ELSEVIER
Chemical Engineering Journal 85 (2002) 161–167
Chemical Engineering Journal
www.elsevier.com/locate/cej

Production of large crystals with a narrow crystal size distribution by a novel WWDJ batch crystallizer

Gu Shan[a], Koichi Igarashi[a], Hideo Noda[b], Hiroshi Ooshima[a,*]

[a] *Department of Bioapplied Chemistry, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan*
[b] *Kansai Chemical Engineering Co. Ltd., 9-7, 2-chome, Minaminanamatsu-cho, Amagasaki, Hyogo 660-0053, Japan*

Received 25 August 2000; received in revised form 28 December 2000; accepted 10 January 2001

Abstract

A novel batch crystallizer has been developed and used for the crystallization of L-aspartic acid, resulting in large product crystals with a narrow crystal size distribution.

The batch crystallizer was equipped with a slurry sprinkler fixed on the shaft of an impeller, and a double-deck jacket. The slurry sprinkler, known as Wall Wetter, is specially designed for agitating the slurry and sprinkling it on the wall of the crystallizer headspace which is covered by the upper jacket. It was expected that by setting the upper jacket temperature at an appropriate high temperature, fine crystals could be dissolved during the fall of slurry along the wall, and consequently the crystal size distribution would shift to the large side. L-aspartic acid was chosen as an example to demonstrate this process. L-aspartic acid was crystallized at an initial supersaturation ratio (C/C_s) of 1.7 with no seeds. The classification exponent n and characteristic size D_e of product crystals, which were evaluated by the Rosin Rammler Sperling Bennet (RRSB) distribution function, were 3.9 and 302 μm, respectively, compared with 2.2 and 237 μm, respectively, in a control crystallization experiment not using the Wall Wetter. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Crystallization; Crystal size distribution; L-aspartic acid; Wall Wetter; Batch crystallizer; WWDJ batch crystallizer

1. Introduction

Crystallization from solution is an important separation and purification process, which can be used to obtain solid products of high purity. Industrial crystallization is expected to produce solids having not only a certain composition but also a certain crystal size distribution (CSD), because CSD often determines handling and many end-use properties. A product with a unimodal and narrow size distribution and large mean size is often desired. This can be achieved batch-wise or continuously. Batch crystallization is becoming increasingly important in the processing of a large variety of fine chemicals and pharmaceuticals.

It is well known that CSD is dependent on the primary nucleation, growth kinetics, and also on secondary nucleation which is mainly caused by collision between crystals and the impeller in the crystallizer [1]. It is also well known that the geometrical configuration of the crystallizer has a considerable effect on CSD [2,3]. Several experiments dealing with CSD show the effect of mixing conditions [4,5]. Franke and Mersmann [6] showed that nucleation is influenced by the inhomogeneity of the supersaturation field which seems to depend on the mixing conditions, etc., and, in consequence, affects the CSD of produced crystals.

Many efforts have been made to obtain a unimodal and narrow CSD, with one of the earliest studies on the control of CSD in batch cooling crystallization being made by Griffiths [7]. Griffiths proposed maintaining the supersaturation at a level within the metastable region during the cooling operation, such that only the growth of seeds could be expected without nucleation. In order to realize such a crystallization strategy, a programmed cooling operation was proposed instead of natural cooling [8] and subsequently this has been extensively used [9,10]. Kubota et al. [11–13], however, pointed out that a sufficient and appropriate amount of seed gives a large mean size of product crystals with a unimodal CSD regardless of the cooling process, i.e. not only in controlled cooling but also in natural cooling.

Another way to obtain a large mean crystal size with a unimodal CSD is to dissolve fine crystals [14,15]. Rohani et al. [16] controlled CSD in a batch cooling crystallizer with an outside-circulation type of fine crystal dissolver. However, it is difficult to clean the inside of pipes and pumps in such a crystallizer after each batch operation. This is a serious problem in the production of pharmaceuticals.

---

[*] Corresponding author. Tel.: +81-6-6605-2700; fax: +81-6-6605-2701.
E-mail address: ooshima@bioa.eng.osaka-cu.ac.jp (H. Ooshima).

