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# Crystallization of RDX by Drowning-Out Combined with Fines Dissolution and Cooling Process

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**ABSTRACT:** A new process of drowning-out combined with fines dissolution and cooling crystallization (the DFC process) was proposed to recover 1,3,5-trinitro-1,3,5-triazinane (RDX) from RDX/ $\gamma$ -butyrolactone solution with relatively large crystal size and high yield. In this process, fine crystals induced by drowning-out are dissolved into the solution by heating so that the dissolved solute can contribute to grow seed crystals by cooling. The DFC process is repeated to reach the desired yield. Estimation of the amount of antisolvent for drowning-out is made by a simple mass balance model in which the mass of fine particles produced by drowning-out equals to that dissolved. Considering dissolution of seeds at the fines dissolution stage, an empirical parameter  $\alpha$  which is smaller than 1 was employed for the estimation of the optimum amount of antisolvent added.  $\alpha = 1$  indicates that effect of dissolution of seeds is negligible. In the present work, initial seeds were prepared by rapid injection of 15 g of water into a saturated RDX/ $\gamma$ -butyrolactone solution of 30 °C. Heating temperature for fines dissolution and cooling temperature for further crystal growth were 40 and 20 °C, respectively. In those operating conditions with  $\alpha = 0.8$ , the average crystal size of RDX with the yield of 90% was 67.6  $\mu\text{m}$ , which was a remarkably improved result when compared with that of 40.4  $\mu\text{m}$  by drowning-out only.

## 1. INTRODUCTION

Crystallization is one of widely used separation techniques for achieving the extraction of a solute from a saturated solution.<sup>1–3</sup> In working with materials which have a high temperature-dependent solubility, cooling crystallization is commonly used since this method permits a large crystal size and narrow crystal size distribution (CSD) with high yields. However, if the solubility is reasonably high at low temperature, product yield would be quite low. In this case, crystallization by drowning-out in which supersaturation is created by adding an antisolvent is effective to improve the overall yield.<sup>4–8</sup> However, despite the high yield, the drowning-out have a troublesome in the control of the level of supersaturation due to extremely high local supersaturation which is primary cause of the generation of very fine crystals.<sup>4</sup>

There are a few reports on the combined processes of cooling crystallization with drowning-out.<sup>9–11</sup> In general, those processes are shown to provide improved size as well as high yield of final product compared with conventional cooling or drowning-out processes. Seed generation by antisolvent addition before cooling is a typical example of a combined process.<sup>9</sup> However, the main target of such processes is not to improve product yield, but to control the population density of seeds. Lindenbergh et al. proposed a combined cooling and drowning-out crystallization process with a model-based optimization method, which is to minimize operating time and number of newly generating nuclei.<sup>10</sup> Their process was shown to provide an improved size of the final product compared with a similar process with no optimization such as rapid addition of antisolvent in the beginning or the end. In the present work, direct nucleation control is the key inspiration. In the direct nucleation control, during the crystal growth stage such as cooling or antisolvent addition, unintentionally induced

fine crystals are dissolved by heating or solvent addition to maintain initial population density of crystals.<sup>11–14</sup> Direct nucleation control is useful to improve CSD, even if operating profiles are not predetermined.

In the present work, a new technique named as the DFC process, a combined process of drowning-out with a fines dissolution process by heating and followed by a cooling process, is proposed. If seeds exist in a batch crystallizer, the DFC process is operated by the following procedure: (1) drowning-out is performed by the rapid addition of antisolvent, and then fine crystals are forcibly induced; (2) the solution is heated to dissolve again those fines; however, initial seeds should be not dissolved completely; (3) cooling crystallization is performed to grow the remaining seeds; (4) those processes are repeated until the desired yield is obtained. The main advantage of the DFC process over conventional crystallization processes is that relatively large-sized crystals will be obtained with a very high yield similar to that by a drowning-out process. Because fine particles induced by drowning-out are dissolved into the solution, dissolved solute can contribute to the growth of the remaining seeds by cooling.

The goal of the present work is the development of the DFC process for the recovery of 1,3,5-trinitro-1,3,5-triazinane (RDX; also known as cyclotrimethylene trinitramine), from  $\gamma$ -butyrolactone with water as an antisolvent. In our previous works, cooling crystallization of RDX from  $\gamma$ -butyrolactone were carried out to improve crystal quality such as crystal size and reduction of inclusion.<sup>15,16</sup> However, even at an ambient

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temperature of 20 °C, the solubility of RDX is 13.4 g/100 g  $\gamma$ -butyrolactone. Therefore, the DFC process could be useful to recover RDX from the waste solution of RDX/ $\gamma$ -butyrolactone, the resultant of RDX production by cooling crystallization. In this work, the DFC process was performed to produce RDX crystals as large as possible. Often smaller crystals hinder filtration of the slurries, therefore larger crystals are desired to facilitate subsequent downstream processes.<sup>17</sup>

This paper describes, first, a measurement of RDX solubility in  $\gamma$ -butyrolactone/water solution. Solubility is the most basic and important thermodynamic property and used in the determination of operating profiles. Second, an internal seeding technique which is one of the processes to induce centers of crystallization without external addition of seed is introduced.<sup>9,16</sup> Finally, a simple mass balance model equation is proposed for the determination of the suitable operating profile of the DFC process.

