

## The Influence of Process Parameters on the Granulometric Properties of Pentaerythritol in Batch Crystallization

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Pentaerythritol is a widely used organic chemical; which is used in the production of high – quality alkyd resins, lacquers, lubricant additives. The quality of obtained crystals is influenced by many factors that determine its granulometric properties. Selection of the operating conditions which result with desired crystal size distribution is very important. Commonly, the unseeded cooling crystallization is controlled by selecting the appropriate cooling profile.

Batch crystallizations of pentaerythritol from water solution were carrying out at four different cooling profiles: natural, linear, optimal and step. Crystal size distribution can be explained by the supersaturation changes during the experiment. The step and optimal cooling profile achieves a high level of maximum supersaturation which causes agglomeration and crystals with wide and bimodal size distribution. At linear cooling profile, supersaturation is increased rapidly and reached maximal value at nucleation point, afterwards supersaturation decreased. Obtained supersaturation isn't too high, and resulted crystals aren't agglomerate, but on the other hand the wide crystal size distribution is obtained. Optimal cooling profile provides the constant, not too high driving force for longer period of time, and resulted crystals meet requested characteristics – the narrow crystal size distribution without agglomeration.

Further more, the granulometric characteristics of obtained crystals are influenced by retention time and mixing intensity. Extended retention time causes obtaining of bigger crystals, when decreasing of mixing speed, because of unfavorable hydrodynamic conditions – low mixing rate, causes obtaining of smaller crystals. The shape of crystals isn't changed regardless of the cooling profile.

### 1. Introduction

Crystal size distribution (CSD) control is particularly important in fine chemistry where batch crystallizations are generally carried out to obtain products with high value added used afterwards in different formulations. In order to produce the desired product size, the batch process must be controlled at certain operating conditions. In batch cooling crystallization without seeding, the determination of the operating conditions includes the specifications of the cooling profile, hydrodynamics conditions and batch time.

Significant improvement in CSD and operation can be achieved by controlling supersaturation levels during the batch crystallization process. Programmed cooling could be designed so that the optimum rate of supersaturation generation could be achieved at all stages of the batch run. Some of results demonstrated that supersaturation control during a batch run was beneficially for increasing crystal size, reducing the batch cycle time and markedly narrowed the CSD (Myerson, 2002).

In this study, batch crystallization of pentaerythritol from water solution was conducted at four different cooling profiles, two different intensity of mixing and different batch time.

## 2. Experimental

All experiments were carried out in a jacketed batch crystallizer. The crystallizer is equipped with the four-pitched blade impeller and four wall baffles (width of about 1/12 of the vessel), and thermostat. The inner diameter of crystallizer (flat bottom) is 0.1 m. The working volume is 0.73 dm<sup>3</sup>. The four-pitched blade impeller used in this study draws the material to be mixed from above, and generates axial flow in the vessel. During experiments concentration of solution was determinate by gravimetric method. . In defined time intervals the samples were taken with syringe filter needle. Mass content pentaerythritol in water solution was determined by difference between the samples weight before and after drying. Samples were weighted on the balance (500 g +/- 0.0001 g).

A saturated solution of pentaerythritol was prepared by dissolving definite amount of pentaerythritol in the distilled water. The initial concentration of solution (0.17 mass % PE in water solution) was the same for all experiments. Solution was then heated above the equilibrium temperature to ensure that all amount of PE is dissolved. To avoid presence of any impurities clear solution was filtered before putting it into crystallizer. Temperature of solution was measured by means of digital thermometer. The solubility curve was determined experimentally:

$$w_s = 0.0368 \cdot \exp^{0.025 \cdot T} \quad (1)$$

### 2.1 Cooling profile

Batch crystallization of aqueous solution of pentaerythritol has been carried out with four different cooling profiles: natural, linear, optimal and step. The cooling profiles, shown of Figure.1, were controlled by circulating water from the thermostat (*Julabo F12*).

Natural cooling profile was performed by pumping cooling water of a constant temperature of 20 °C through the jacket. Saturation aqueous solution of pentaerythritol was cooled from above 60 to 35°C (Doki et al., 2001).

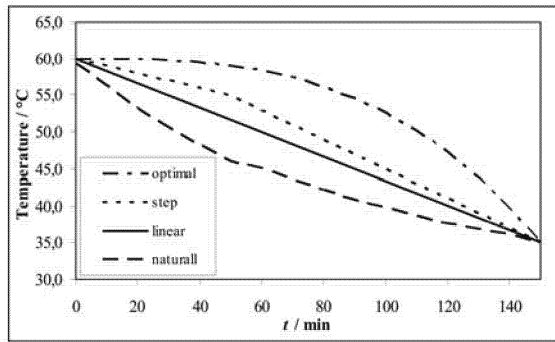


Figure.1. Cooling profiles followed in batch cooling crystallizations

At optimal cooling profile temperature was lowered along with controlled cooling curve: (Hojjati et al., 2005)

$$\frac{(T(t) - T_0)}{(T_0 - T_{fin})} = \left(t / t_{fin}\right)^4 \quad (2)$$

The step cooling profile was significantly lower in the first phase before nucleation process, after that the cooling rates increased. In the first phase cooling rate was 5.8 °C/h and in the second phase 12.8°C/h. Cooling rate at linear cooling profile was 10°C/h. Temperature was lowered from 60 °C to 35 °C and the batch time was 150 minutes for all cooling profiles.