1385-8947/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S1385-8947(01)00153-X

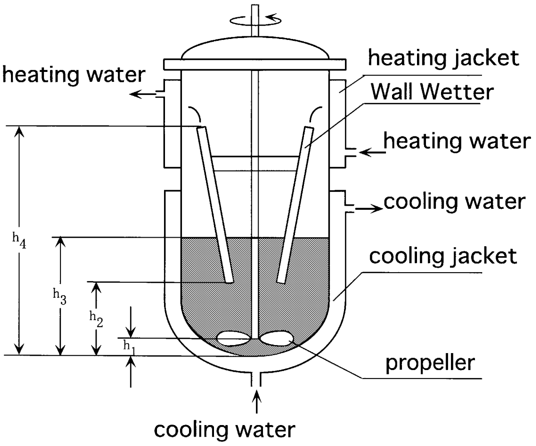

Fig. 1. Schematic diagram of WWDJ batch crystallizer.

In the present paper, we propose a novel batch crystallizer, the structure of which is quite simple as shown later. It is easy to wash and clean the inside of the vessel, as there is no outside-circulation line and no pump. The crystallizer allows the production of large crystals with a narrow CSD, this being achieved by the fractional dissolution of fine crystals and growth of large crystals, which occur simultaneously in the batch vessel. Furthermore, the same end result can be achieved even when crystallization is carried out without seed crystals. We show an example of the benefit of the proposed batch crystallizer through the crystallization of L-aspartic acid performed without seeds.

2. Experimental procedure

2.1. A novel batch crystallizer (WWDJ batch crystallizer)

The newly developed WWDJ (Wall Wetter/double-deck jacket) batch crystallizer is illustrated in Fig. 1, and its dimensions are shown in Table 1. The crystallizer is a cylindrical glass vessel with a round bottom, covered with a double-deck jacket. The working volume of this crystallizer, corresponding to the volume of the part covered by the lower jacket, is 1.5 l. The crystallizer was equipped with a four-blade propeller down the middle of the vessel. It was also equipped with a Wall Wetter that was developed by one of the present authors (Noda) [17]. The Wall Wetter is a slurry sprinkler, namely a device specially designed for sprinkling slurry or a solution on the wall of the crystallizer headspace. The Wall Wetter adopted in this study comprised two channel bars with a J-shaped cross-section as shown in Fig. 2. The device was fixed to the agitation shaft at a given angle. Agitation was provided by the propeller and also by the Wall Wetter. The slurry was raised along the channel by centrifugal force and sprinkled on the upper wall, then fell down the wall. During the fall, it can be expected that crystals dissolve partially so that fine crystals disappear, if the upper jacket temperature is higher than that of the lower jacket. The surviving large crystals are also expected to grow further, at the expense of fine crystals, after returning to the lower crystallization phase.

Table 1
Dimension of crystallizer and process condition of the experiment

Inner diameter of crystallizer (cm)	14.0
Height of the upper jacket (cm)	10.0
Height of the lower jacket (cm)	17.0
Height of the space between the two jacket (cm)	2.0
h_1: The distance between the bottom and the propeller (cm)	3.4
h_2: The distance between the bottom and the lowest part of Wall Wetter (cm)	8.3
h_3: The distance between the bottom and the solution level (cm)	13.6
h_4: The distance between the bottom and the top of Wall Wetter (cm)	19.2
Volume of solution (l)	1.5

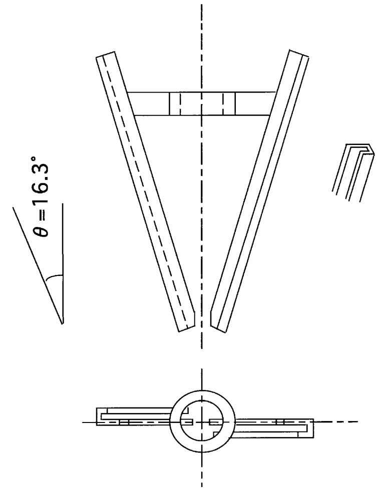

Fig. 2. Geometrical configuration of Wall Wetter.

The crystallization temperature was adjusted to a given value by controlling the rotation speed of the Wall Wetter and the temperature of the double-deck jacket, where the temperature of the upper and lower jackets is separately controlled.