## 2. MATERIALS AND METHODS

**2.1. Materials.** RDX (99.9%) supplied by Hanwha Co., Korea, was used without further purification. Commercial grade  $\gamma$ -butyrolactone (99+, Sigma-Aldrich, USA) was used as a solvent for RDX. The triple-distilled water produced by a distillation apparatus (Younglin, Ultra 370 series, Korea) was used as an antisolvent.

**2.2. Experimental Apparatus.** As shown in Figure 1, the experiments were carried out in a double-jacketed 100 mL glass

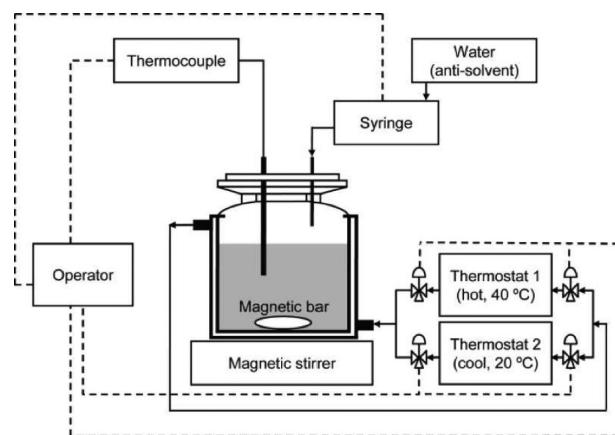


Figure 1. Experimental setup of the DFC process.

crystallizer with a magnetic stirrer (a Teflon-coated magnetic bar, diameter, 60 mm). The agitation speed of 250 rpm was chosen to suspend crystals without any generation of bubbles due to vortex formation during crystallization. In this configuration, grinded or broken crystals by abrasive mixing with the stirrer bar were not observed. The temperature of the solution in the crystallizer was controlled with two thermostats by circulating heating and cooling water separately; that is, each thermostat (Polyscience, model 9710, USA) was maintained with constant temperature during operation of the DFC process. It helps swift temperature control without any complicated process control devices. In the DFC process, antisolvent was injected by one-pot using a syringe. The temperature of antisolvent was also maintained with the same temperature of the solution inside the crystallizer by a thermostat.

The RDX suspension taken from the crystallizer was filtered over a glass filter funnel equipped with an aspirator. The filtered

RDX crystals were washed with triple-distilled water three times. Then, the RDX crystals were dispersed onto a Petri dish. The collection of samples from a filter funnel was carefully made with an antistatic spoon and spatula made of Teflon. The RDX crystals on a Petri dish were dried in a desiccator with silica gel. It was found that the weight of the sample measured was not changed after 12 h drying.

**2.3. Solubility Measurements.** The solubility of RDX was measured at the temperature of 20, 30, and 40 °C. At a given temperature, an excess quantity of RDX was injected into pure  $\gamma$ -butyrolactone or cosolvents ( $\gamma$ -butyrolactone + water) with water content of 10–50 wt %. The solution with RDX slurry was mildly agitated at constant temperature for 24 h, and then the solution was stabilized without agitation. After the stabilization over 2 h, the upper clear solution was decanted from the solution. The sample solution was carefully evaporated in a vacuum drying oven without rapid boiling. RDX solubility was calculated by the weight difference between initial solution and residual mass, which was assumed to be pure RDX.

Figure 2 shows that the solubility of RDX increases with increasing temperature and concentration of solvent. In this

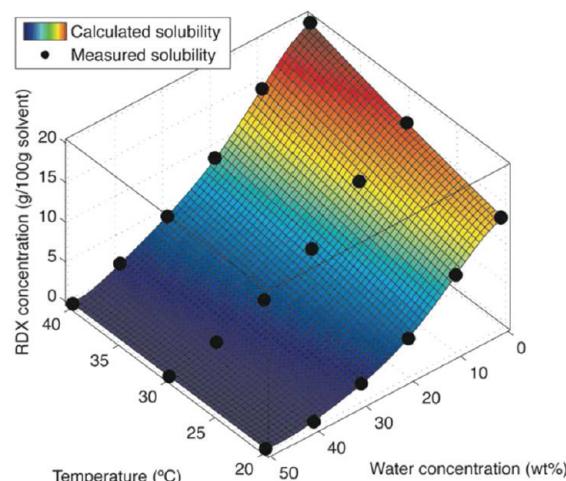


Figure 2. Measured and calculated solubility of RDX in  $\gamma$ -butyrolactone/water solution.

