Chemical Engineering Journal 81 (2001) 307–312

Chemical Engineering Journal

www.elsevier.com/locate/cej

Short communication

Influences of seed crystals on agglomeration phenomena and product purity of *m*-chloronitrobenzene crystals in batch crystallization

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Received 31 August 1999; received in revised form 26 January 2000; accepted 31 January 2000

Abstract

Changes in the fraction of agglomerates, agglomeration kinetics and product purity of *m*-chloronitrobenzene (CNB) crystals with the number and size of seed crystals were examined in batch crystallization experimentally, and influences of seed types (ground and well-defined) on agglomerate purities were discussed. From the fraction of agglomerates and agglomeration kinetics, it was found that agglomeration occurred more frequently when the number of seed crystals was larger and its size was smaller. The amount of purity decrease by agglomeration was smaller for the smaller number of seeds and for the larger ones. As the number of the elementary crystals constituting agglomerates was smaller, the purity of agglomerates was higher. With ground crystals, more frequent agglomeration occurred and the purity of agglomerates was lower than those for the well-defined crystals. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Agglomeration phenomena; Agglomerate purity; Batch crystallization; Seed crystals

1. Introduction

Product particles from suspension type crystallizers are often agglomerated, and purity of such products is in general, lower than that expected from the phase equilibrium. It is said that the purity of product particles become lower when crystals are agglomerated [1,2]. Therefore, the decreasing of the product purity by agglomeration is a serious problem to the chemical and pharmaceutical industry. The mechanism of purity decrease by agglomeration is not clearly understood.

The purity decrease of single crystals mainly occurs by inclusion of mother liquor into the crystals and by its adhesion on the crystal surfaces. Formation of inclusions was observed by Murata and Honda [3] for fixed single crystals of *m*-CNB growing in *m*-CNB–*o*-CNB binary melts. Matsuoka et al. [4] reported that the inclusion factor that is defined as the fraction of mother liquor included by a crystal increased with the growth rates of *m*-CNB crystals.

For agglomerates, the purity can further decrease by entraining mother liquor during agglomeration [5]. Misra and White [6] observed mother liquor included among Bayer aluminum trihydroxide crystals by a tracer method. Matsuoka et al. [7] reported an empirical correlation between purity of agglomerated β-isopropylnaphthalene (β-IPN) crystals and mass of deposits or the initial melt supercooling in a batch crystallization. Funakoshi et al. [5] proposed the correlations between the fraction or purity of agglomerates and particle size of products in a batch crystallization, and discussed the mechanism of purity decrease by agglomeration.

The influences of the characteristics of seed crystals on agglomeration phenomena and agglomerates purity, however, are not discussed in detail. The purpose of this study is to examine the changes of agglomeration phenomena and purity of agglomerates with the number and size of seed crystals quantitatively for the system of *m*-CNB–*o*-CNB in a batch crystallization. Moreover, based on their results the influences of type of seeds on purity of agglomerates was discussed.

2. Experimentals

All experiments were conducted by use of the *m*-CNB–*o*-CNB simple eutectic system. The experimental apparatus and analyzing methods of product particles were described in detail elsewhere [5].

200 g melt of 0.95 mass fraction of *m*-CNB and 0.05 mass fraction of *o*-CNB was placed in a crystallizer, and was cooled to a predetermined temperature to provide an initial

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PII: S1385-8947(00)00200-X

Nomenclature

K_a	agglomeration rate coefficient (m^3/s)
L	particle size (m)
L_A	number-based mean size of agglomerates (m)
L_N	number-based mean size of non-agglomerates (m)
M_m	mass of melt (kg)
M_s	mass of seed crystals (kg)
N	number of product particles (#)
n	number of elementary crystals (#)
N_A	number of agglomerates (#)
N_N	number of non-agglomerates (#)
N_s	number of seed crystals (#)
$N(\theta)$	number of particles at time θ (m^{-3})
ΔT_r	remaining supercooling (K)
w_{Ai}	purity of agglomerates of size i (–)
w_N	purity of non-agglomerates (–)
$w_m(\theta)$	melt composition at time θ (–)
w^*	equilibrium melt composition (–)
Φ_{Agg}	fraction of agglomerates (–)
θ	time (s)
$\sigma(\theta)$	supersaturation at time θ ($=\{w_m(\theta)-w^*\}/w^*$) (–)

supercooling of 1.0 K, agitating at 400 rpm with a marine propeller type impeller. Then seed crystals were added which had been prepared by the method mentioned later. After a given time, the crystalline particles were separated from the melt with a glass filter attached at the bottom of the crystallizer and were then centrifuged.

