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Agglomeration Control of 1,4-Diazabicyclo (2.2.2)Octane Crystals by Operating Variables in Cooling Crystallization

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The agglomeration of crystallized 1,4-diazabicyclo(2.2.2)octane was investigated in a turbulent agitated semibatch reactor. To modify the agglomeration of 1,4-diazabicyclo(2.2.2)octane, the crystallization operating factors, including the stirring rate, cooling rate, feed concentration, and aging, were studied. The mean particle size of the 1,4-diazabicyclo(2.2.2)octane in the product suspension increased with decreasing feed concentration and cooling rate. The products were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The product obtained at the condition of crystalline concentration of 1.80 g/mL, stirring rate of 200 rpm, and cooling rate of 0.3 K/min is hard to agglomerate.

Keywords Agglomeration control; cooling crystallization; 1,4-diazabicyclo(2.2.2) octane crystals; operating variables

Introduction

1,4-diazabicyclo(2.2.2)octane (CAS No.: 280–57–9, DABCO) is a pure white powdered crystal under standard conditions. DABCO exhibits certain unusual properties which are due to its bicyclic or "cage" structure [1]. It is an important intermediate and end product in the chemical industry, which is used mainly as a catalyst in the production of polyurethane foams [2]. A number of methods are known in the literature for preparing and isolating this compound as a product of commercially acceptable purity [3]. Typically, DABCO is isolated from the reaction mixture as a white crystalline hygroscopic product containing a small amount of byproduct amine compounds. In the final purification step, the DABCO recrystallizes from solution [4, 5]. The purified commercial powdery crystalline DABCO product of the desired low content of organic amine impurities, when stored in commercial-size drums for even short periods, particularly in moderately warm environment, tended to develop a caking or blocking problem.

Cooling crystallization is frequently used for the separation and purification of materials in the fine chemical, food, pharmaceutical, and biochemical industries. However, the benefits of this type of crystallization are invariably frustrated by agglomeration that

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entraps the impurities and mother liquor among the agglomerated particles. Thus, crystal agglomeration has drawn much attention in crystallization studies [6, 7]. Agglomeration degree of crystals depends on the particle size and elevated agitation reduces the agglomeration degree of big particles. Particle mean size exhibits a maximum with increasing agitation intensity, which is explained from the perspective of antisolvent dispersion and crystal agglomeration/disruption [8–10].

The crystal size distribution (CSD) is one of the important factors in the agglomeration. Accordingly, the present study examined the influence of the crystallization operating variables on agglomeration, including stirring rate, cooling rate, and concentration of crystalline solution of DABCO crystals produced using the cooling method. In addition, the role of aging on crystal size distribution was also investigated.

Experimental Section

White crystalline TEDA powder was obtained from Shijiazhuang Hejia Health Productions Co., Ltd., China, and had a melting point of (159.25 ± 0.5) K. Its mass fraction purity, determined by gas chromatography (GC, SP 6890 with an FID detector, 30 m CP-Sil-5 Chrompack column, i.d. 0.25 mm, coating 0.25 lm, column temperature 200°C, injector temperature 200°C, and FID temperature 250°C), is higher than 99.75%. It was dried under a vacuum at 313.15 K for 24 h and stored in a desiccator. The ethanol used for experiments were obtained from Tianjin Chemical Reagent Co., Ltd., Tianjin (City), China, which has a minimum purity of 99.5 mol% [11].

The crystallization conditions were modified in terms of stirring rate, cooling rate, and concentration of the crystal. As such, the stirring rate was varied from 150, 200, and 250 rpm, the cooling rate was varied from 0.5, 0.3, and 0.2 K/min, and the concentration of products was varied from 2.30, 2.01, and 1.80 g/mL. The size distributions of immediate and 2-h aging sampling after cooling crystallization were tested under the same condition of stirring rate (200 rpm), cooling rate (0.3 K/min), and concentration of crystalline solution (1.80 g/mL).