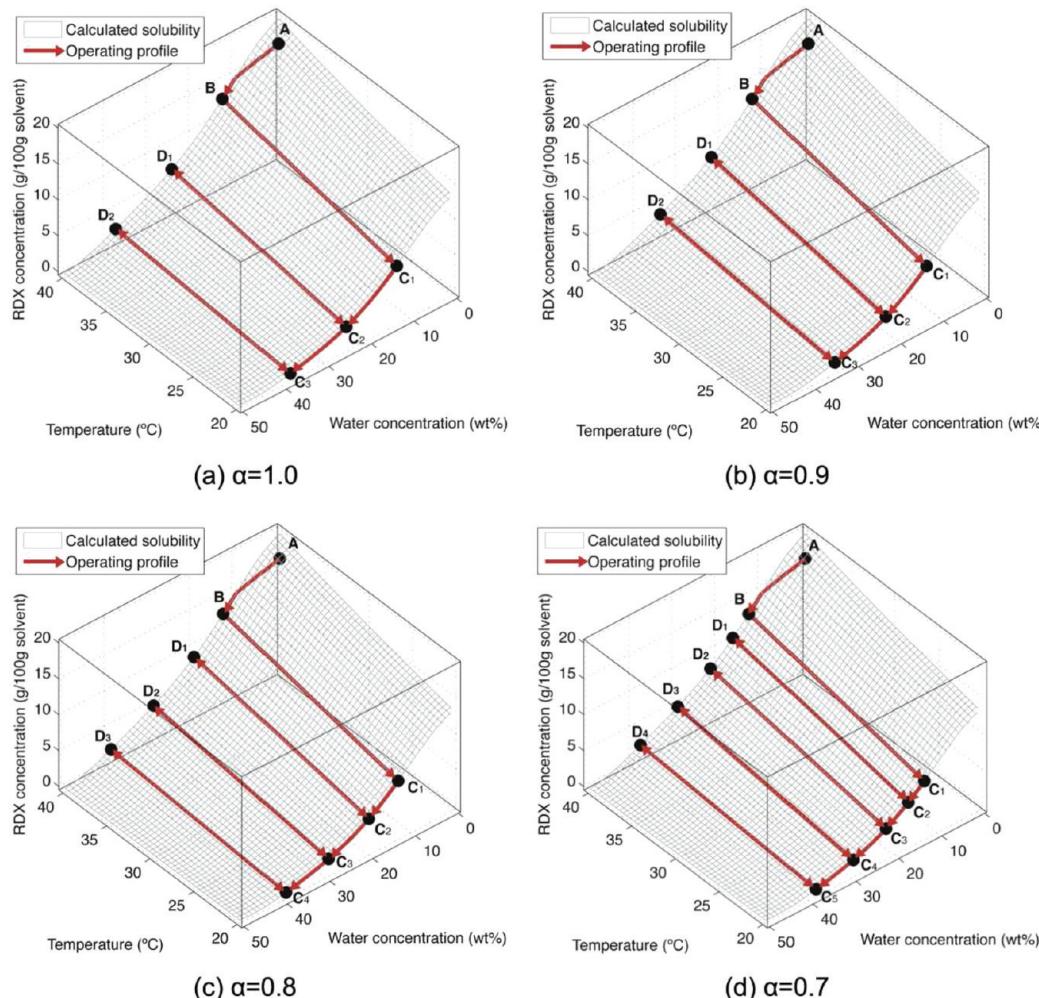
figure, the solubility is represented as a surface by a two-dimensional (2D) polynomial. In this correlation, 14 coefficients of 2D polynomial of  $2 \times 5$  order listed in Table 1 were determined by fitting the experimental data in a least-squares method.

$$\begin{aligned} c^*(T, w) = & p_{0,0} T^0 w^0 + p_{1,0} T^1 w^0 + p_{2,0} T^2 w^0 \\ & + p_{1,1} T^1 w^1 + p_{0,2} T^0 w^2 + p_{2,1} T^2 w^1 + p_{1,2} T^1 w^2 \\ & + p_{0,3} T^0 w^3 + p_{2,2} T^2 w^2 + p_{1,3} T^1 w^3 + p_{0,4} T^0 w^4 \\ & + p_{2,3} T^2 w^3 + p_{1,4} T^1 w^4 + p_{0,5} T^0 w^5 \end{aligned} \quad (1)$$

where  $c^*$  is the solubility in g per 100 g solvent on a solute free basis,  $T$  is temperature in °C, and  $w$  is water concentration in wt % on a solute free basis.  $p_{xy}$  is the coefficient which is the element of the  $x$ th column and  $y$ th row. The coefficient of determination,  $R^2$ , is 0.9999 for RDX/ $\gamma$ -butyrolactone/water system. It should be noted that the polynomial is valid in the temperature ranging from 20 to 40 °C and for water concentration from 0 and 50 wt %. Equation 1 may be expressed as a single variable equation with second or fifth order polynomial when  $w$  or  $T$  is constant.