Two different types of crystals were used as seeds, i.e. well-defined and ground crystals. The well-defined crystals were prepared by spontaneous nucleation from acetone solutions containing about 0.6 mass fraction of *m*-CNB, and only those having a block shape were selected under a microscope. Finally, they were taken from the sieve fraction of 4.2×10^{-4}–5.9×10^{-4} and 8.4×10^{-4}–1.19×10^{-3} m, the mean size being 5.1×10^{-4} and 1.0×10^{-3} m, respectively. The ground crystals were made by crystallization of the pure *m*-CNB melt, ground in a mortar and sieved by the 4.2×10^{-4}–5.9×10^{-4} m sieves (the mean size was 5.1×10^{-4} m). Each purity of the well-defined and the ground crystals was unity in mass fraction.

The experimental conditions are shown in Table 1. In order to discuss the influences of the characteristics of seed crystals on the fraction of agglomerates, agglomeration kinetics and product purity in this study, the number, N_s, size, L_s, and types of seed crystals were changed, where the number of seed crystals was estimated from the mass of seed crystals, M_s. To formulate the agglomeration kinetics, experiments with different durations, θ, were conducted (Run 2, 5 and 6).

Table 1
Experimental conditions

Run	Seed types	M_s (kg)	N_s (#)	L_s (m)	θ (s)
1	Well-defined	1.0×10^{-4}	9.1×10^{2}	5.1×10^{-4}	600
2	Well-defined	1.0×10^{-3}	9.1×10^{3}	5.1×10^{-4}	600
3	Well-defined	5.0×10^{-3}	4.7×10^{4}	5.1×10^{-4}	600
4	Well-defined	1.0×10^{-3}	1.1×10^{3}	1.0×10^{-3}	600
5	Well-defined	1.0×10^{-3}	9.1×10^{3}	5.1×10^{-4}	150
6	Well-defined	1.0×10^{-3}	9.1×10^{3}	5.1×10^{-4}	300
7–1∼3	Ground	1.0×10^{-3}	–	5.1×10^{-4}	600

3. Results and discussion

3.1. Influences of the number and size of seed crystals on agglomeration phenomena

To see the effects of mixing conditions, a few preliminary runs were carried out at rotation speeds of 200, 400 and 600 rpm, other conditions being kept the same as Run 7. At 200 rpm, dispersion of particles was not sufficient and settled down at the bottom of the crystallizer; however, no significant differences in particle dispersion and the resulting PSD were observed between 400 and 600 rpm. Therefore, the rotation speed was set at 400 rpm throughout the experiments.

Fig. 1 shows differences of the particle size distributions (PSD) of products for the case of different numbers of seeds and their size. The agglomerates and non-agglomerates were distinguished by their appearances as described previously [5]. Table 2 shows the number-based mean size of agglomerates, L_A, and of non-agglomerates, L_N, and the fraction of agglomerates, Φ_{Agg}, which is defined as the ratio of the number of agglomerates, N_A, to the sum of those of the agglomerates and non-agglomerates, N_A+N_N, i.e. $\Phi_{Agg}=N_A/(N_A+N_N)$, for each run.

It was found that the larger the number of seed crystals, the smaller the mean sizes of agglomerates and non-agglomerates. The measured remaining supercoolings of the melt at the end of experiments are included in Table 2 showing that they are larger for those having smaller initial total surface area of the seed crystals. The initial total surface area is obviously proportional to $N_s\times L_s^2$ for the well-defined seeds. The average number of crystals constituting agglomerates, defined as the elementary crystals, was larger for the case of the larger number of seed crystals. The mean size of agglomerates, however, was smaller because of the smaller elementary crystals.