After crystallization, three samples of the products in the reactor were quickly filtered using vacuum, and then the particles were redispersed in pure acetone to measure the particle size distribution (Mastersizer/E, Malvern Instruments, Malvern, U.K.). The sample of DABCO products was examined by scanning electron microscopy (SEM, Leica SEM, Stereoscan 400, Leica Microsystems AG, Wetzlar, Germany) and X-ray powder diffraction (XRD, Rigaku D/MAX 2500, JP).

Results and Discussion

Effects of Stirring Rate

Stirring rate is a significant parameter which affects hydrodynamics in the crystallizer. A low stirring rate may weaken dispersal and mixing in the facility and is prone to local supersaturation. High supersaturation is favorable for nucleation while against crystal growth, which induces primary nucleation and decreases the size of local crystals. A high stirring rate may reinforce the turbulent shearing force, which enhances the collision possibility and strength between crystal and propeller, crystal and crystal, and crystal and wall. The particles are easy to break down and the rate of secondary nucleation increases, which leads to the development of smaller crystal size as well. Nevertheless, it may be relatively regular in this case, i.e., the coefficient of variation (CV) decreases.

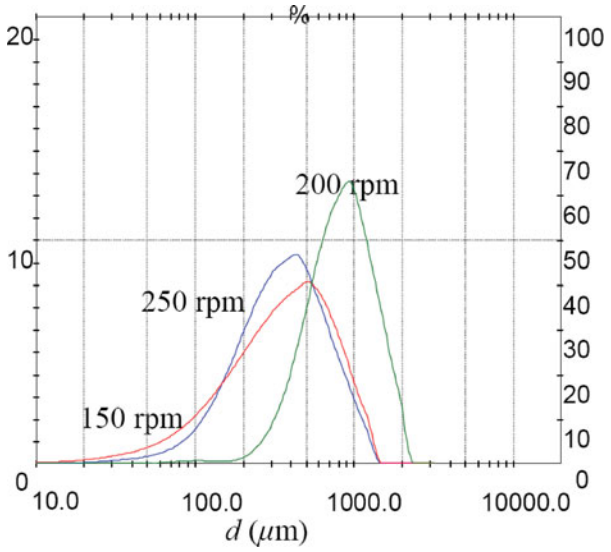


Figure 1. Effects of stirring rate on CSD graph at the concentration of crystalline solution of 1.80 g/mL and the cooling rate of 0.3 K/min.

Figure 1 shows the pore distribution, as a function of stirring rate whereas all other parameters are held constant. It can be inferred from the earlier figure that generally the particle size of the final product varies dramatically with examined stirring rates. The ideal particle size and distribution of 1,4-Diazabicyclo[2.2.2]octane crystal product can be obtained when the stirring rate is 200 rpm.

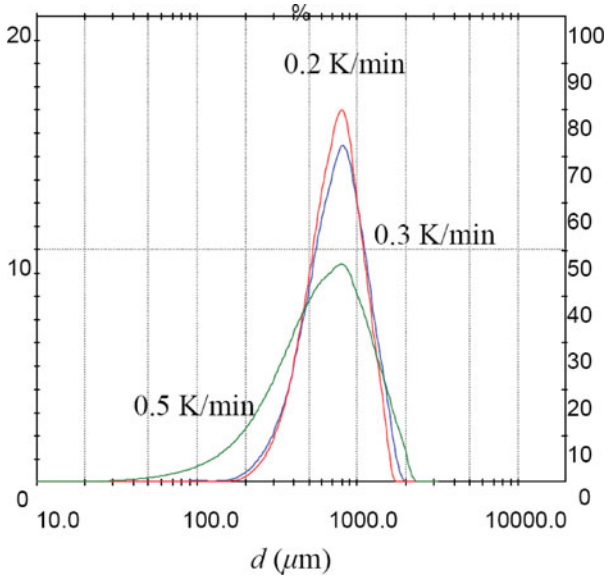


Figure 2. Effect of cooling rate on the CSD at the concentration of crystalline solution of 1.80 g/mL and stirring rate of 200 rpm.