Crystal size distribution was determined by the sieve analysis and their shape by light microscope *Motic 2000*.

### 3. Results and discussion

Figure 2. shows the dependence of supersaturated variation and cumulative CSD to different cooling profiles.

During natural and linear cooling rates supersaturation increases sharply until reaching the nucleation point, than decreases (Doki et al. 2001.).

During step and optimal cooling rate, supersaturation is maintained at lower values for longer period of time which provides good conditions for crystal growth (Qu et al., 2004).

Obtained CSD are bimodal for all cooling rates profiles (4 cooling profiles), which shows the secondary nucleation regardless different cooling rate.

The narrowest CDS and the smallest crystals were obtained by the optimal cooling rate. All cooling rates last equally, 150 min, but during optimal cooling profile nucleation occurs at the latest, (aprox. 60 min). It shows that crystals obtained during optimal cooling rate grows for shorter period of time and CSD is moved to finer fractions, although the most favorable conditions for the crystal growth was achieved.

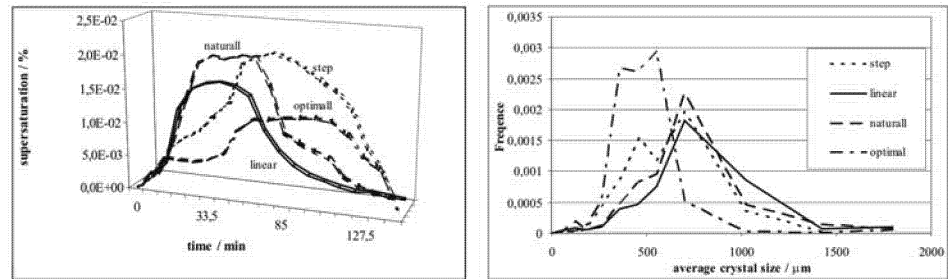


Figure.2. The influence of the cooling profile on the granulometric properties of crystals: a) supersaturation; b) CSD

In order to determine influence of mixing intensity on obtained crystals granulometric properties, additional experiments were carried on. For linear and step cooling rate additional experiments have been performed at 100 rpm. At both cooling rates, during lower mixing intensity, smaller crystals were obtained, although supersaturation level wasn't changed significantly (Fig. 3.). Some lower supersaturation was achieved with lower mixing intensity for both cooling rates, and in accordance to time of achieving maximal supersaturation, could be concluded that nucleation occurred on similar temperatures. Low mixing intensity caused unwanted hydrodynamics conditions for crystal growth. When the crystals achieved a certain size (become to heavy), felled on the bottom on the reactor where couldn't grow properly. CSD are shift toward smaller particles.

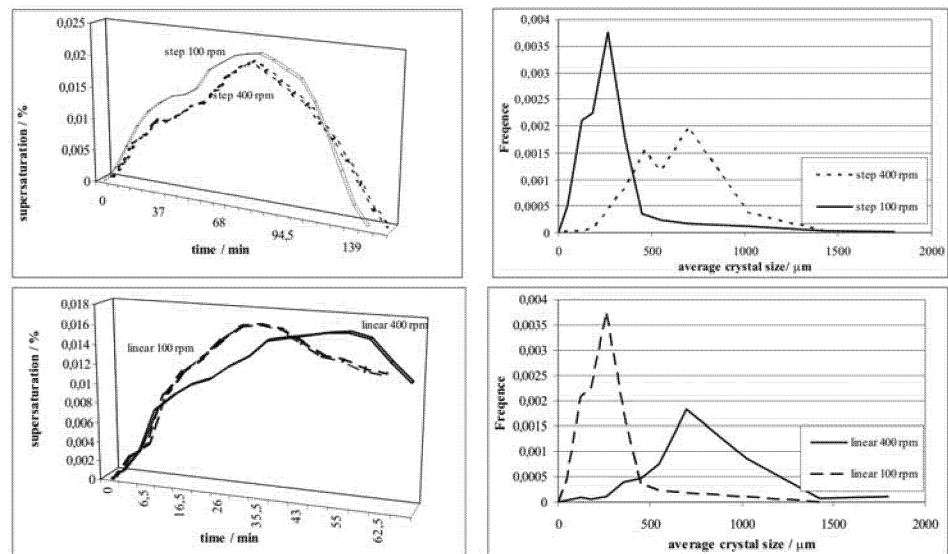


Figure.3. The influence of the mixing rate on the granulometric properties of crystals: Step cooling rates a) supersaturation; b) CSD; linear cooling rates c) supersaturation; d) CSD

The applicability of the logarithm-normal and Rosin-Rammler-Sperling-Bennett functions for the obtained crystal size distribution was tested. Better level of correlation was achieved for RRSB function.

