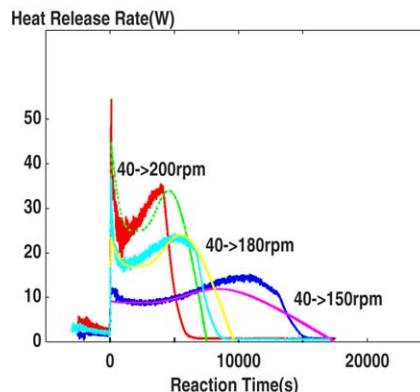


Fig. 1. Simulation of heat release rate profile.

The fitting were done in the time range from the point when the agitation speed increased up to the critical agitation speed of mixing of two phase, N_c .

The prediction result using the Eq. (7) is well fitted to the experimental data. Fig. 1 shows the experimental and the calculated values of the heat release rate).

2. Experiments

2.1. Equipments

2.1.1. Reaction calorimeter

The reaction is observed using a reaction calorimeter, the Mettler RC1 with the glass vessel reactor AP01, which is equipped with temperature sensors, a calibration heater, and a reflux condenser. The temperatures of reactant in the vessel, coolants around the vessel and in the reflux condenser, and feeding material are monitored. The amount fed into the reactor is also monitored using a mass balance. Fig. 2 gives the sketch of RC1.

2.1.2. Focused beam reflectance measurement

For evaluating the particle size distribution, focused beam reflectance measurement (FBRM) was used. An FBRM probe is inserted into a reaction calorimeter vessel. A laser beam is projected through the sapphire window of the FBRM probe

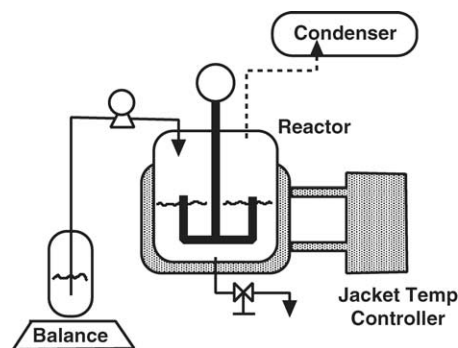
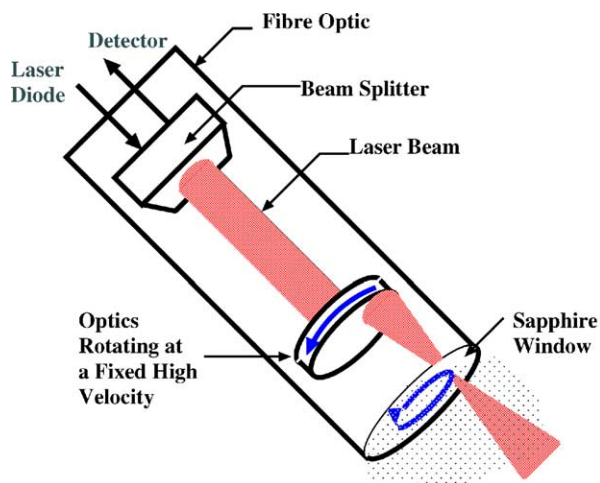


Fig. 2. Reaction calorimeter RC1.



Probe at approx. 45deg angle to turbulent well-mixed flow.

Fig. 3. FBRM principle.

and highly focused just outside the window surface. This focused beam is then moved so it follows a path around the circumference of the probe window. The focused beam is moving at a high rate of speed (2–6 m/s, depending on the application) so that particle motion is insignificant to the measurement. Fig. 3 gives the sketch of FBRM.

As particles pass by the window surface, the focused beam will intersect the edge of a particle. The particle will then begin to backscatter laser light. The particle will continue to backscatter the light until the focused beam has reached the particle's opposite edge. The backscatter is collected by the FBRM optics and converted into an electronic signal.

2.1.3. Visualization

For observing images of droplets in liquid–liquid heterogeneous solution both in process and in real time, Mettler Toledo particle vision and measurement (PVM), a in-process imaging system was used.

2.2. Reaction procedure

Reaction system consists of followings;

- continuous phase: 3.6 mol/l NaOH aq. solution
 - dispersed phase: *n*-butyric anhydride 1 mol
- (i) 88 g (2.2 mol) of NaOH was dissolved into 600 g of water in a vessel of RC1 as continuous phase solution. The reactant temperature was controlled to the desired temperature (300 K) under 40 rpm of agitation speed.
 - (ii) After the thermal equilibrium was reached, 158.2 g (1.0 mol) of *n*-butyric anhydride had been fed for 10 min.
 - (iii) After measuring heat generation behavior under 40 rpm for 30 min, the agitation speed was accelerated up to 200 rpm with 1.0 rpm/s.

3. Results and discussion

Sauter Diameter, which is used for the calculation of the surface area (Eq. 3), is expressed by the followed equation.

$$d_{32} = \frac{\sum n \times L^3}{\sum n \times L^2} \quad (8)$$

where d_{32} is the Sauter Diameter [m], n the number of particles in each size [–], L the particle size [m].

The value measured by FBRM does not measure particle size directly. It is called a chord length. A chord length is a straight line between any two points on the edge of a particle or particle structure (agglomerate). So, if we need the absolute value of particle size distribution, a conversion is required with some assumption on the particle shape, etc. But for discussing on just the change of the particle size, a chord length has enough information for the discussion. In this paper, we used modified Sauter Diameter (Fig. 4), derived from chord length instead of particle size.