Table 1. Parameters of the 2D Polynomial Describing the Solubility of RDX

$p_{xy}$	0	1	2	3	4	5	$y$
$x$	0	9.31	$-2.79 \times 10^{-1}$	$-4.22 \times 10^{-2}$	$2.51 \times 10^{-3}$	$-5.00 \times 10^{-5}$	$3.49 \times 10^{-7}$
1		$1.44 \times 10^{-1}$	$1.53 \times 10^{-2}$	$-6.41 \times 10^{-4}$	$4.30 \times 10^{-6}$	$2.71 \times 10^{-8}$	
2		$2.88 \times 10^{-3}$	$-3.45 \times 10^{-4}$	$1.16 \times 10^{-5}$	$-1.19 \times 10^{-7}$		

Figure 3. Operating profiles of the DFC process in RDX/ $\gamma$ -butyrolactone/water system (amount of first injection water = 15.0 g).

**2.4. Nucleation by Internal Seeding.** Figure 3 represents an example for the operating profile of batch crystallization by the DFC process. Before crystals are developed in the solution, there must exist a number of nuclei or seeds that act as centers of crystallization.<sup>1</sup> In the present work, an internal seeding technique was adopted to produce seeds as follows. A saturated RDX/ $\gamma$ -butyrolactone solution at 30 °C was prepared and the solution was kept at the temperature of 40 °C with a stabilization time of 30 min. And then water was injected (period A–B) to induce nucleation. The solution with those fine crystals was cooled to the temperature,  $T_{\text{cool}}$ , of 20 °C (period B–C<sub>1</sub>) for further growth of those seeds. Here the population density of seed crystals is directly proportional to the amount of injection water. The desired amount of first injection water was determined by a trial and error to obtain large sized crystals and uniform CSD after crystal growth stage.

**2.5. Operation by the DFC Process.** The DFC process is a repeating process as mentioned above. The beginning of  $i$ th cycle in the DFC process is ( $i + 1$ )th drowning-out (period C<sub>1</sub>–C<sub>2</sub>, C<sub>2</sub>–C<sub>3</sub>, ..., and C <sub>$i$</sub> –C <sub>$i+1$</sub> ) with  $i = 1, 2$ , and so on. It should be noted that first drowning-out (period A–B) is performed for the internal seeding.

In general, antisolvent injection induces further growth of seeds as well as the generation of new fines. In the present work, however, the growth of seeds is assumed to be negligible because of the very high local supersaturation immediately induced by the one-pot injection of antisolvent. This kind of rapid injection of antisolvent may be assumed to contribute to the generation of new fines only. Indeed, intensive nucleation was observed as soon as water was injected. In addition, the growth of existing seed crystals was not noticeable after the rapid injection of water. Therefore, the amount of crystallized solid phase by ( $i + 1$ )th drowning-out,  $m_{\text{c},i+1}$ , is assumed to be

equal to that of fines produced by  $(i + 1)$ th drowning-out,  $m_{cf,i+1}$ ; that is,

$$m_{cf,i+1} = m_{df,i+1} \quad (2)$$

During  $(i + 1)$ th drowning-out, the cooling temperature,  $T_{cool}$ , is fixed with 20 °C. Therefore,  $m_{cf,i+1}$  is readily estimated by the following equation based on mass balance:

$$\begin{aligned} m_{cf,i+1} &= c^*(T_{cool}, w_i)(m_s + \sum_{k=1}^i m_{as,k}) \\ &\quad - c^*(T_{cool}, w_{i+1})(m_s + \sum_{k=1}^{i+1} m_{as,k}) \end{aligned} \quad (3)$$

where  $w_i$  indicates the weight percent (wt %) of antisolvent on a solute free basis after  $i$ th drowning-out,  $m_s$  is the amount of solvent,  $m_{as,i}$  is the amount of injected antisolvent at  $i$ th drowning-out. Here  $w_i$  can be estimated by the following equation, because solvent is not added further.

$$w_i = \frac{(\sum_{k=1}^i m_{as,k})}{(m_s + \sum_{k=1}^i m_{as,k})} \quad (4)$$

After the  $(i + 1)$ th drowning-out,  $i$ th fines dissolution (period C<sub>2</sub>–D<sub>1</sub>, C<sub>3</sub>–D<sub>2</sub>, ..., and C<sub>i+1</sub>–D<sub>i</sub>) was carried out by heating. However, it should be noted that seed crystals are also dissolved by heating:

$$m_{d,i} = m_{ds,i} + m_{df,i} \quad (5)$$

where  $m_d$ ,  $m_{ds}$ , and  $m_{df}$  are the amount of dissolved solute, seeds, and fines, respectively. Subscript,  $i$  indicates fines dissolution of the  $i$ th DFC process. In the present work, the heating temperature,  $T_{hot}$ , was fixed at 40 °C. Therefore,  $m_d$  can be estimated by the following equation:

$$\begin{aligned} m_{d,i} &= c^*(T_{hot}, w_{i+1})(m_s + \sum_{k=1}^{i+1} m_{as,k}) \\ &\quad - c^*(T_{cool}, w_{i+1})(m_s + \sum_{k=1}^{i+1} m_{as,k}) \end{aligned} \quad (6)$$