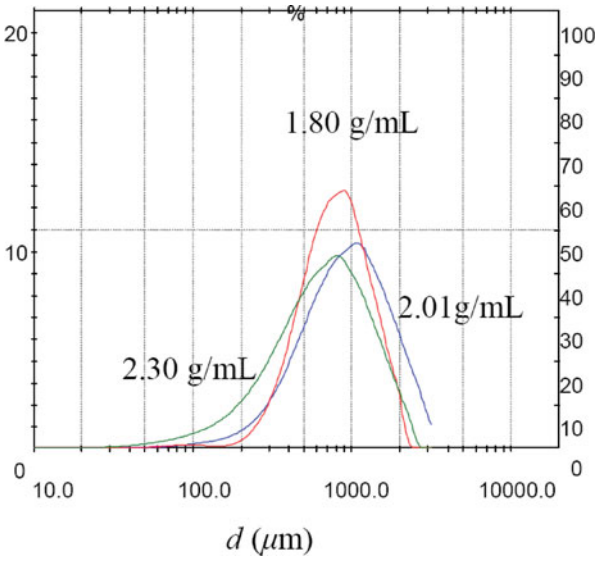


Figure 3. Effects of concentration of crystalline solution on the CSD at the cooling rate of 0.3 K/min) and the stirring rate of 200 rpm.

Effects of Cooling Rate

It is the supersaturation that drives the crystallization process. It's of the greatest importance during the quality control of the crystal product. Constant supersaturation is generally the goal of process control during crystallization. The emergence of supersaturation in cooling–crystallization is mainly provided by cooling. Therefore, the higher the cooling rate, the higher the supersaturation, and the greater the driving force of nucleation.

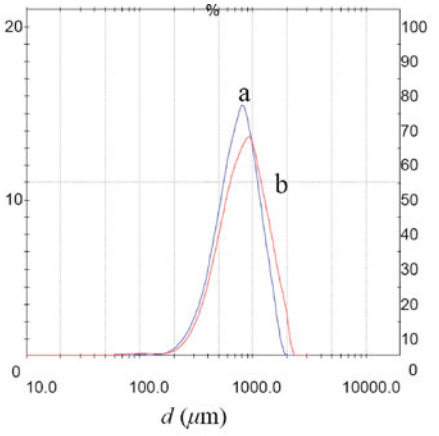
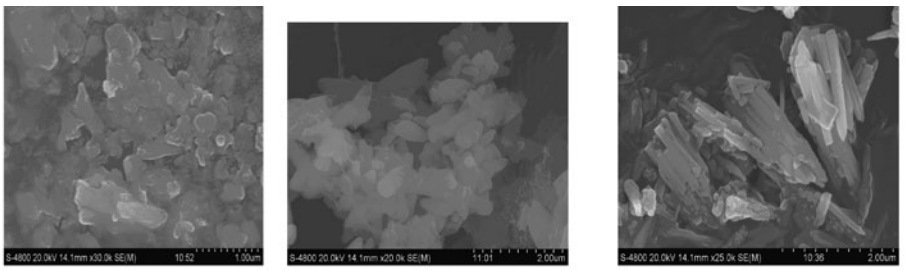


Figure 4. Effect of aging on the CSD at the condition of the stirring rate (200 rpm), cooling rate (0.3 K/min), and concentration of crystalline solution (1.80 g/mL).

As shown in Fig. 2, there is a significant change in size distribution along with the cooling rate. The worst primary size and size distribution of the crystal are observed when the cooling rate is 0.5 K/min. When it comes to 0.3 K/min and 0.2 K/min, both primary sizes are fairly good and acceptable size distribution of crystal products are obtained whose CSD indicators are close. Based on a comprehensive consideration of production efficiency and crystallization time, 0.3 K/min is selected as the cooling rate.