In the previous paper [5], change of Sauter Diameter over time is expressed empirically (Eq. (5)). But ϕ factor on the paper ($\phi \approx 0.2$) is quite different from our experiments ($\phi \leq 0.03$).

To confirm the availability of the equation on the our experimental condition, the equation was applied to the experimental results of FBRM with the nonlinear least-squares Marquardt–Levenberg algorithm (Fig. 5).

The d_{32eq} , k_3 and k_4 were given as follows;

$$d_{32eq} = 90, k_3 = 1.8 \times 10^4, k_4 = -0.8 \quad (9)$$

From the result of FBRM, the number of three chord length ranges, which are 1–10, 10–100, and 100–1000 μm , were calculated and plotted (Fig. 6). This shows

- (i) the number of larger particles range (100–1000 μm) decreases gradually,
- (ii) the number of smaller particles range (1–10 μm) increases gradually,

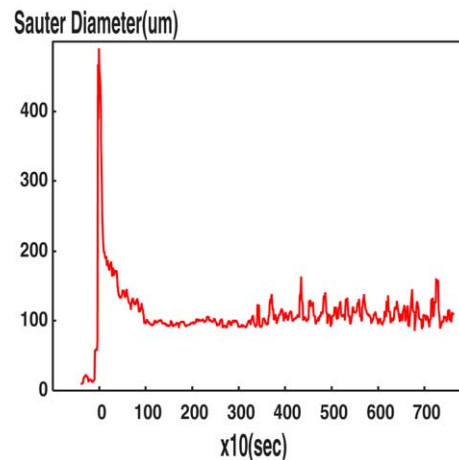


Fig. 4. Modified Sauter Diameter.

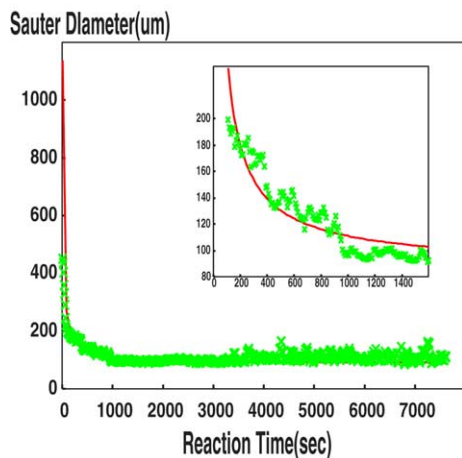


Fig. 5. Fitting result for Sauter Diameter.

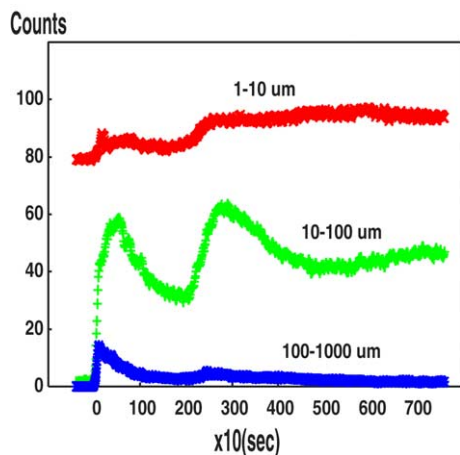


Fig. 6. Particle size distribution.

(iii) the number of middle size particles range (10–100 μm) repeats increase and decrease.

The strange behaviour of middle size particles range must be important to examine the reaction mechanism of heterogeneous reaction.

Another method to observe droplets size change, which is PVM, could not show good results of droplets size distribution because definition of droplets in the field of view is quite difficult.

But PVM gives another information on the strange trend of the middle size droplets. The photos from PVM shows the middle range particles generation (Fig. 7). The particles seems not to be droplets or bubbles but to be solid crystals agglomerations. They might be sodium butyrate.

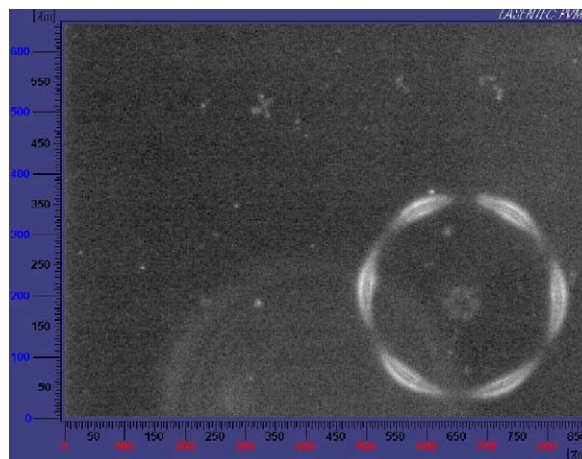


Fig. 7. PVM observation.

4. Conclusion

Modified Sauter Diameter was derived from the chord length measured by FBRM, and was fit to the equation based on the parameter ϕ . It seems that the mean diameter change over time may be fitted to the above approximate equation.

Otherwise, the calculated number of three chord length ranges, which are 1–10, 10–100, and 100–1000 μm , shows

- (i) the number of larger particles range (100–1000 μm) decreases gradually,
- (ii) the number of smaller particles range (1–10 μm) increases gradually,
- (iii) the number of middle size particles range (10–100 μm) repeats increase and decrease.

The strange behaviour of middle size particles range must be important to examine the reaction mechanism of heterogeneous reaction.

The photos from PVM seem to show generation of solid crystals agglomerations.

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