To estimate the amount of dissolved fines only,  $m_{df}$ , an empirical adjusting parameter,  $\alpha$ , was employed as follows:

$$\begin{aligned} m_{df,i} &= \alpha c^*(T_{hot}, w_{i+1})(m_s + \sum_{k=1}^{i+1} m_{as,k}) \\ &\quad - c^*(T_{cool}, w_{i+1})(m_s + \sum_{k=1}^{i+1} m_{as,k}) \end{aligned} \quad (7)$$

When  $\alpha$  is equal to 1,  $m_{df,i}$  is equal to  $m_{d,i}$ . It indicates that undersaturation induced by heating contributes to only dissolution of fines with no dissolution of seeds. On the other hand,  $\alpha$  value smaller than 1 indicates partial dissolution of seeds with fines dissolution. Strictly speaking,  $\alpha$  may be a function of CSD, crystal population density, solution composition, and so on. Therefore, it is very difficult to consider all factors to find an optimum value of  $\alpha$ . However, it is very difficult to consider all factors influencing  $\alpha$ , and thus that is determined by a trial and error. In the present work, it

was found that uniform CSD of final product is obtained when  $\alpha$  is smaller than an optimized value.

For the uniform CSD, all fines must be dissolved. Therefore, the amount of injected antisolvent may be determined to be

$$m_{cf,i+1} = m_{df,i} \quad (8)$$

Consequently, the amount of antisolvent injected can be estimated by the following equation obtained by combining the equations 2, 3, 7, and 8.

$$\begin{aligned} &c^*(T_{cool}, w_i)(m_s + \sum_{k=1}^i m_{as,k}) \\ &= \alpha c^*(T_{hot}, w_{i+1})(m_s + \sum_{k=1}^{i+1} m_{as,k}) \end{aligned} \quad (9)$$

After fines dissolution,  $(i + 1)$ th cooling (period D<sub>1</sub>–C<sub>2</sub>, D<sub>2</sub>–C<sub>3</sub>, ..., and D<sub>i</sub>–C<sub>i+1</sub>) is performed for the growth of the remaining seed crystals. All cooling processes are conducted to the fixed cooling temperature,  $T_{cool}$ . It should be noted that first cooling is performed at the internal seeding step (period B–C<sub>1</sub>). Finally, the DFC cycle is repeated until the desired yield is reached.

**2.6. Product Characterization.** At least 500 crystals of RDX were measured by image analysis from the optical micrographs to obtain average crystal size and CSD. The average length of the diameters measured at 2° of intervals with passing through the object's centroid was used to determine the characteristic length of the crystals. The CSD was plotted on a log-linear graph, where the horizontal axis is marked off on a log scale (crystal size) and the vertical axis on an arithmetic scale (percentage).

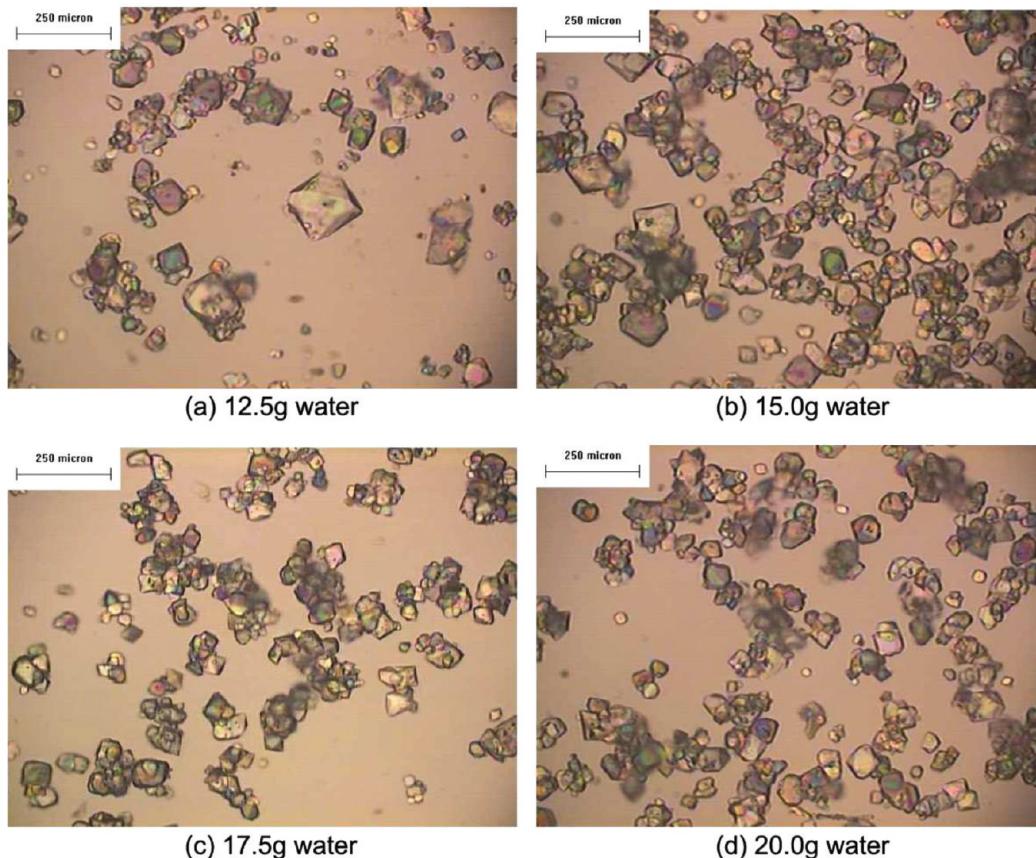
The total number of crystals per unit volume of solution,  $N_T$ , was estimated by the following equation.

