Kinetics of the seeded batch cooling crystallization

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The influence of the seed size, loadings and the batch time on crystallization kinetics and granulometric properties of the obtained pentaerythritol crystals has been investigated. Experiments have been performed in the laboratory batch cooling crystallizer (Rushton dimensions). The solubility curve and the metastable zone width have been determined at the defined cooling profile. In order to compare the obtained results, an experiment of unseeded crystallization was performed. The experiments have been performed within the metastable zone width.

For estimation of the growth kinetics, from the desupersaturation curve during batch seeded experiments, the Garside et al. method was used. The crystal growth is controlled by the surface integration (polynuclear or birth and spread mechanism of grow), since the values of the exponent of growth, g, are very high (g>2).

The crystal size distribution can be approximated with the RRSB function. The smaller seed size and lower seed loadings leads to a uni-modal size distribution of the final crystals and the higher crystal growth rate. Decreasing the batch time from 80 min to 35 min, improves the final crystal size distribution. (unimodal for lower seed loadings).

1. Introduction

Crystallization is one of the most complex separation processes due to numerous simultaneous processes (momentum, heat and mass transfer, phase change, dissolution, agglomeration, breakage,...) (Myerson, 2002). The obtained crystals are of the specific purity and granulometric characteristics (shape, size, and crystal size distribution). The crystal quality is very sensitive to cooling rate, mixing intensity, system geometry, type of crystallization process and impeller used for mixing. Crystals of the desirable granulometric properties can be obtained only if the thermal and the hydrodynamic conditions are selected very carefully (Gates, 2003). In order to minimize excessive primary nucleation, crystallization has to be conducted within the metastable zone width. Excessive nucleation yields too many small crystals and an unacceptable crystal size distribution. For the same reason, secondary nucleation (contact nucleation, breakage, mixing) has to be suppressed as much as possible (Gates, 2003). At the optimal process conditions, regular shape crystals with the unimodal narrow size distribution will be produced (Chong et al, 2004). Hydrodinamic conditions have to

provide good flow of the solution past the heat transfer surfaces and satisfactory handling of the crystals being formed (Mersmann, 1988). In other words, to support crystal growth, it is very important that crystal surface area is accessible at locations where the supersaturation is generated.

1.1 Seeded crystallization

The crystallization process (nucleation and growth) can be controlled by adding a certain number of seed crystals of a uniform size, L_s, in the crystallizer at the saturation temperature (Myerson, 2002). Process has to be conducted at low supersaturation lewel, within the metastable zone width. Seeded crystallization process is influenced by the way in which the seeds are produced, seeding policy, seed quantity and loadings (Hojjati et al, 2005). The size and mass of seeds influences the crystal size distribution and the crystal growth rate (Lung-Sommariba et al). Seeds must often be very small and often are produced by milling. Seed size distribution has to be narrow. If the supersaturation is maintained below the metastable zone upper limit, than the spontaneous nucleation will be avoided and only the seed crystals will grow. Consequently, produced crystal size distribution will be narrow. Some materials tend to form agglomerates. In that case crystals with less uniform size distributions (bimodal) will be obtained. Required seed mass can be calculated by the equation (Lung-Sommariba et al):

$$\frac{m_c}{m_s} = \left(\frac{L_c}{L_s}\right)^3 \tag{1}$$

where

m_c and m_s are the produced crystals and seed mass,

L_c and L_s are the final crystal and seed size.

The value of the L_c/L_s has to be between 1 and 5 (seed mass represents 2-5 % of the final theoretical mass of crystals that can be obtained for the desired working conditions).

1.2 Estimation of crystal growth kinetics

Garside and al., 1982, proposed a method for estimation of the growth kinetics from the desupersaturation curve. The method assumes that no nucleation occurs, so the solution concentration change is due to crystal growth only. If the secondary nucleation is suppressed, kinetic parameters, the power g and constant k_g, can be estimated from the equations:

$$g = \frac{2 \cdot F \cdot \Delta C_0}{3 \cdot \rho \cdot \overline{L}_0 \cdot A_{T0}} + \frac{\Delta C_0 \cdot \Delta \ddot{C}_0}{\Delta \dot{C}_0} \tag{2}$$

$$k_g = \frac{-\Delta \dot{C}_0}{A_{T0} \cdot \Delta C_0^g} \tag{3}$$

ΔC_0 - superaturation at time zero; $\Delta \dot{C}_0, \Delta \ddot{C}_0$ - first and second derivatives of the desupersaturation curve at time zero; F – shape factor ratio (β/α); $\overline{L}_0$ - average seeds size; A_{T0} – seeds surface area at time zero.