2.2. Crystallization

Crystallization of L-aspartic acid from aqueous solution was carried out. The L-aspartic acid used in this experiment was of reagent grade and was purchased from Wako Pure Chemical Industries (Japan).

The WWDJ-crystallizer was used in two modes of crystallization, namely PWW-mode crystallization and P-mode crystallization. PWW-mode crystallization was performed using the crystallizer with the Wall Wetter and a propeller. P-mode crystallization was performed without the Wall Wetter as a control experiment against PWW-mode crystallization, i.e. in P-mode crystallization, the crystallizer was used as a conventional batch crystallizer.

The PWW-mode crystallization was performed as follows. The upper jacket was adjusted to a high temperature and the lower jacket was adjusted to a low temperature so that crystallization could be achieved at a given intermediate temperature. The initial concentration of L-aspartic acid was 5.18 mg/ml in all crystallization experiments. A solution (1.7 l) was prepared by dissolving a given amount of L-aspartic acid in distilled water at a temperature slightly higher than the desired saturation temperature. Then 1.5 l of solution was quickly introduced into the crystallizer while the Wall Wetter and the propeller were rotating at the same low speed. Agitation was then adjusted to a selected speed. A steady crystal dispersion phase was formed in the solution by spontaneous nucleation at an early stage. A sample (5 ml) of slurry was withdrawn at regular intervals. The crystals were immediately separated by filtration and the filtrate was used for the determination of L-aspartic acid concentration by UV absorption at 210 nm. When the concentration reached the desired value, all crystals were recovered by filtration as fast as possible, dried at room temperature in air for 12 h, then used for the measurements of the crystal size distribution.

2.3. Measurement of temperature in crystallizer

The crystallizer was operated in the PWW-mode, where the upper jacket was adjusted to a high temperature and the lower jacket was adjusted to a low temperature. Tap water was placed in the crystallizer instead of crystal slurry and the Wall Wetter and the propeller were rotated at a same speed. After the temperature of the bulk water became constant, the temperature was measured at the six points of the crystallizer shown in Fig. 3a using a copper–constantan thermocouple of 0.2 mm in thickness as a sensor. Points A and B are the top and bottom positions of the water falling down on the surface of the wall covered with the upper jacket. Point C is the center of the bulk water. By molding the thermocouple to the surface of the inner wall of the crystallizer, the wall temperature was measured at Points D, E, and F. As easily anticipated, since the thermocouple contacts with not only the wall surface but also the falling water, it is difficult to measure the wall temperature accurately. The data were nevertheless helpful in understanding the crystallization behavior as described later.

2.4. Determination of CSD

The dry crystals recovered above were classified by sieving and the crystal size distribution by weight was obtained. Nine sieves of 710, 500, 420, 297, 160, 105, 74, 53 and 37 μm aperture size were used in this experiment.

The Rosin Rammler Sperling Bennet (RRSB) distribution was used for the evaluation of CSD:

$$R(D_\mathrm{p}) = 100\exp\left[-\left(\frac{D_\mathrm{p}}{D_\mathrm{e}}\right)^n\right] \qquad (1)$$