$$N_T = \frac{1}{V_S f_V \rho_c} \frac{N_m M_T}{\sum_{k=1}^{N_m} L_k^3} \quad (10)$$

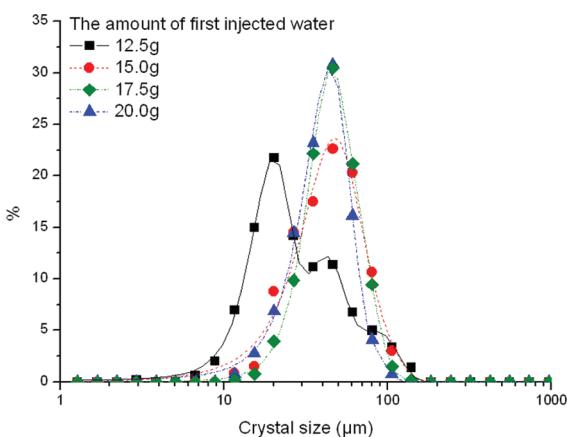
where  $V_S$  is the volume of solution in a batch crystallizer,  $f_V$  and  $\rho_c$  are the volume shape factor and the crystal density (1.82 g/cm<sup>3</sup>), respectively. Here volume shape factor is defined as  $f_V = M / (\rho_c L^3)$ , where  $M$  and  $L$  are the mass and characteristic length of crystal, respectively.  $N_m$  and  $M_T$  are the total number of measured particles and the total mass of crystals in one batch, respectively.  $L_k$  is the size of each crystal measured. In the present work,  $f_V = 0.38$  was obtained by the following method: with the use of a strip of an adhesive tape with attached crystals, the number of crystals per unit area and average characteristic length of crystal were measured by image analysis from optical microphotograph. The total mass of crystal on the adhesive tape is calculated by the difference between the mass of the adhesive tape with and without attached crystals. The total number of crystals on the adhesive tape is a multiple of the total area of the adhesive tape and the number of crystals per unit area. Subsequently, volume shape factor is estimated by using the average mass and characteristic length of the crystal with the crystal density.

### 3. RESULTS AND DISCUSSION

**3.1. Internal Seeding.** Figure 4 and Figure 5 show the optical micrographs of RDX crystals obtained after the first cooling process with the amount of injection water and their CSDs, respectively. In general, the morphology of RDX



**Figure 4.** Optical micrographs of RDX crystals obtained after the first cooling (point  $C_1$ ) with an amount of injection water.

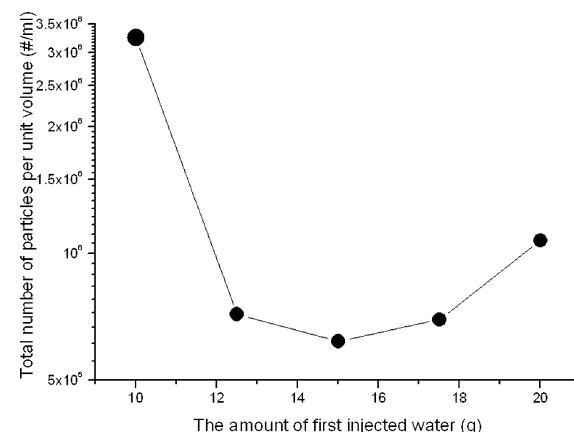


**Figure 5.** CSDs of RDX obtained after first cooling (point  $C_1$ ) with amount of injection water.

obtained in the present work is shown to be a bihexagonal pyramid, similar to that in previous reports.<sup>18,19</sup> When the amount of water was 12.5 g (Figures 4a and 5), bimodal CSD was obtained, and this may be attributed to a lower population density of seed crystals. If the number of seed crystals is not enough, the limit of the metastable zone is experienced during the cooling process because of the slow rate of desupersaturation.<sup>1</sup> As a result, many fine crystals are formed by primary nucleation during cooling. On the other hand, when the amount of injection water was larger than 15.0 g, crystal sizes were found to be relatively uniform. If the size of seeds were the same, the final crystal size of product increased by decreasing the population density of seeds. Therefore, the population

density of seeds was investigated to determine the desirable amount of injection water.

