

A STUDY OF THE DROPLET SIZE DISTRIBUTIONS AND THE REACTION HEATS IN LIQUID-LIQUID HETEROGENEOUS REACTION PROCESS

Yasuhiro Fujimoto

National Institute of Industrial Safety, Umezono 1-4-6, Kiyose-si, Tokyo 204-0024, Japan;
email: fuji@anken.go.jp

In heterogeneous liquid-liquid reaction processes, explosions have been reported. An aim of this study is to simulate the accident stories, which were guessed to 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 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.

KEYWORDS: reaction calorimeter, heterogeneous reaction, droplet size

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 events. 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 which 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, it was guessed that the accident triggered by the faster agitation speed than one in the latest successful batch. The reason for the modification of the control sequence of agitation was to improve productivity by the faster reaction. As the result, the reaction temperature might finally achieve the boiling point and the bubbling might start. After that, the slower agitation couldn't make the reaction rate smaller any more because of 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 with agitating condition.

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 area.

Furthermore, the time profile calculation of the reaction heat release rate also was tried^[3]. On the induction process of the equation for the model, the equation of the droplet 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 order to predict the heat release rate on any time, the method which could lead the equation to predict, is proposed^[4] using an empirical equation of time versus droplet size^[6] with the experimental results from a reaction calorimeter RC1. The hydrolysis of an anhydride is selected as a model reaction.

The empirical equation depends on data under the smaller ϕ factor, volumetric fraction of the dispersed phase, than our experiments' factor (the bigger). That is the reason why some experiments to evaluate change of droplet size distribution over reaction time have been done with FBRM.

AN OVERVIEW OF DROPLET SIZE AND HEAT RELEASE RATE IN HETEROGENEOUS LIQUID-LIQUID REACTION

The heat rate as a function of reaction time in a heterogeneous reaction 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 when it is a diffusion controlled reaction.

The surface area of the dispersed phase per unit volume, A [m^{-1}] is expressed as below.

$$A = \frac{6\phi}{d_{32}} \quad (1)$$

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

$$d_{32eq} = k_1(1 + k_2\phi)We^{-\gamma}L \quad (2)$$

where d_{32eq} [m] means the particle size in the equilibrium state, ϕ [-] means the volumetric fraction of the dispersed phase. k_1 , k_2 , γ [-] mean factors.

We [-] means the Weber number,

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

where ρ [kg/m^3] means the specific density of continuous phase, σ [N/m] means the interfacial tension of two phases, N [s^{-1}] means the substantial agitation speed which is calculated from " $N_{\text{observed}} - N_{\text{critical}}$ ". N_{observed} means the observed agitation speed, N_{critical} means the critical agitation speed on mixing of the two phase liquids. At the N_{critical} ,

the flow in a vessel changes laminar state to turbulent state. L [m] means the diameter of the stirrer.

Furthermore, If the dispersed phase liquid could react with the continuous phase liquid and the reacted materials dissolve into the continuous phase liquid, the volumetric fraction was assumed as follows.

$$\phi(t) = \phi_0 e^{k_5 t} \quad (4)$$

where $\phi(t)$ [-] means the volumetric fraction of the dispersed phase as a function of reaction time. ϕ_0 [-] means the initial value of the volumetric fraction of the dispersed phase. k_5 [-] means a factor.

The above equations (Eq. 2,3) could derive particle size as a function of reaction time (t [s]) from the start of the agitation. This is because the followed empirical equation was proposed^[6].

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

where $d_{32}(t)$ [m] means the particle size on the any time from the start of the agitation, k_3 , k_4 [-] mean factors.

The above empirical equations (Eq. 2,5), were derived under very small ϕ factor's condition, which is approximately below 0.03.