The lower fraction was proposed for the smaller number of seed crystals. The fraction, however, was larger for Run 2 than that for Run 3. It was considered by Sakamoto et al. [8] and David et al. [9] that agglomeration was influenced by the supersaturations in addition to the number of suspended particles. The consuming rates of the supercooling in a melt for Run 3 was five times faster than for Run 2. Moreover, the fraction of agglomerates increased with the particle size for

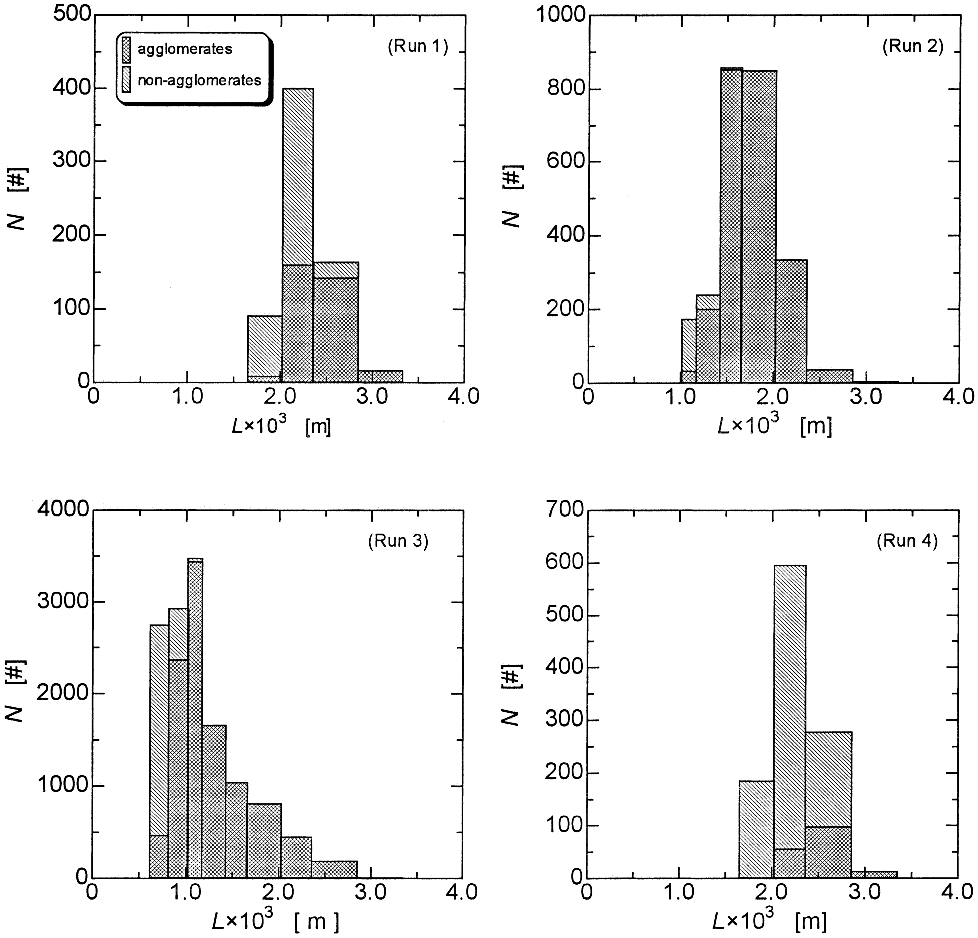


Fig. 1. Particle size distributions of products for Run 1–4.

all runs, as seen in Fig. 1. This tendency was the same with copper sulphate pentahydrate crystals reported by Zumstein and Rousseau [10].

The agglomeration rate was defined as the decreasing rate of particle number since no nucleation was observed during experiments. It was then calculated from the changes in the particle numbers measured at different times (Runs 2, 5 and 6) and was correlated by the following equation which was adopted for the NaCl experiments [11].

$$-\frac{\mathrm{d}N(\theta)}{\mathrm{d}\theta} = K_\mathrm{a}\sigma(\theta)^3 N(\theta)^2 \tag{1}$$

Table 2
Mean size, fraction of agglomerates, agglomeration rate coefficient and remaining supercooling

Run	L_A[a] (m)	L_N[b] (m)	Φ_Agg (–)	K_a (m^3/s)	ΔT_r (K)
1	2.41×10^{-3}	2.14×10^{-3}	0.485	5.0×10^{-6}	0.90
2	1.74×10^{-3}	1.15×10^{-3}	0.926	7.3×10^{-6}	0.79
3	1.25×10^{-3}	7.60×10^{-4}	0.783	1.2×10^{-6}	0.71
4	2.50×10^{-3}	2.20×10^{-3}	0.158	3.7×10^{-8}	0.85

[a] L_A: number-based mean size of agglomerates.