Total number of crystals per unit volume of solution, which is estimated by eq 10, versus the amount of injection water was plotted in Figure 6. This figure clearly shows that the total



**Figure 6.** Total number of crystals per unit volume solution versus amount of first-injection water.

number of crystals increases with decreasing the amount of water injected when the amount of injection water is smaller than 12.5 g, because the main driving force to induce fine crystals is primary nucleation by cooling in the present operating condition. On the other hand, when the amount of injection water is larger than 15.0 g, primary nucleation by cooling seems to be suppressed and nucleation is induced by

the reduction of solubility by drowning-out. As a result, population density of seeds was directly proportional to the amount of injected water. In this way, 15.0 g was determined as the optimum amount of first-injection water, because a uniform CSD with large crystals and a smaller population density of seeds were obtained.

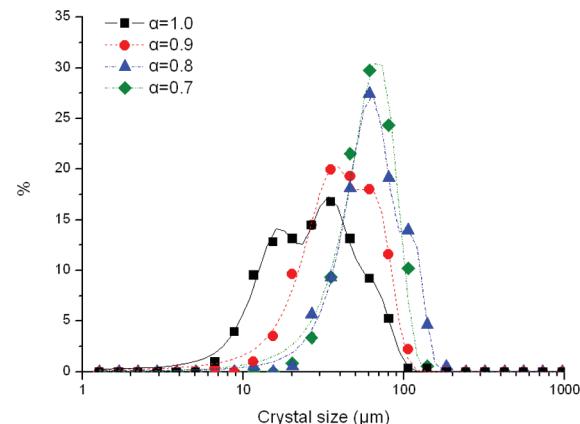
**3.2. DFC Process.** Using the MATLAB *fzero* solver, eq 9 was solved with  $\alpha$  values of 0.7, 0.8, 0.9, and 1.0. In this calculation, the desired yield and the amount of first-injection water were chosen to 85% and 15.0 g, respectively. Heating and cooling temperatures were fixed at 20 and 40 °C, respectively. It is obvious that the amount of injection water for each step of the drowning-out process is decreased with decreasing  $\alpha$  as listed in Table 2. Therefore, as  $\alpha$  becomes smaller, more DFC

**Table 2. The Amount of Injection Water of *i*th Drowning-out with Various  $\alpha$**

parameter, $\alpha$	amount of injection water, $m_{as,i}$				
	$i = 1$	$i = 2$	$i = 3$	$i = 4$	$i = 5$
1.0	15.0	18.2	28.1		
0.9	15.0	14.2	23.7		
0.8	15.0	9.8	16.6	23.2	
0.7	15.0	5.1	8.0	13.9	19.9

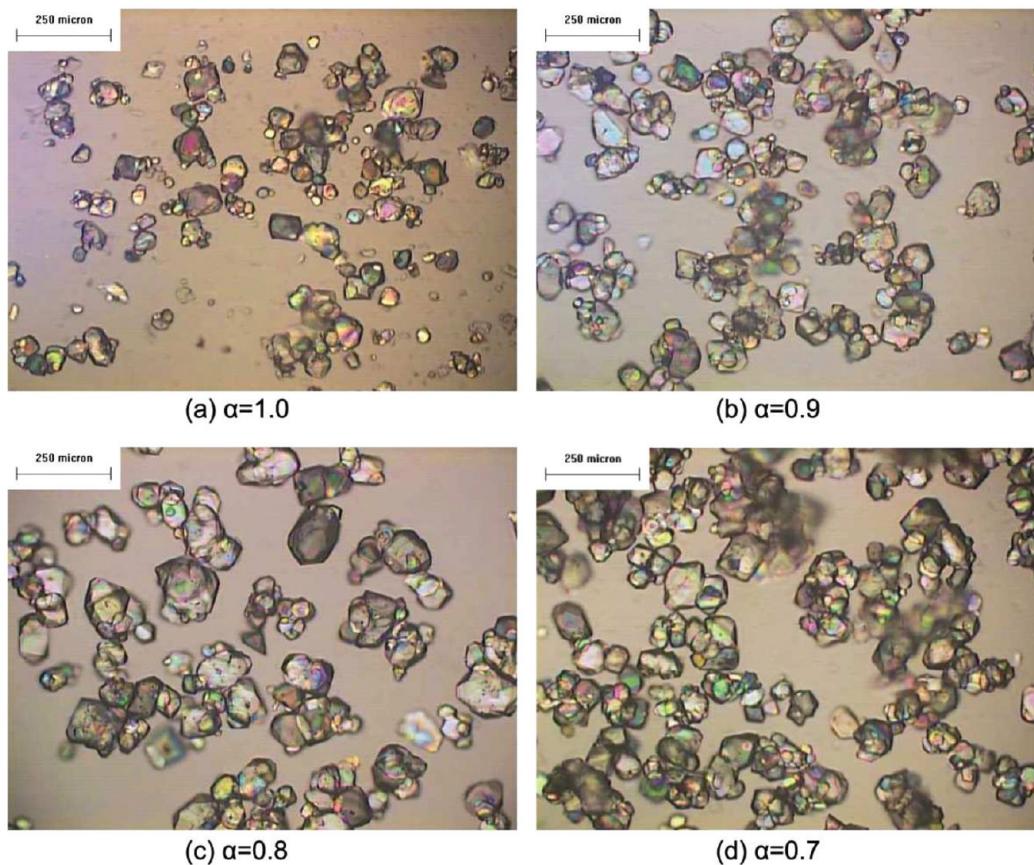
runs are required to reach the desired yield. If the product quality were the same, a large  $\alpha$  is desirable because the total operating time is decreased.