So,

$$d_{32}(t) = k_1 (1 + k_2 \phi_0 e^{k_5 t}) \left(\frac{\rho}{\sigma} N^2 L^3 \right)^{-\gamma} L (1 + k_3 (Nt)^{k_4}) \quad (6)$$

Then, the equations, (Eq. 1, 4, and 6) could derived to the equation of heat rate as a function of reaction time.

$$Qr(t) = KA(t)V = \frac{K6\phi_0 e^{k_5 t} V}{k_1 (1 + k_2 \phi_0 e^{k_5 t}) \left(\frac{\rho}{\sigma} N^2 L^3 \right)^{-\gamma} L (1 + k_3 (Nt)^{k_4})} \quad (7)$$

where $A(t)$ [m^{-1}] means the surface area of the dispersed phase per unit volume as a function of reaction time. V [m^3] means the volume of the dispersed phase. K [W/m^2] means a factor.

RESULTS AND DISCUSSION

Sauter diameter, which is used for the calculation of the surface area (Eq. 1), is expressed by the followed equation.

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

where d_{32} [m] is the sauter diameter, n [-] is the number of particles in each size, d_i [m] is the area mean size of each particles.

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, which length strongly depend on the particle shape.

So, if we need the area mean size distribution, a conversion is required with some assumption on the particle shape, etc. Droplet shape of liquid seems to be sphere. And the chord length of spherical shape particles are similar to the area mean size. So, for discussing on just the change of the droplet size, a chord length has enough information for the discussion. In this paper, we used modified sauter diameter, derived from chord length instead of area mean particle size.

In the previous paper (Eq. 2,5), change of Sauter Diameter over time is expressed empirically. But ϕ factor on the paper ($\phi \leq 0.03$) is quite different from our experiments ($\phi \approx 0.2$).

To confirm the availability of the equation (Eq. 6) on the our experimental condition, The equation was applied to the experimental results of FBRM measurements on RC1 and DRS with the nonlinear least-squares Marquardt-Levenberg algorithm. 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, $N_{critical}$. The calculated value is well fitted to the experimental data (Figures 1, 2).

The k factors were given as follows;

The $N_{critical}$ values are $1.0 [s^{-1}]$ in RC1 and $2.0 [s^{-1}]$ in DRS. The impeller's width L values are $0.1 [m]$ in RC1 and $0.08 [m]$. The assumed σ is $10^{-2} [N/m]$. The assumed ρ is $10^3 [kg/m^3]$. The γ factor for calculating weber number is assumed to $0.6^{[5]}$.

The above values of k_1, k_2, k_3, k_4 both from RC1 and from DRS, are almost same. Furthermore, to compare them to previous papers' values, they have same order.

Table 1. k factors

Reactors	k_1	k_2	k_3	k_4	k_5
RC1	0.040	4.0	41	-0.69	-10
DRS	0.011	3.9	68	-0.45	-1.1
(lit.)	$0.06^{[5]}$	$3.75^{[5]}$	$16^{[6]}$	$-0.53^{[6]}$	-

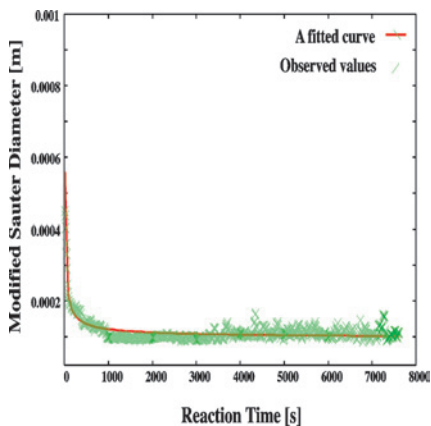


Figure 1. Fitting result for modified sauter diameter in RC1

On the other hand, the values of k_5 in the assumed equation (Eq. 4) are quite different. It means that the reaction rate in DRS is slower than the rate in RC1 in spite of the similar weber numbers in RC1 and DRS. The reason must be the occurrence of drop coalescence because of different shape of impellers.

