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Modelling and simulation of crystallization processes in a FC-Crystallizer.

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Abstract

While designing chemical engineering processes it is important to understand the processes kinetics. The kinetics of the process is determined by the formation of fragments and their subsequent growth. The formation of fragments has been controlled by secondary nucleation. There are various types of secondary nucleation, but the most important source of secondary nuclei in crystallisation is attrition. Attrition is also known as contact nucleation occurs as a result of crystal-target collision. The ultimate objective is to quantitatively describe a crystallization process, which is governed by the formation and growth of attrition fragments. The calculations can be used to select optimum process conditions for a product of certain quality.

Keywords: Suspension crystallization; Attrition mechanism; Crystallisation with fines dissolution

1. Introduction

Lately FC-Crystallizers are widely used in chemical engineering processes. They have many prerogatives in comparison with others crystallizers. In the near future to design and operate industrial crystallizers will be a helpful means. The purpose of this thesis is investigation, mathematical modelling and simulation of the crystallizartion process with the controlled attrition of crystals in the FC-Crystallizer under variation of the process conditions.

While designing chemical engineering processes it is important to understand the processes kinetics. The crystallization kinetics is determined basically by nucleation and growth kinetics. The nucleation of well dissolvable substances with small supersaturation and coarse crystals is controlled by attrition (secondary nucleation). There are various types of secondary nucleation, but the most important source of secondary nuclei in crystallisation is attrition. Attrition, also knows to as contact nucleation, occurs as a result of crystal-target collision. The ultimate objective is to quantitatively describe a crystallization process, which is governed by the formation and growth of attrition fragments. For these purpose 3 variants of the crystallization process are considered: process only with crystals attrition; crystallization with crystals attrition and their subsequent growth; crystallization with crystals attrition and fines dissolution. While modelling each of these processes was subdivided in separate zones. Mass, energy and population balances have been calculated for each zone. A recent paper presented en attrition model to explain the formation of fragments and their growth in suspension crystallizers (Gahn and Mersmann, 1997)[1]. This model was used for modelling of the secondary nucleation mechanism. The model considers the impact of crystals on a hard body and their abrasion. These attrition processes are described by mechanical properties of materials and conditions of attrition process. A number of experiments have been carried out with the crystallizing system ammonium sulphate under variation of the experiments conditions for each case of process in the lab-scale. The model parameters have been determined in the process of experimenting. With the help of these parameters simulations and calculations for various experimental conditions have been performed and compared with the experimental findings. With the help of these calculations optimum conditions of the process may be selected for a product of certain quality.

2. Mathematical modelling

The purpose of the modelling is an opportunity to predict the median crystals size and the particle size distribution. The particle size distribution is very significant, because it decisively influences downstream processes and correlates with certain product properties. In the future, modelling may be a helpful tool to design and operate crystallizers, which reliably meet the demands of the customers. Three variants of the crystallization process were quantitatively described and calculated:

1. Process only with crystals attrition.
2. Crystallization with crystals attrition and their subsequent growth.
3. Crystallization with crystals attrition and fines dissolution

While modelling each of the processes was subdivided in separate zones. The process only with crystals attrition was subdivided in attrition and mixing (crystallizer) zones. The process with crystals attrition and their subsequent growth was subdivided in mixing, cooling, attrition, growth (crystallizer) and sampling zones. The process with crystals attrition and fines dissolution was subdivided in mixing 1, separating, fines dissolution, cooling, attrition, mixing 2, growth (crystallizer) and sampling zones. Mass, energy and population balances have been made up and calculated for each zone.

For investigation and modelling of the crystallization processes a continuously operated 5-liter-FC-laboratory crystallizer has been installed. The crystallizer uses a particularly gentle pump to circulate the crystals at minimal attrition. By using this crystallizer the attrition behaviour of crystals has been investigated by imposing to them additional mechanical stress with the help of an impingement device implemented in the loop. This device consists of a nozzle and an orthogonal positioned cylinder as a target (Figure 1). The crystals attrition was being produced by their impingements with this cylinder.

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[1] Gahn, C., Mersmann, A., 1997, Theoretical prediction and experimental determination of attrition rates. Trans. Instn. Chem Engng, 75A, 125-131

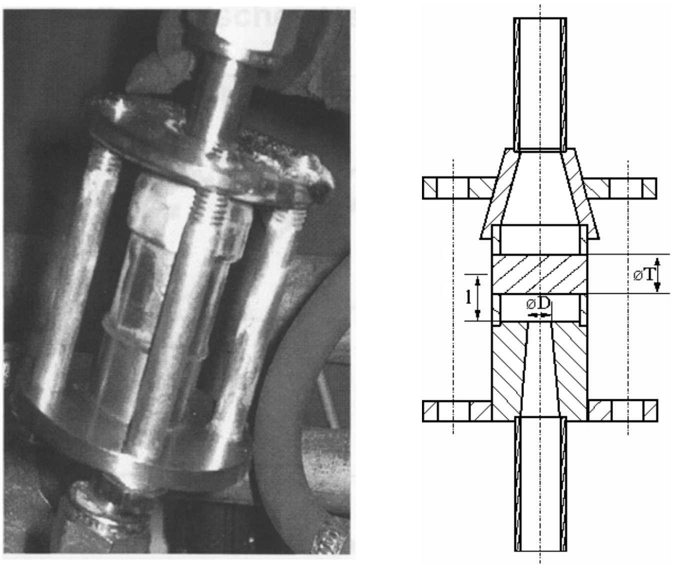

Figure 1. Device for crystals attrition.