Figure 7 and Figure 8 shows the optical micrographs of RDX obtained by the DFC process with various  $\alpha$  and their CSDs,



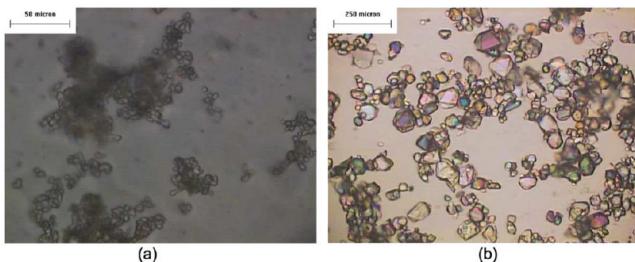
**Figure 8.** CSDs of RDX produced by the DFC process with various  $\alpha$ .

respectively. If the large  $\alpha$  values were employed, the fine particles are not dissolved completely during the fines dissolution step. Therefore, many fine particles still remained and the original seeds could not grow enough. In this work, when  $\alpha$  was 0.9 and 1.0, such unwanted fine crystals were observed as can be seen from Figure 7 panels a and b, and CSDs in Figure 8. On the other hand, when fine particles were completely dissolved by employing  $\alpha$  smaller than 0.8, relatively large crystals and uniform CSD were obtained. Therefore, considering crystal size, CSD, and operating time, the  $\alpha$  value was chosen to be 0.8. The average size of the RDX crystals of the present experiments with  $\alpha = 0.8$  was 67.6  $\mu\text{m}$ , and the overall product yield was about 90 wt %.



**Figure 7.** Optical micrographs of the RDX crystals produced by the DFC process with various  $\alpha$ .

For comparison, experiments with conventional drowning-out were performed with RDX/ $\gamma$ -butyrolactone saturated solution of 30 °C. Two methods in the antisolvent injection were employed: injections by one-pot and by a constant feeding rate. In the experiment with the one-pot injection, 64.6 g water, that is the same value with the amount of the total injection water in the DFC experiment with  $\alpha = 0.8$ , was poured rapidly into the saturated solution. On the other hand, in the experiments with constant feeding rate, 64.6 g water was fed with constant rate during 55 min that is the total process time of the DFC experiment with  $\alpha = 0.8$ . Optical photographs of RDX crystals by those methods were shown in Figure 9.



**Figure 9.** Optical micrographs of RDX crystals produced by conventional drowning-out.

The average size of RDX crystals produced by drowning-out with rapid injection of water was  $3.3\ \mu\text{m}$  (Figure 9(a)). This size is too small compared with that by the DFC process. Average size of RDX crystals produced by water injection with constant flow rate was  $40.4\ \mu\text{m}$  (Figure 9(b)). Although this size is much larger than that by a rapid antisolvent injection, it is still smaller than that produced by the DFC process.

#### 4. CONCLUSIONS

The DFC process, the drowning-out combined with fines dissolution and cooling process, was applied to the crystallization of RDX from  $\gamma$ -butyrolactone. The fines dissolution process was found to be a proper conjunction technique between drowning-out and cooling crystallization for taking out the merits of the former process (high yield) and the latter (large crystal size). During the DFC process, fine particles induced by drowning-out should be completely dissolved at the fines dissolution stage. In the present work, this requirement was resolved by adopting an empirical parameter,  $\alpha$ , to the mass balance model (eq 9). The average crystal size RDX produced by the DFC process with  $\alpha = 0.8$  was  $67.6\ \mu\text{m}$ , and the production yield was 90%. When the conventional drowning-out was performed with the same batch time and amount of antisolvent with those conditions, RDX crystals with a size of  $40.4\ \mu\text{m}$  were obtained. Therefore, it is concluded that the DFC process would be an effective method to recover RDX with improved CSD and overall yield from an industrial waste solution of RDX/ $\gamma$ -butyrolactone. However, the exact value of dissolved fines cannot be estimated by  $\alpha$ , only because  $\alpha$  is just an empirical constant. In the future, when the kinetics of dissolution and crystallization of RDX by drowning-out will be investigated in detail, the amount of dissolved fines may be quantitatively estimated to calculate the amount of injected water at each drowning-out step and the number of DFC cycles.

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##### Notes

The authors declare no competing financial interest.

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