[b] L_N: number-based mean size of non-agglomerates.

where supersaturation $\sigma(\theta)$ is defined as $\{w_\mathrm{m}(\theta) - w_\mathrm{m}^*\}/w_\mathrm{m}^*$ and $w_\mathrm{m}(\theta)$ was calculated from the mass balance and the growth rate equation for the *m*-CNB–*o*-CNB system. The value of K_a thus determined was 7.3×10^{-6} m^3/s for Runs 2, 5 and 6, and those for other runs are similarly calculated and are shown in Table 2. As the seed size was larger, the agglomeration rate coefficients were smaller and the fraction of agglomerates was lower. These values of K_a for *m*-CNB crystals for all runs were smaller than those for NaCl crystals where $K_\mathrm{a}=1.9\times10^{-5}$–$9.8\times10^{-4}$ m^3/s [11]. The particle size was about a few mm in this study, while it was about a few tens μm for NaCl crystals.

From the fraction of agglomerates and the agglomeration kinetics, it is found that frequent agglomeration occurred when the number of seed crystals was larger and its size was smaller.

3.2. Influences of seed crystals on product purity

Since as shown in Fig. 1, the size of product particles is mainly controlled by agglomeration, purity of the agglomerates is correlated as a function of particle size, and is shown in Fig. 2. The ordinate indicates the amount of purity de-

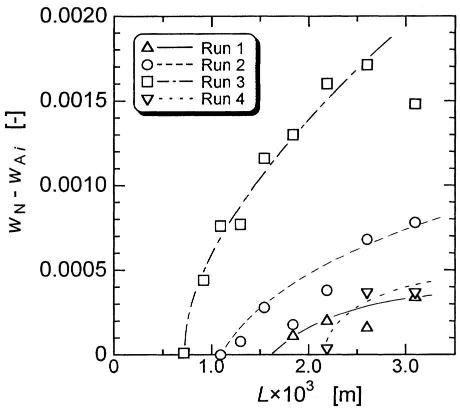


Fig. 2. Amount of purity decrease by agglomeration.

crease by agglomeration, that is the difference between the purity of agglomerates of size i (i.e. on the ith sieve), w_{Ai}, and that of elementary crystals, w_N, i.e. w_N–w_{Ai}, where w_N is assumed to be equal to the purity of non-agglomerates at the mean size since the size of the elementary particles of agglomerates is almost equal to the mean size. The amount of purity decrease was larger for the larger number and the smaller size of seeds at the same agglomerate size. The number of elementary crystals was larger for the larger number of seed crystals and for the smaller ones when the size of agglomerates was same. The increasing ratios of w_N–w_{Ai} with agglomerates size were larger as the mean size of non-agglomerates was smaller.

It is clearly shown that the purity decrease is more substantial when agglomerates size is smaller. This can be explained that the number of elementary crystals has significant effects on purity decrease through the entrainment of mother liquor during agglomeration. Fig. 3 illustrates the relation between the purity and the numbers of elementary crystals, n, for Run 3, where n is defined as the mean number of crystals constituting the agglomerates existing on the ith screen. w_{Ai} decreased with the increasing of n. The similar correlation between the purity of the whole products and the average number of the elementary crystals was found for the case of NaCl crystals [11]. Comparison of Fig. 3 with Fig. 2 shows that the purities of agglomerates decreased rapidly with the increase of their size, however, these decreased slightly with the increasing of the number of elementary crystals. Although the size of agglomerates increased with the number of elementary crystals as reported previously [5], the ratio of size increase was reduced with increasing of the number of them. This implies that larger agglomerates are more densely packed with the elementary crystals.