On the figure 4. parameters of RRSB function are shown; location parameter,  $x_{63}$  and distribution parameter,  $n$ . The granulometric characteristics of obtained crystals are influenced by retention time and mixing intensity. Extended retention time causes production of bigger crystals  $x_{63}$ , and wider CSD (Hash et al., 2008). The wider CSD confirmed that secondary nucleation occurs.

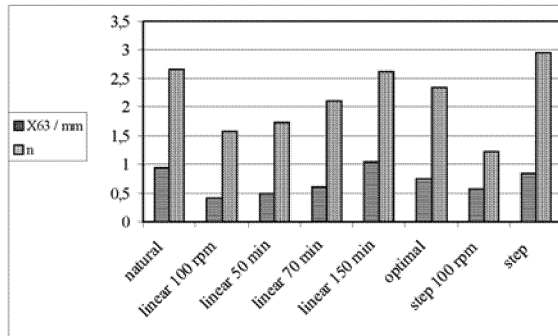


Figure.4. Parameters of RRSB function for all conditions

Figure 5. shows shapes of obtained crystals for all cooling rates. The basic shape of the crystals wasn't changed regardless cooling rates, but during step and natural cooling rates formation of the agglomerates was noticed. High supersaturation levels (Figure 2) were achieved for the mentioned cooling profiles. Consequently, crystals tend to form agglomerates.

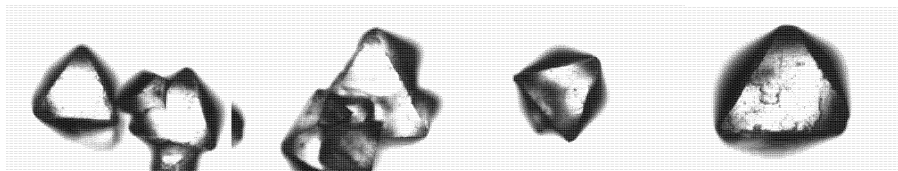


Figure.5. pentaerythritol crystals taken on light microscope a) natural; b) step; c)optimal; d) linear cooling rates

#### 4. Conclusions

The step and natural cooling profile achieves a high level of maximum supersaturation which causes agglomeration and crystals with wide and bimodal size distribution. At linear cooling profile, obtained supersaturation isn't too high, and resulted crystals aren't

agglomerate, but on the other hand the wide CSD is obtained (because of the secondary nucleation). Optimal cooling profile provides the constant, not too high driving force for longer period of time, and resulted crystals meet requested characteristics – the narrow crystal size distribution without agglomeration (reduced secondary nucleation) (Yang et al., 2006).

Further more, the granulometric characteristics of obtained crystals are influenced by retention time and mixing intensity. Extended retention time causes production of bigger crystals, when decreasing of mixing speed, because of unfavorable hydrodynamic conditions – low mixing rate, causes obtaining of smaller crystals. The shape of crystals isn't changed regardless of the cooling profile.

## 5. Symbols

$n$  – distribution parameter of RRSB function

$t$  – time, min

$T$  – temperature, °C

$w$  – mass fraction, %

$x$  – location parameter of RRSB function, mm

## References

- Doki N., Kubota N., Sato A., Yokota M., 2001, Effect of cooling mode on product crystal size in seeded batch crystallization of potassium alum, *Chem. Eng. J.* 81, 313-316.
- Hash J., Okorafor O.C., 2008, Crystal size distribution (CSD) of batch salting-out crystallization process for sodium sulphate, *Chem. Eng. and Process.* 47, 622-632.
- Hojjati H., Rohani S., 2005, Cooling and seeding effect on supersaturation and final crystal size distribution (CSD) of ammonium sulphate in a batch crystallizer, *Chem. Eng. and Process.* 44, 949-957.
- Myerson A.S., 2002, *Handbook of Industrial Crystallization*, Butterworth-Heinemann, Boston
- Qua H., Pöllänen K., Louhi-Kultanen M., Kilpiöb T., Oinasc P., Kallas J., 2005, Batch cooling crystallization study based on in-line measurement of supersaturation and crystal size distribution, *J. Crystal Growth*, 275, e185-e1862.
- Yang G., Louhi-Kultanen M., Sha Z., Kallas J., 2006, Determination of Operating conditions for Controlled Batch Cooling Crystallization, *Chem. Eng. Technol.* 29, 200-205.