As indicated above, all investigated cases of the crystallization process have the attrition zone. The modelling of this zone is the most complicated. It was necessary to describe quantitatively the attrition of crystals in a special device (see Figure 1). For the modelling of this zone the Gahn-model[1] was selected as a basis. The Gahn-model describes the attrition of crystals that happens in the case of their impingements with an impeller. A discussion about the assumptions made and the mathematical derivation of the model can be found in Gahn and Mersmann (1997)[2]. The possibilities and the limitations of the model can be found in Gahn and Mersmann (1999)[3]. The model of this zone is given bellow.

2.1 Mathematical model of the crystals attrition.

Equation of particle number conservation:

$$\frac{\partial n(L,t)}{\partial t} = \frac{1}{\tau}\left(n^{in}(L,t) - n(L,t)\right) + n_{attr}(L,t) \qquad (1)$$

The net source term as result of attrition, n_{attr}, is composed of three terms, which relate to the various steps of the attrition process: a sink term for the parent crystals that are subject to attrition, $n_{attr,1}$, a source term reflecting the birth of a single crystal, slightly smaller than the parent crystal, $n_{attr,2}$, and a source term for the attrition fragments, $n_{attr,3}$.

$$n_{attr}(L,t) = -n_{attr,1}(L,t) + n_{attr,2}(L,t) + n_{attr,3}(L,t) \qquad (2)$$

The sink term for parent crystals subject to attrition, $n_{attr,1}$, follows from:

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[1] Gahn, C., 1997, Crystals hardness and her influence on the kinetics in suspension crystallizers, PhD Thesis, TU Munchen, 145 (in German).

[2] Gahn, C. and Mersmann, A., 1997, Theoretical prediction and experimental determination of attrition rates, Trans. Instn. Chem Engng, 75A, 125-131.

[3] Gahn, C. and Mersman, A., 1999, Brittle fracture in crystallization processes part A and part B, Chemical Engineering Science, 54, 1273-1292.

$$n_{attr,1}(L,t) = \frac{1}{\tau}\eta(L)n(L,t)h(W_p(L) - W_{p,\min}) \quad (3)$$

The source term reflecting the birth of a single crystal, slightly smaller than the parent crystal, $n_{attr,2}$, is obtained by the following equation:

$$n_{attr,2}(L,t) = \frac{1}{\tau}\int_{L^{/}=L}^{\infty}\delta(L - L^{*}(L^{/}))\eta(L^{/})n(L^{/},t)h(W_p(L^{/}) - W_{p,\min})dL \quad (4)$$

In these equations, h, denotes the Heavyside function, δ, denotes the Dirac distribution, $L^{/}$, denotes the size of the parent crystal, L, denotes the size of an attrition fragment and, L^{*}, is the size of the parent crystal's remnant after the attrition event. The size of this remnant is a function of the parent crystal's size prior to the collision and the volume of the attrition fragments formed by that collision:

$$L^{*}(L^{/}) = \sqrt[3]{L^{/3} - \frac{V_{attr}(L^{/})}{k_v}} \quad (5)$$

The source term for the attrition fragments, $n_{attr,3}$, is given by the following equation:

$$n_{attr,3}(L,t) = \frac{1}{\tau}\int_{L^{/}=L}^{\infty} \begin{matrix} h(L_{fr,\max}(L^{/}) - L_{fr,\min})N_{fr}(L^{/})q_{fr}(L^{/}) \\ \eta(L^{/})n(L^{/},t)h(W_p(L^{/}) - W_{p,\min}) \end{matrix} dL \quad (6)$$

The other necessary parameters can be found in Gahn and Mersmann (1999)[1].

3. Research results

For the investigation of the crystallization process with the crystals attrition a number of experiments have been carried out with the crystallizing system ammonium sulphate under variation of the operating conditions in the lab-scale. All experiments have been carried out in 5.85 liters FC-Crystallizer of the crystallization temperature of 25°C and concentration 0.4346 kg/kg, for mean specific power input 0.1 W/kg and diameter of the target 0.01 m. The other operating conditions listed in Table 1. The calculation for various experimental conditions have been performed and compared with the experimental findings. All the results can be subdivided into two parts:

- Results, which describes dynamic behaviour;
- Results, which corresponds with the stable state.