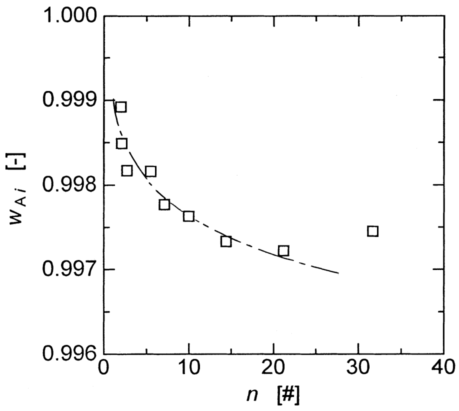


Fig. 3. Correlations between agglomerates purity and the number of elementary crystals.

For Run 2, the mean sized agglomerates was constituted by about four elementary crystals and its purity was 0.9994. Comparison of Run 3 with Run 2 leads that the purity of agglomerates was lower for the smaller elementary crystals when the number of elementary crystals was same (n=4). The reason is that the elementary crystals for Run 3 agglomerated more densely than for Run 2, from the observations of their appearances.

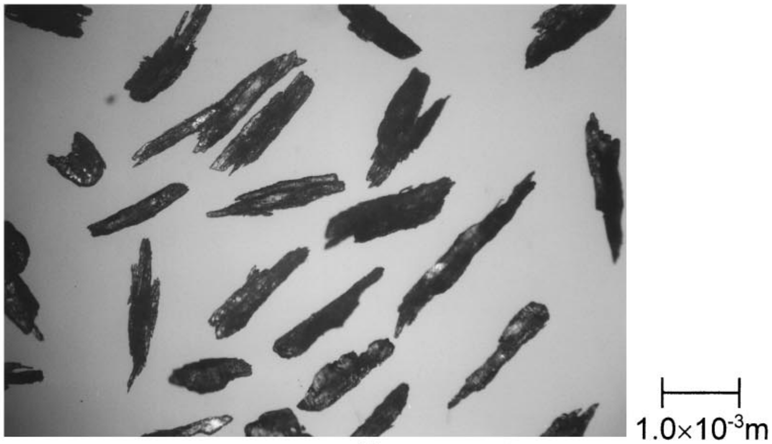
3.3. Comparison between the ground seeds and the well-defined seeds

In industrial crystallization, it is impossible to control shapes, number and size of seed crystals strictly. In order to examine the influence of types of seed crystals on the PSD and appearance and purity of products, ground crystals were also used in this study.

The appearances of the ground crystals used as seeds is shown in Fig. 4(a). They were spindle shaped and their surfaces were very rough. Fig. 5 shows an example of the PSD of products from the ground crystals (Run 7–3). Compared with the PSD for the case of well-defined seeds (Fig. 1(b)), there are many particles in Run 7–3 smaller than that grown up from seed crystals. It was observed that the agglomerates, where an example of them was shown in Fig. 4(b), were constituted by many and variously sized crystals in contrast to the agglomerates produced with the well-defined crystals. Therefore, it is confirmed that secondary nucleation occurred for the case of the ground crystals.

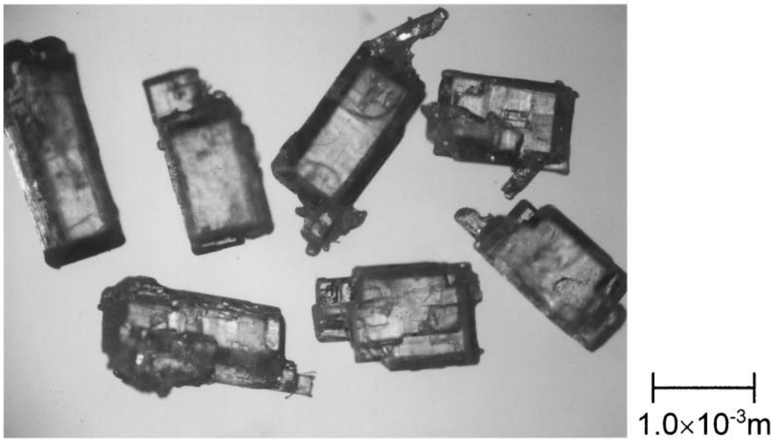
Although there were single crystals that looked one particles in products obtained for the case of the ground crystals, their surfaces were much rougher than the non-agglomerates obtained for the well-defined crystals, as seen in Fig. 4(c). Moreover, when the single crystals obtained for the ground crystals were melted, it was observed that they separated into a number of small parts, while non-agglomerates became smaller keeping on their original shape. This suggests that the distinction of single crystals from agglomerates was difficult when the ground crystals were used as seeds.