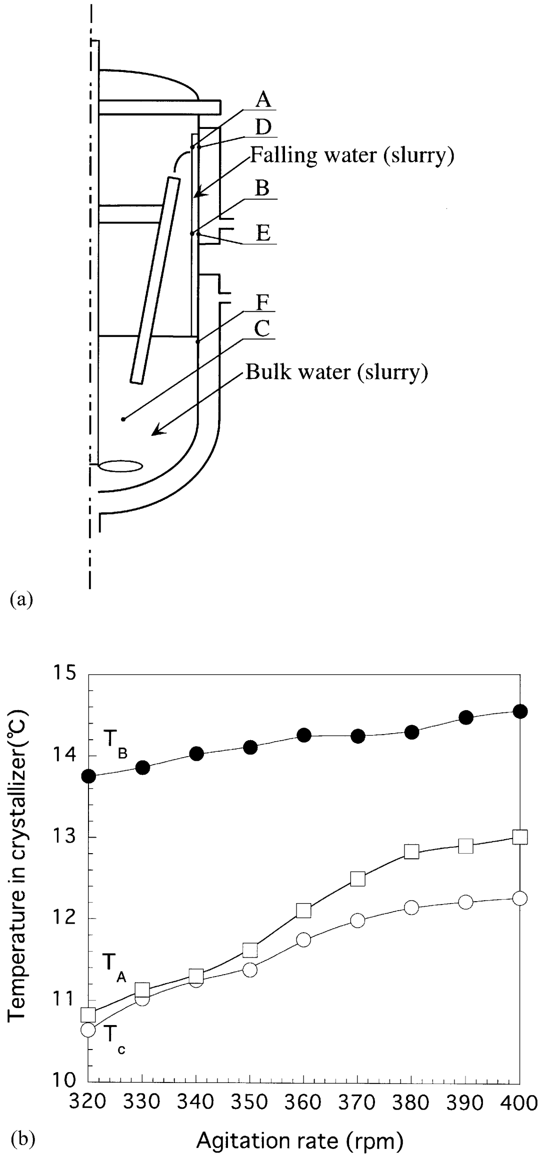

Fig. 3. (a) Determining point of solution temperature in crystallizer; (b) the relationship between the solution temperature and rotation rate of Wall Wetter.

where $R(D_\mathrm{p})$ is the cumulative weight percentage of crystals larger than the size of D_p, D_e the size of crystals corresponding to $R(D_\mathrm{p}) = 36.8\%$ of the product oversize fraction and n the classification exponent. The larger the value of n is, the narrower the CSD. A graph of $\ln(\ln(100\,R(D_\mathrm{p})))$ plotted against $\ln(D_\mathrm{p})$ gives a straight line according to the following equation:

$$\ln\left[\ln\left[\frac{100}{R(D_\mathrm{p})}\right]\right] = n\ln(D_\mathrm{p}) - n\ln(D_\mathrm{e}) \qquad (2)$$

The values of D_e and n can be obtained graphically from this plot.

2.5. Measurement of amount of crystals sprinkled by the Wall Wetter

Using the Wall Wetter and the propeller equipped in an open cylindrical glass vessel having the same geometry with the inner vessel of the WWDJ batch crystallizer except for short-cut wall of the headspace, the amount of slurry sprinkled was measured and compared among crystals having different sizes. 3.33 g/l slurry of L-aspartic acid crystals classified by sieving was prepared at 25°C using a saturated solution as dispersant. The slurry (1.5 l) was quickly introduced into the vessel pre-adjusted to 25°C, and immediately sprinkled over the wall of the vessel at 350 rpm for 1.0 min. The sprinkled slurry was gathered by a receiver and its density was determined. The slurry density was evaluated as a sprinkled slurry density ratio (SSDR in %) defined by Eq. (3).

$$\mathrm{SSDR} = 100\,\frac{\text{sprinkled slurry density}}{\text{initial bulk slurry density}} \tag{3}$$

A small SSDR indicates that the crystals are difficult to sprinkle.

3. Results and discussion

3.1. Temperature in crystallizer

In order to examine how large a difference can be produced between the crystallization temperature and the fine crystal dissolution temperature in the crystallizer operated in PWW-mode, temperature was measured at six points in the crystallizer shown in Fig. 3a. As described in Section 2, tap water was used instead of crystal slurry. The temperatures of the upper and lower jackets were fixed at 30.0 and 5°C, respectively. These jacket temperatures were arbitrarily chosen as an example. In Fig. 3b, the temperatures of water at Points A, B, and C in the crystallizer are shown as a function of the rotation speed of the Wall Wetter. The temperature of water at Point A, T_A, was close to that at Point C, T_C. The T_C increased from 10.6 to 12.3°C with an increase in the rotation speed of the Wall Wetter from 320 to 400 rpm. The temperature of water at Point B, T_B, was highest and changed from 13.7 to 14.6°C over the same range of rotation speed. The wall surface temperatures of the crystallizer at Points D, E and F, are 20.6 ± 0.6, 23.9 ± 0.8 and 5.5 ± 0.2°C, respectively, regardless of rotation speed, between 320 and 400 rpm. This means that a temperature gradient should be formed between the surface of the wall and the slurry falling on the wall, and also between the surface of the lower wall and the bulk slurry in the crystallization. Thus, an inhomogeneity in supersaturation level should be naturally created in the slurry falling on the wall of the headspace and also in the bulk slurry.