Effects of Concentration of Crystalline Solution

As shown in Fig. 3, changes in crystal size of the final product vary with changes in initial concentration. In the experimental condition, the primary particle size decreases as initial concentration increases. This may be derived from the high suspension density of the crystalline liquid under increasing initial concentration. High suspension density enhances the collision among particles as well as between crystals and internal parts of the agitator and crystallizer, which is favorable for secondary nucleation and leads to decreasing



(a) (b) (c)

a: crystalline concentration of 3.20 g/mL, stirring rate of 200 rpm, and cooling rate of 0.3 K/min

b: crystalline concentration of 1.80 g/mL, stirring rate of 300 rpm, and cooling rate of 0.3 K/min

c: crystalline concentration of 1.80 g/mL, stirring rate of 200 rpm, and cooling rate of 0.3 K/min

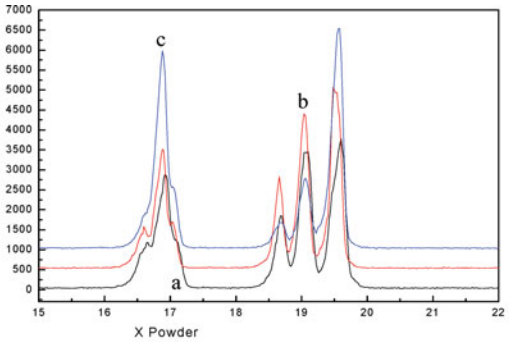
Figure 5. SEM images of 1,4-diazabicyclo(2.2.2)octane.

primary particle size in size distribution. In order to obtain appropriate crystal size and size distribution, 1.80g/mL was chosen as the optimum initial concentration.

Effects of Aging

Aging indicates that when solid particles disperse in its saturated solution, small ones tend to dissolve while soluble solute precipitates on the large ones, that is, small particles dissolve while large ones expand. In principle, it makes product size distribution narrower. The driving force of aging is the solubility difference between large and small particles in solution.

It can be inferred from Fig. 4 that no sensible difference on size distribution was observed when changing the aging time. The primary crystal size from immediate sample after crystallization is in the same range of that from aging for 2 h. Viewing from CV value,



a: crystalline concentration of 3.20 g/mL, stirring rate of 200 rpm, and cooling rate of 0.3 K/min

b: crystalline concentration of 1.80 g/mL, stirring rate of 300 rpm, and cooling rate of 0.3 K/min

c: crystalline concentration of 1.80 g/mL, stirring rate of 200 rpm, and cooling rate of 0.3 K/min

Figure 6. XRD patterns of 1,4-diazabicyclo(2.2.2)octane.

the size distribution after aging is relatively narrower. In practice, this step can be omitted in order to save operation time.

Effects of Crystallization Process to 1,4-Diazabicyclo[2.2.2]octane Agglomeration

With the function of excessive driving force, 1,4-Diazabicyclo[2.2.2]octane tends to agglomerate, leading to lumps of products, as shown in Figs. 5(a) and (b). Applying the condition of crystalline concentration of 1.80 g/mL, stirring rate of 200 rpm, and cooling rate of 0.3 K/min, products were obtained without obvious agglomeration, as shown in Fig. 5(c).

Powder X-ray diffraction was applied to examine these samples. Their crystalline structures and phases were analyzed, as shown in Fig. 6. It can be inferred from the previous figure that the phases of peaks at the same diffraction angle are coincident, so are their shapes, which refers to the same interior crystal structure. Moreover, the intensity of diffraction peaks of sample c is obviously higher than that of sample a and sample b, meaning the higher crystallinity of sample c, compared to sample a and sample b.

Conclusions

The effects of factors in cooling crystallization to the quality of product were studied. It can be concluded that the optimum process is stirring rate of 200 rpm, cooling rate of 0.3 K/min, and initial crystalline concentration of 1.80 g/mL. Under this condition, the apparent quality of product has been obviously improved and 1,4-Diazabicyclo[2.2.2]octane product is less possible to agglomerate. Both agglomeration time and duration of 1,4-Diazabicyclo[2.2.2]octane are prolonged.

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