The purities of agglomerates made of the ground crystals were lower than those for the well-defined crystals, as shown in Fig. 6. Since Runs 7–1∼7–3 were conducted at the same experimental conditions, the solid dots in Fig. 6 show the reproducibility of purity of agglomerates for ground crystals. Moreover, purity of agglomerates kept decreasing with their size for the case of the ground seeds. When the ground crys-



(a) seed crystals ($\bar{L}$ =5.1×10^{-4}m)

(b) agglomerates ($\bar{L}$=1.4×10^{-3}m)



(c) single crystals ($\bar{L}$=9.2×10^{-4}m)

Fig. 4. Seed crystals and agglomerates and single crystals obtained for ground crystals.

tals were added as seeds, there were a large number of particles in a melt that were smaller than the crystals originated from the seeds, and they were born due to secondary nucleation such as the initial breeding. Therefore, it is considered that frequent agglomeration have occurred and consequently the amount of mother liquor entrained during agglomeration became larger for ground crystals than for well-defined crystals.

For industrial crystallization, secondary nucleation occurs by initial breeding and contact nucleation in the seeded suspension crystallizers. As the larger number and smaller crystals grown up from the nuclei are suspended in a mother

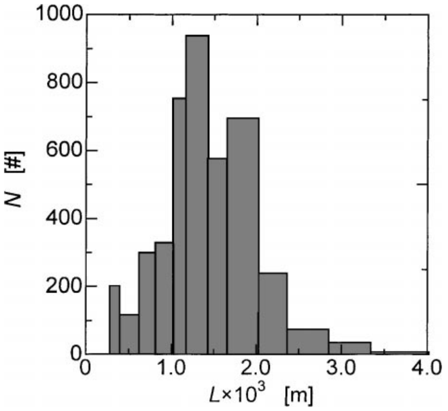


Fig. 5. Particle size distribution of products for ground crystals (Run 7–3).

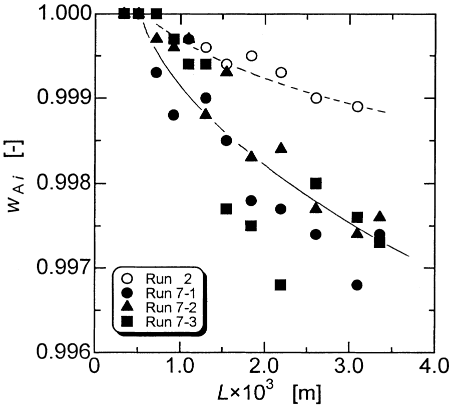


Fig. 6. Differences of agglomerates purities with seed types.

liquor, agglomeration occurs frequently by those crystals. Consequently, it is considered that the further purity decrease occurs in a mother liquor by agglomeration of such particles.

4. Conclusions

Changes in the fraction of agglomerates, agglomeration kinetics and product purity of *m*-CNB crystals with the number and size of seed crystals in a batch crystallization were examined experimentally and the influences of seed types on agglomerates purity were discussed. From the relations between the fractions of agglomerates and the operating conditions, it was found that frequent agglomeration occurred when the number of seed crystals was larger and its size was smaller. The agglomeration kinetics were correlated as a function of the number of particles and the supersaturation in a melt, and the agglomeration rates coefficient was smaller for the larger seeds.

As the number of seed crystals was larger and its size was smaller, the amount of purity decreases by agglomeration was larger. The purity of agglomerates decreased with the increase of the number of elementary crystals constituting agglomerates. The amount of mother liquor entrained during agglomeration became larger when the elementary crystals agglomerated more densely.

When the ground crystals were used as the seeds, agglomeration occurred more frequently and the purity of products was lower because the number of smaller particles in a melt by secondary nucleation was larger.

Acknowledgements

The authors thank Dr. H. Uchida for his cooperation in computer programming.

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