3.2. Setting of an operational condition of WWDJ batch crystallizer for the production of large crystals with a narrow CSD

As described above, our purpose in the present study was to show an example that the WWDJ-crystallizer allows the production of large crystals with a narrow CSD, comparing with a conventional batch crystallizer. For this purpose, we arbitrarily chose a set of values for the following three operational parameters, namely the temperature of the upper and lower jackets and the rotation speed of the Wall Wetter. The temperature of the upper and lower jackets was fixed at 30 and 5°C, respectively. A rotation speed of the Wall Wetter was chosen considering the dissolution of sprinkled crystals and the amount of slurry sprinkled per unit time. The driving force of the dissolution of crystals should be the temperature difference between T_B and T_C. Fig. 3b shows that the difference between T_B and T_C is almost same regardless of the rotation speed of the Wall Wetter. This means that the driving force of the dissolution of crystals is almost same regardless of the rotation speed. The amount of slurry sprinkled per unit time depends on the rotation speed of the Wall Wetter. However, an excessive rotation speed causes uncontrolled sprinkling of the slurry. On the other hand, a slow rotation speed decreases the quantity of the sprinkled slurry. From the visual observation, we chose 350 rpm as a possible rotation speed for later experiments. At 350 rpm, the amount of sprinkled solution was 72 ml/min and the temperature at Points A, B and C was 11.6, 14.2 and 11.2°C, respectively. As a result, we chose 11.2°C as a crystallization temperature.

3.3. Crystallization of L-aspartic acid in the WWDJ batch crystallizer

Crystallization of L-aspartic acid was performed in the WWDJ batch crystallizer. Fig. 4 shows the change of

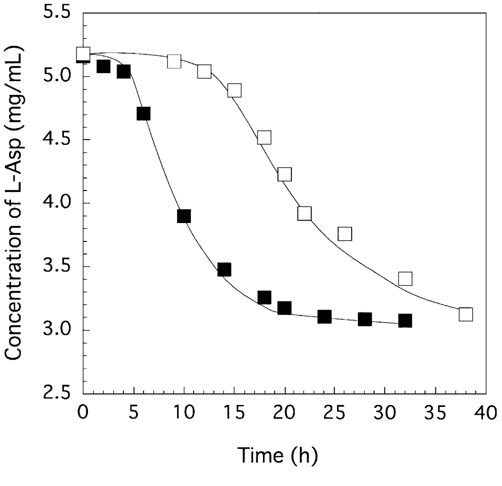

Fig. 4. The change of concentration during crystallization. Operation: (■) PWW-mode; (☐) P-mode.

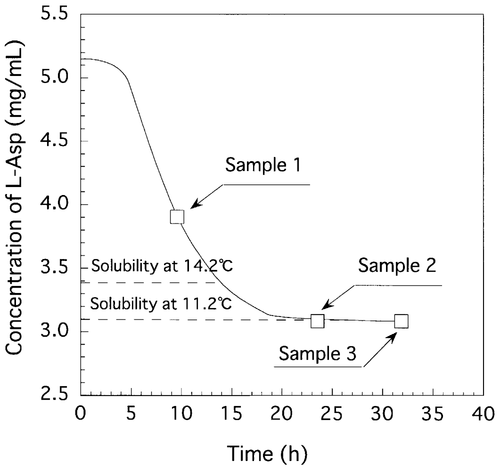

Fig. 5. The harvest of crystal in PWW-mode crystallization.

L-aspartic acid concentration during the crystallization. The solubility at 11.2°C was 3.10 mg/ml. A waiting time was observed in the PWW-mode and P-mode crystallization, and the former was shorter than the latter. The difference in waiting time between the two operation modes may be explained by the difference in the nucleation temperature. As described above, in the PWW-mode operation the bulk supersaturated solution contacts the cold surface of the wall covered with the lower jacket, but in the P-mode operation the temperature of the solution (T_c) is equal to that of the wall surface (T_F). The low temperature in the vicinity of the lower wall surface in the PWW-mode operation must have accelerated the nucleation. Incidentally, the initial supersaturation ratio estimated at T_F of 5.5°C is 1.22 times larger than that at T_C of 11.2°C. The crystallization rate after the waiting time in the PWW-mode operation was slightly larger than that in P-mode operation. These results show that the WWDJ batch crystallizer is useful for shortening the crystallization time.