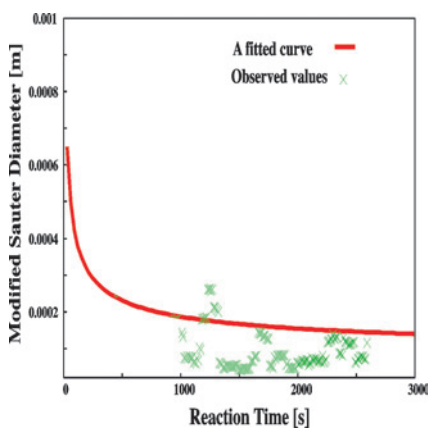


Figure 2. Fitting result for modified sauter diameter in DRS

CONCLUSION

Modified sauter diameter is derived from the chord length measured with FBRM. And the modified sauter diameter as a function of the reaction time was fitted to the equation based on the parameter ϕ .

The values of k_1, k_2, k_3, k_4 are derived from the fitting, and ones from RC1 are almost same as ones from DRS. Previous papers' values have same order as our values. This means the assumption which is using the Eq. (2,5) obtained in the agitation system under smaller ϕ factor condition is considered reasonable and proper.

Furthermore, on the values of k_5 which is assumed as a factor of parameter ϕ as a function of reaction time, ones from RC1 are different from DRS in spite of the similar weber numbers in RC1 and DRS. The reason must be the occurrence of drop coalescence because of different shape of impellers.

REFERENCES

1. E. Miyata et al., *J. Japan Society for Safety Eng.*, 37, p. 164–171 (1998)
2. M. Suzuki et al., *Proc. 1st Conference of the Association of Korean–Japanese Safety Engineering Society*, p.190–193, Kyongju (1999)
3. E. Miyata et al., *Proc. 28th Safety Engineering Symposium*, p. 105–108, Tokyo (1998)
4. Y. Fujimoto, *Proc. Asia Pacific Symposium on Safety 2001*, Vol. 2, p. 167–170, Kyoto (2001)
5. P.H. Calderbank, *Trans. Inst. Chem. Eng.*, 36, p. 443 (1958)
6. M. Kuriyama, et al., *Trans. Inst. Chem. Eng.*, 74, p. 431 (1996)
7. Y. Fujimoto, *Proc. 6th Annual Symposium, Mary Kay O'Connor Process Safety Center*, p. 487–493, Texas (2003)
8. Helene Nogent, et al., *J. Loss Prevention in the Process Ind.*, 15, p.445 (2002)

APPENDIX

EQUIPMENTS

Reaction Calorimeter, RC1

The reactions were observed using reaction calorimeters. The first one is the RC1 by Mettler-Toledo with the glass vessel reactor AP01, which is equipped with temperature sensors, a calibration heater, and a reflux condenser. The vessel volume is 2.5 liter. The reactions ran by mixing with an anchor-type glass stirrer, which impeller's width L is 0.1 [m], was equipped.

The temperatures of reactant in the vessel, feeding material, and coolants around the vessel and the reflux condenser are monitored. The amount fed into the reactor is also monitored using a mass balance. Figure 3 gives the sketch of RC1.

Reaction Calorimeter, DRS

The other calorimeter is a hand-made calorimeter system, DRS, which uses two same reactors (sample and reference). The measurement principles are as similar to DRC's ones^[8].

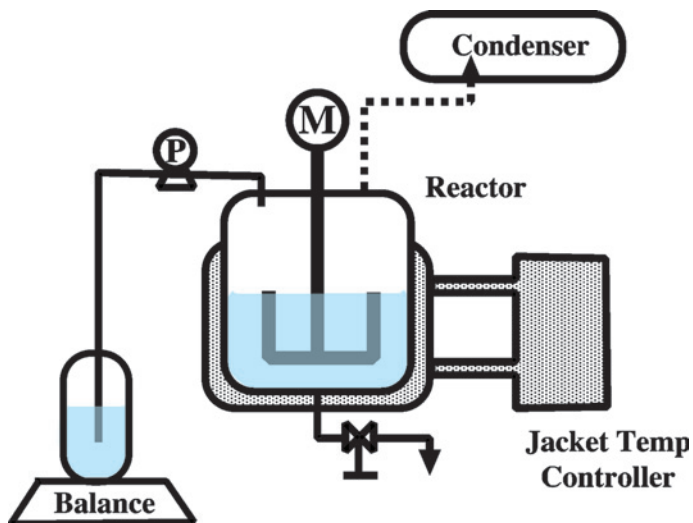


Figure 3. A sketch of reaction calorimeter RC1

A vessel volume is 0.5 liter. The glass bar with a semicircular Teflon impeller as a stirrer, which width L is 0.08 [m], was equipped. Figure 4 gives the sketch.