The derivatives $\Delta \dot{C}_0, \Delta \ddot{C}_0$, are obtained by fitting the desupersaturation curve to a polynomial of the form:

$$\Delta C = a_0 + a_1 \cdot t + a_{2 \cdot t^2}$$ (4)

So that $\Delta C_0 = a_0$, $\Delta \dot{C}_0 = a_1$ and $\Delta \ddot{C}_0 = 2 \cdot a_2$.

2. Experimental

Batch cooling crystallization of the pentaerythritol from the aqueous solution was carring out in the Rushton dimensions crystallizer equipped with four baffles and axial flow impeller (four pitched blade impeller). The size and the mass of the seed was selected and calculated from the average crystal size obtained by unseeded experiment. Finer fractions of industrially prepared pentaerythritol were used as seed. Defined mass of seed was introduced to the crystallizer at the saturation temperature. All experiments have been carried out at the same linear cooling rate (16 °C/hr). The solubility curve and the metastable zone width were determined experimentally. Since the metastable zone width is very narrow at higher mixing rates, mixing rate was set to 400 rpm. Produced crystals were rinsed with cold acetone. Crystal size distribution was determined by the sieve analysis and their shape by light microscope.

3. Results and discussion

The influence of the mass and the average size of the seed, and the batch time on the granulometric properties of the obtained pentaerythritol (PET) crystals and the growth kinetics have been investigated on the laboratory scale. Granulometric properties of the crystals produced by the seeded crystallization were compared with the crystals produced by unseeded crystallization. During all experiments concentration of the solution was changed within the metastable zone width, so the primary nucleation was suppressed. Small amount of new nuclei were produced due to secondary nucleation (contact). The highest value of the maximal supersaturation was achieved for the unseeded experiments (Table 1) because of secondary nucleation. Increase of the seed size and decrease of the seed mass, cause decrease of the maximal supersaturation. During seeded crystallization solution is at a relatively low supersaturation so that growth of the seed crystal is preferred to nucleation of new crystals.

Table 1. Maximal supersaturation levels and kinetic parameters

L_s, µm	Seed mass, g	Initial seed surface area, m^2	Maximal supersturation, kg PET/kg water	k_g	g
Unseeded	0	-	0,0456	-	-
90	0,55	$0,26 \cdot 10^{-1}$	0,0167	$1,32 \cdot 10^{38}$	25,60
90	1,60	$0,76 \cdot 10^{-1}$	0,0215	$6,26 \cdot 10^{-5}$	1,79
125	1,80	$0,62 \cdot 10^{-1}$	0,0146	$2,93 \cdot 10^{6}$	6,81
180	4,50	$1,07 \cdot 10^{-1}$	0,0134	$6,65 \cdot 10^{-5}$	2,97

For estimation of the growth kinetics, from the desupersaturation curve during batch seeded experiments, the Garside et al. method was used (equations 2 and 3). The crystal growth is controlled by the surface integration (polynuclear or birth and spread

mechanism of grow) (Myerson, 2002), since the values of the exponent of growth, g, are very high ($g>2$) (Table 1). Both parameters decrease with the increase of the seed size and mass. The crystal growth rate is inversely proportional to seed size and loadings.

The influence of the seed mass and size on the crystal size distribution is shown on figure 1. Only for the smallest seed size (90 µm) the unimodal narrow CSD is obtained. Since the growth rate depends on the seed size additional nucleation (contact, breakage) occurred. This additional nucleation is very intense, so large numbers of nuclei were formed momentarily, resulting with broadening of the CSD with the increase of the seed size. Unseeded experiments results with the widest CSD due to high level of supersaturation and consequently very intense nucleation.
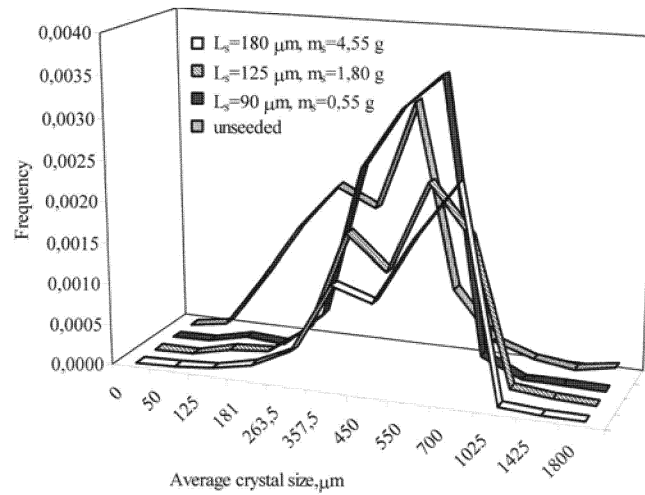