Median crystals size, supersaturation and particle sizes distribution have been determined for the investigation of the dynamic behaviours. The calculated crystallization process and the experimental process must reach the stable state for the full comparison of the calculated and experimental median sizes and supersaturations. The dynamic behaviour of the crystallization process with the crystals attrition and their subsequent growth is given as example bellow.

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[1] Gahn, C. and Mersman, A., 1999, Brittle fracture in crystallization processes part A and part B, Chemical Engineering Science, 54, 1273-1292.

Table 1. Operating conditions.

Operating conditions	Attrition				Crystallization	Fines dissolution			
Volumetric flow [l/h]	378	368; 324	381; 292	390	350				
Feed temperature [˚C]	-				50				
Feed concentration [kg/kg]	-				0.45283				
Feed mass flow [kg/h]	-				10.969				
Dissolution temperature [˚C]	-				-	35			
Volume of the vessel for dissolution [l]	-				-	2			
Seed crystals sizes [µm]	355-560	560-800	800-1000	1000-1250	200-350	200-560	200-800		
Axial velocity by impact [m/s]	6.45	6.25; 5.55	6.53; 5	6.7	6.1	3.2			
Separator diameter [m]	-				-	0.025	0.05		
Fines dissol. velocity [l/h]	-				-	4.5	26	17	13

Figure 2 shows the dynamic behaviour of experimental and calculated parameters.

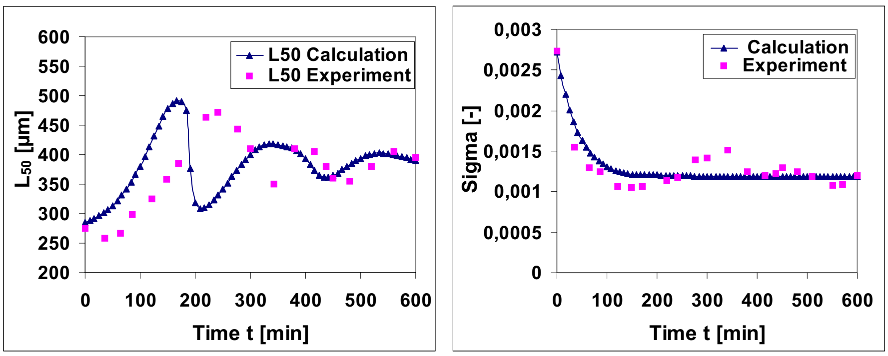

Figure 2. The Comparison of calculated and experimental median crystals sizes and supersaturations.

The comparison of calculated and experimental results for the stable state is presented in Table 2.

Table 2. Calculated and experimental values of the median sizes and supersaturations for different operating conditions

	Operating conditions			Experiments results			Calculation results	
Experiments	L_{seed} [μm]	v_{ax} [m/s]	R [-]	L_{50} [μm]	$L_{99,.9}$ [μm]	σ [-]	L_{50} [μm]	σ [-]
Attrition-1	355-560	6,45	1	268	955	-	250	-
Attrition-2	560-800	6,25	1	241	713	-	230	-
Attrition-3	560-800	5,55	1	481	1397	-	450	-
Attrition-4	800-1000	6,53	1	442	1468	-	430	-
Attrition-5	800-1000	5	1	325	1159	-	500	-
Attrition-6	1000-1200	6,7	1	414	1552	-	410	-
Crystallization-1	200-350	6,1	1	390	990	- [a]	415	0.0012
Crystallization-2	200-350	6,1	1	415	1000	0.0012	415	0.0012
Fines dissol. -1	200-560	3,2	1,5	607	1354	0.0034	440	0.0013
Fines dissol. -2	200-800	3,2	3,9	748	1343	- [a]	540	0.0016
Fines dissol. -3	200-800	3,2	2,9	760	1483	0,004	501	0,0014
Fines dissol. -4	200-800	3,2	2,5	637	1281	- [a]	483	0,0014

[a] These parameters have been not measured.

4. Conclusions

A mathematical model of attrition process has been developed. It describes quantitatively impacts of crystals with the hard body (orthogonal positioned cylinder in the attrition device). This attrition model was used for the modelling of three variants of crystallization process. The results obtained for ammonium sulphate indicate that the model is consistent. However, the model has been applied only to one substance and only to one crystallizers type. The future investigations are necessary to draw the process more exactly.

References

Bermingham, S.K., 2003, A design procedure and predictive models for solution crystallization processes, DUP Science, 267.

Gahn, C., 1997, Crystals hardness and her influence on the kinetics in suspension crystallizers, PhD Thesis, TU Munchen, 145 (in German).

Gahn, C. and Mersmann, A., 1997, Theoretical prediction and experimental determination of attrition rates, Trans. Instn. Chem Engng, 75A, 125-131.

Gahn, C. and Mersman, A., 1999, Brittle fracture in crystallization processes part A and part B, Chemical Engineering Science, 54, 1273-1292.

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