3.4. Crystal size distribution

The crystals were recovered during the same crystallization as that shown in Fig. 4 and their CSD were measured. In Fig. 5, the recovering-points are represented with the L-aspartic acid concentration curve obtained in the PWW-mode crystallization.

The CSD of sample 1 is shown in Fig. 6a and b, and the characteristic parameters in CSD are presented in Table 2.

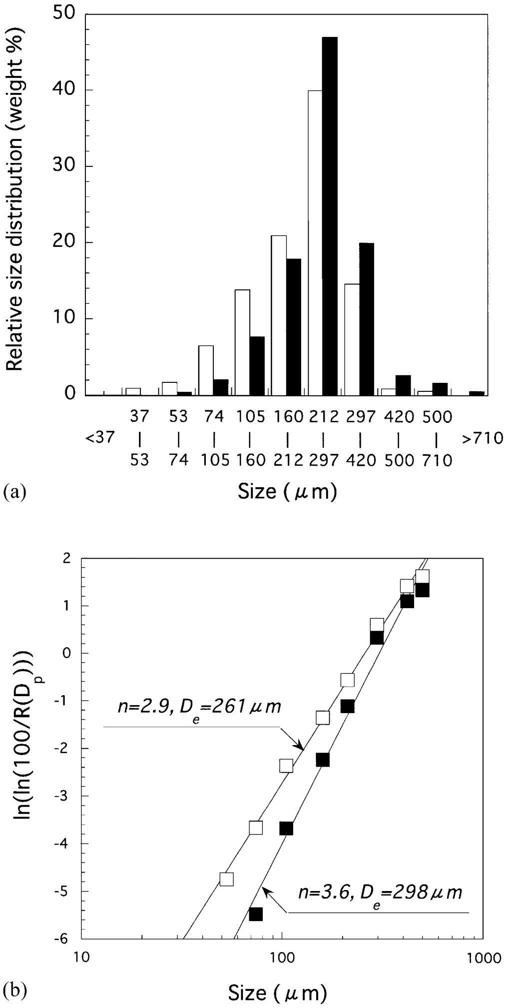

Fig. 6. Crystal size distribution of L-Asp crystals (sample 1). (a) Crystal size distribution: (■) PWW-mode; (□) P-mode. (b) CSD evaluated by RRSB distribution function: (■) PWW-mode; (□) P-mode.

In the PWW-mode crystallization, the quantity of fine crystals less than 160 μm was significantly reduced and a narrow CSD was attained. Furthermore, the characteristic size of crystals (D_e) became larger than that in the P-mode crystallization. These results suggest that fine crystals were dissolved and survivor crystals grew in the PWW-mode crystallization.

However, there is a complication. When the crystals of sample 1 were recovered, the solution was still in the supersaturated state, because the L-aspartic acid concentration

Table 2
Changes in CSD during crystallization: comparison of CSD between PWW-mode and P-mode operation

Sample	Concentration (mg/ml)	Crystallization time (h)		n (–)		D_e (μm)	
		PWW-mode	P-mode	PWW-mode	P-mode	PWW-mode	P-mode
1	3.9	10	22	3.6	2.9	298	261
2	3.1	24	34	3.6	2.2	302	237
3	3.1	32	42	3.9	2.1	336	221