Focused Beam Reflectance Measurement, FBRM

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 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 m/s to 6 m/s, depending on the application) so that particle motion is insignificant to the measurement.

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 (Figure 5).

REACTION PROCEDURE

Reaction system were consists of following contents;

- continuous phase: NaOH aq.solution.
- dispersed phase: n-butyric anhydride (reagent).

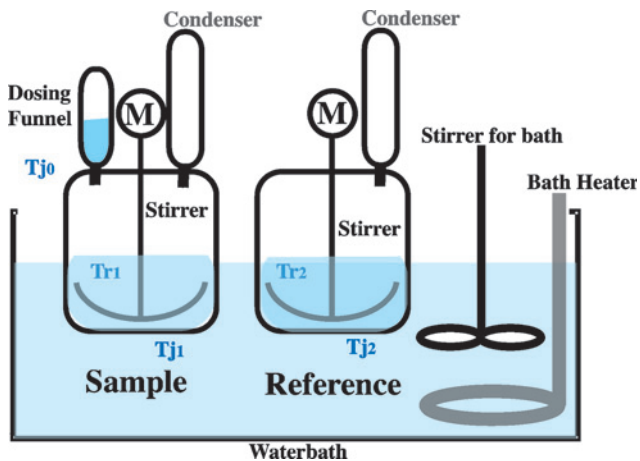
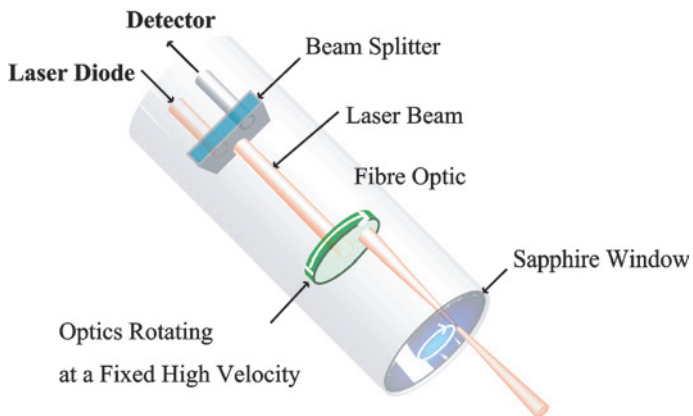


Figure 4. A sketch of hand-made reaction calorimeter DRS



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

Figure 5. A sketch of FBRM

RC1

1. 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 0.7 s^{-1} (40 rpm) of agitation speed.
2. After the thermal equilibrium was reached, 158.2 g (1.0 mol) of n-butyric anhydride had been fed for 10 minutes.
3. After measuring heat generation behavior under 40 rpm for 30 min, the agitation speed was accelerated up to the desired agitation speed, which is 1 s^{-1} (60 rpm)– 3.3 s^{-1} (200 rpm), with 1.0 rpm/s.

DRS

1. 22 g (0.55 mol) of NaOH was dissolved into 150 g of water into the vessel of the sample as continuous phase solution and into the reference vessel as reference solution. The water bath temperature was controlled to the desired temperature (300 K) under 0.7 s^{-1} (40 rpm) of agitation speed.
2. After the thermal equilibrium was reached, 39.6 g (0.25 mol) of n-butyric anhydride had been fed in 10 seconds into the sample reactor.
3. The agitation speed of the sample and reference reactor were accelerated up to the desired agitation speed, which is 1.5 s^{-1} (90 rpm)– 3.3 s^{-1} (200 rpm) within 1 minute.