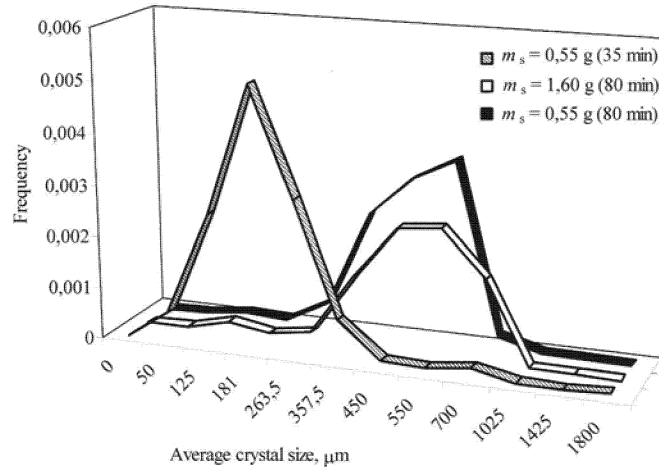Figure 1. The influence of the seed size and mass on the CSD (τ=80 min)

Figure 2. The influence of the seed mass and the batch time on the CSD (L_s=90 µm)

In order to produce crystals with unimodal narrow size distribution, the batch time was decreased from 80 to 35 min. Size and quantity of the produced crystals were smaller, and unimodal CSD's were obtained for all seeded experiments. Bimodal CSD was obtained only for unseeded experiment, which means that secondary nucleation occurs at short batch time also (process was also carried out within the metastable zone width). The initial surface area of the seeds grows with the quantity of seeds added to the solution (Table 1). Larger surface competes for grow, higher supersaturation was achieved and consequently bigger crystals were produced. Modal crystal diameter is pretty much the same for all experiments at the given batch time (~180 mm for 35 min, and 550 for 80 min), but the mode fraction is highest for the smallest seeds.

The applicability of the LN and RRSB function for the CSD description was tested. Since both functions can be used for description of the CSD (almost the same correlation coefficient ~ 0,98), another criteria was used to select the appropriate mathematical function. Based on the evaluated (from the LN and RRSB function parameters) and experimental values of the specific surface area the adequate function was selected (Table 2.). Since the evaluated values for the LN function differs highly from the calculated values, RRSB function can be used for description.

Table 2. Specific surface area of the obtained crystals for two different experiments duration

$\tau = 35$ min	S_m, cm^2/g			$\tau = 80$ min	S_m, cm^2/g		
L_s, μm	Calculated	LN	RRSB	L_s, μm	Calculated	LN	RRSB
Unseeded	200,42	846,15	164,62	Unseeded	150,23	572,38	110,40
90	275,61	2090,80	297,75	90	92,43	241,52	65,89
125	274,83	3114,45	330,24	125	102,56	284,89	72,87
180	251,02	1555,16	248,74	180	73,14	234,86	57,98

Table 3. RRSB function parameters

$\tau = 35$ min			$\tau = 80$ min		
L_s, μm	x_{63}, mm	n	L_s, μm	x_{63}, mm	n
Unseeded	0,484	1,73	Unseeded	0,602	2,11
90	0,376	1,37	90	0,782	3,56
125	0,390	1,28	125	0,726	3,14
180	0,490	1,47	180	0,924	3,12

Longer batch time and bigger amount of the seeds, results with CSD shifted toward coarser fractions (bigger x_{63}) (Table 3). The shape of the crystals is not influenced by the applied process condition (Figure3).
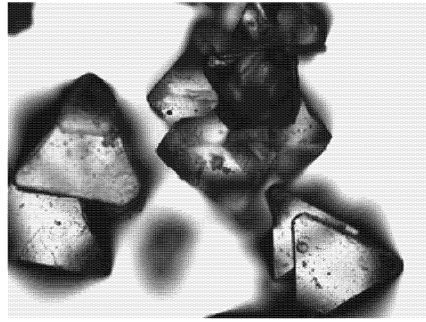
Figure.3. PET crystals taken on light microscope

4. Conclusions

More uniform CSD is obtained with shorter batch time and smaller amount of seeds added in the just saturated solution. The seed size and loadings strongly influences the crystallization kinetics parameters and the produced crystals size distribution. Maximal value of supersaturation is achieved during unseeded crystallization. Its value decreases with the increase of the average seed size, and the decrease of the amount of seeds. Higher values of the size and amount of seeds results with lowering the growth kinetic parameters (k_g and g). High values of parameter g correspond to polynuclear or birth and spread mechanism of growth. CSD can be approximated with the RRSB function. Longer batch time and bigger seed size and mass shifts the CSD to the coarser fractions. The shape of the crystals is not influenced by the applied process condition.

References

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