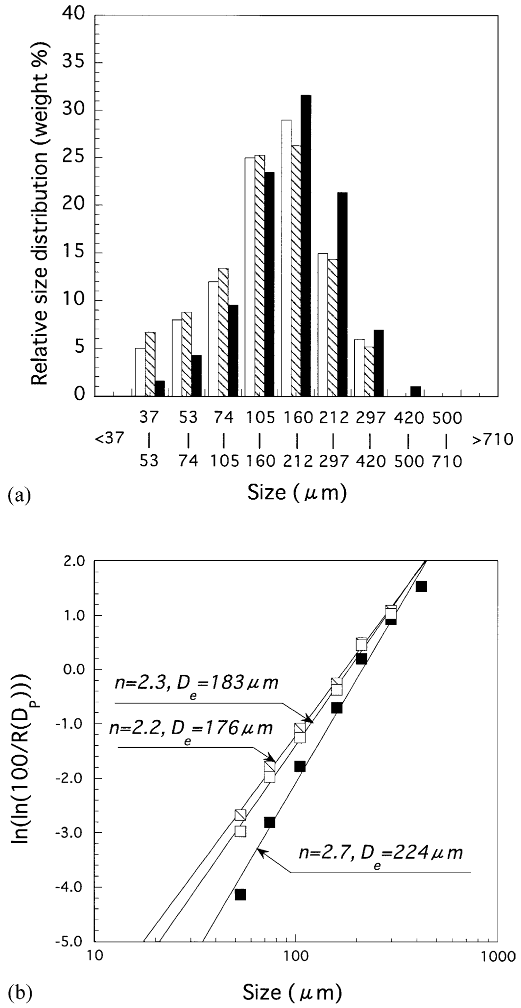

Fig. 7. Changes in CSD of seed crystals of L-Asp for 3 h operation. (a) Crystal size distribution: (☐) control (initial distribution); (■) PWW-mode; (▧) P-mode. (b) CSD evaluated by RRSB distribution function: (☐) Control (initial distribution); (■) PWW-mode; (▧) P-mode.

was still higher than its solubility at the high slurry temperature T_B. Nevertheless, Fig. 6a shows that fine crystals were dissolved. A possible explanation for this is that the high temperature near the surface of the heating wall, larger than 14.3°C of T_B and less than 23.9°C of T_D, played an important role in the dissolution of fine crystals.

The characteristic parameters in CSD for other samples are also presented in Table 2. In PWW-mode crystallization both n and D_e are larger than those in P-mode crystallization, indicating that crystallization in the PWW-mode produces a narrow CSD with large size. The values for sample 3 shown in Table 2 indicate that CSD can be further improved by continuing PWW-mode operation after the complete precipitation of crystals. On the contrary, a long P-mode operation resulted in a wide CSD with small size. This is due to the secondary nucleation and also the formation of fine crystals through attrition of crystals by the impeller.

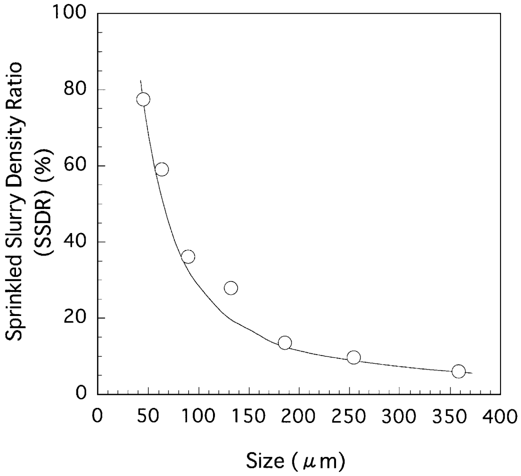

Fig. 8. Preferential sprinkling of fine crystals by Wall Wetter.

The attrition of crystals by the impeller was confirmed by the following experiment. A quantity of L-aspartic acid crystals with a known CSD was added to a saturated solution at 11.2°C in the crystallizer operated in P-mode and in PWW-mode. The crystallizer was operated for 3 h in each mode. The change in CSD is compared in Fig. 7a and b. Crystals became small and the CSD became wide in the P-mode. This is obviously due to the attrition of crystals by the impeller, because in this experiment the primary nucleation never occurs. On the other hand, when the crystallizer was operated in the PWW-mode, crystals became large and the CSD became narrow. This is due to the dissolution of fine crystals and the growth of survivor crystals at the expense of fine crystals.

3.5. Preferential sprinkling of fine crystals by Wall Wetter

The Wall Wetter is an apparatus specially designed for sprinkling slurry onto the wall of the vessel. However, the CSD of the sprinkled crystals should not be always the same as that of crystals leaving in the bulk slurry, because of inhomogeneity of suspension in the bulk slurry [4,18]. We determined the SSDR defined in Section 2 to evaluate the preference in the crystal size for the sprinkling. Fig. 8 shows that crystals less than 150 μm are preferentially sprinkled onto the wall of the crystallizer. This result indicates that crystals smaller than 150 μm are preferentially dissolved on the heating wall. This is an important factor for the effective and preferential removal of fine crystals in the WWDJ batch crystallizer.

4. Conclusion

We propose a novel batch crystallizer equipped with the Wall Wetter (a kind of slurry sprinkler) and a double-deck jacket. The crystallizer was named the WWDJ batch crystallizer. We showed that by using this crystallizer, the size and distribution of product crystals became large and narrow, respectively. This is due to the effective dissolution of fine crystals. Also in the crystallization without seeds, nucleation was accelerated. It can be concluded that the WWDJ batch crystallizer is useful for the production of large crystals with a narrow size distribution.

References

[1] A.M. Neumann, S.K. Bermingham, H.J.M. Kramer, G.M.V. Rosmalen, The effect of the impeller speed on the product crystal size distribution (CSD) a 22 l draft tube (DT) crystallizer, J. Cryst. Growth 198/199 (1999) 723–728.

[2] K. Shimizu, T. Nomura, K. Takahashi, Crystal size distribution of aluminum potassium sulfate in a batch crystallizer equipped with different type of impeller, J. Cryst. Growth 191 (1998) 178–184.

[3] P. Penicot, H. Muhr, E. Plasari, J.S. Villermaux, Influence of the internal crystallizer geometry and the operational conditions on the solid product quality, Chem. Eng. Technol. 21 (1998) 507–513.

[4] Z. Sha, M. Lauhi-kultanen, K. Ogawa, S. Palosaari, The effect of mixedness on crystal size distribution in a continuous crystallizer, J. Chem. Eng. Jpn. 31 (1988) 55–60.

[5] K. Ogawa, An expression of quality of mixedness for multicomponent batch mixing, Kagaku Kougaku Ronbunshu 10 (1984) 261–264 (in Japanese).

[6] J. Franke, A. Mersmann, The influence of the operational conditions on the precipitation process, Chem. Eng. Sci. 50 (1995) 1737–1753.

[7] H. Griffiths, Mechanical crystallization, J. Soc. Chem. Ind. 44 (1925) 7T.

[8] J.W. Mullin, J. Nývlt, Programmed cooling of batch crystallizer, Chem. Eng. Sci. 26 (1971) 369–377.

[9] A.G. Jones, J.W. Mullin, Programmed cooling crystallization of potassium sulphate solution, Chem. Eng. Sci. 29 (1974) 105–118.

[10] W.P. Moore, Optimize batch crystallization, Chem. Eng. Prog. (1994) 73–79.

[11] D. Jagadesh, N. Kubota, M. Yokota, A. Sato, N.S. Tavare, Large and mono-sized product crystals from natural cooling mode batch crystallizer, J. Chem. Eng. Jpn. 29 (1996) 865–873.

[12] D. Jagadesh, N. Kubota, M. Yokota, N. Doki, A. Sato, Seeding effect on batch crystallization of potassium alum under natural cooling mode and a simple design method of crystallizer, J. Chem. Eng. Jpn. 32 (1999) 514–520.

[13] N. Doki, N. Kubota, A. Sato, M. Yokota, Scale-up effect on seeded batch cooling crystallization of potash alum, AIChE J. 45 (1999) 2527–2533.

[14] A.G. Jones, A. Chianese, J.W. Mullin, in: S.J. Jancic, E.J. de Jong (Eds.), Industrial Crystallization, Vol. 84, Elsevier, Amsterdam, 1985, pp. 191–195.

[15] A.G. Jones, A. Chianese, Fines destruction during batch crystallization, Chem. Eng. Commun. 62 (1987) 5–16.

[16] S. Rohani, N.S. Tavare, J. Garside, Control of crystal size distribution in a batch cooling crystallizer, Can. J. Chem. Eng. 68 (1990) 260–267.

[17] H. Noda, H. Yamaji, N. Kuratani, T. Mukaida, M. Ohuchi, Challenge to a process revolution “Wall Wetter” Kagaku Kougaku (Chem. Eng.) 63 (1999) 295–296 (in Japanese).

[18] S.L. Makee, R.A. Williams, A. Boxman, Development of solid–liquid mixing models using tomographic technique, Chem. Eng. J. (Lausanne) 56 (1995) 101–107.