

Design of Continuous Crystallizer with Fines Removal for Melt Crystallization of Caprolactam

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A method of designing a new type continuous crystallizer with fines removal for the suspension melt crystallization of caprolactam is presented. The crystallizer enables one to obtain crystals with a relatively large average size. An algorithm has been developed on the basis of the experimental data obtained from a specially designed crystallizer for suspension melt crystallization. The algorithm is based on a mathematical model of CSD and on derived balance equations and exploits the geometrical similarity between the laboratory crystallizer and its industrial version. The algorithm can be used to calculate: a) the cumulative mass size distribution of the caprolactam crystals in the obtained product, b) median crystal size L_{50} , c) the mass streams in the crystallizer installation and their concentrations and temperatures, d) crystallizer sizes. It can be also used to simulate the effect of fines removal on the size of the produced caprolactam crystals and on the crystallizer sizes.

1. Introduction

The aim of this work was to develop an algorithm for designing a new type continuous crystallizer with fines removal for the suspension melt crystallization of caprolactam. The crystallizer enables one to obtain crystals with a relatively large average size. The purity of the crystals largely depends on their size distribution. Proper crystal size distribution makes the sedimentation, filtration and washing of the crystals easier, which results in a reduction in impurities, and in better operation of the wash columns where the crystals are additionally purified. These were the reasons for which the new type of continuous crystallizer for suspension melt crystallization was developed (Misztal and Verdoes, 1999). The algorithm is based on experimental data obtained from a specially designed crystallizer for suspension melt crystallization with fines removal and on a mathematical description of the CSD caprolactam produced in the crystallizer (Misztal, 2011).

2. Experimental and theoretical data

A diagram of the specially developed experimental crystallizer for suspension melt crystallization, with a working volume of $3.6 \cdot 10^{-3} \text{ m}^3$ is shown in Figure 1. The crystallizer is equipped with a draft-tube heat exchanger (2) and a special agitator consisting of a three-bladed propeller (4) which is connected to two external and internal scrapers (3). A special system of baffles is mounted in the upper part of the crystallizer to create a settling zone. The system consists of six large vertical baffles (1) and an additional cone baffle (5). Such a design makes possible the removal of fines from the crystallizer. The slurry stream (S) is removed from its bottom part while the stream containing fines (F) flows out from the settling zone. The stream with fines passes to a heat exchanger where the fines are remelted. The fines stream is then cooled in another heat exchanger, combined with the feed liquid, additionally cooled in still another heat exchanger, and flows into the bottom part of the crystallizer. The experimental set-up and the experiments were described in an earlier paper on the crystallizer (Misztal, 2011). Caprolactam containing about 1.85 wt.% water was used in the experiments. The crystal size distributions were determined by sieve analysis. During the experiments the operating conditions were changed as follows: a) mean residence time τ of the product crystal slurry from 3028 to 4623 s, b) crystal slurry density M_t from 194.61 to 316.13 kg/m^3 , c)

stirrer speed ω from 3.100 to 3.933 s⁻¹ (and calculated specific power input ε from 88.26 to 170.52 W/m³),
 d) crystallization temperature t_c from 60.80 to 61.95 °C and e) fines destruction rate r expressed as

$$r = \frac{\dot{V}_F + \dot{V}_P}{\dot{V}_P} \quad (1)$$

(where: \dot{V}_F - the fines volumetric flow rate, \dot{V}_P - the product volumetric flow rate) from 2.789 to 7.635. It was found that median crystal size L_{50} varied from $0.948 \cdot 10^{-3}$ to $1.633 \cdot 10^{-3}$ m.

For most of the experiments, semilogarithmic plots of crystal population densities (typical for the crystallizer with fines removal), with two different CSD straight line segments (Randolph and Larson, 1998) as shown in Figure 2, were obtained. Using the plots and the following relations for population density (Juzaszek and Larson, 1977, Rojkowski and Synowiec, 1991):

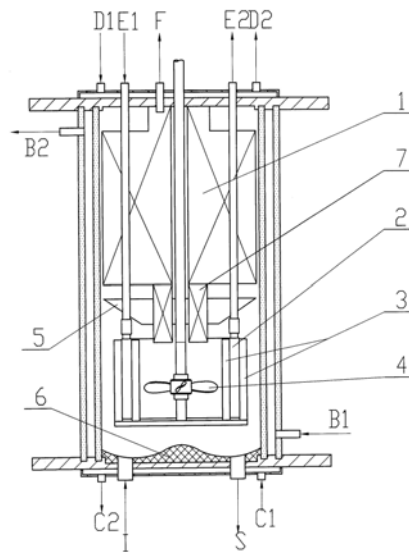


Figure 1: Diagram of experimental crystallizer; 1- baffle, 2- draft-tube heat exchanger, 3- scrapers, 4- three-bladed propeller, 5- cone baffle, 6- shaped bottom, 7- baffle, B1, B2, C1, C2, D1, D2, E1, E2- water, I- inlet, F- fines, S- crystal slurry.

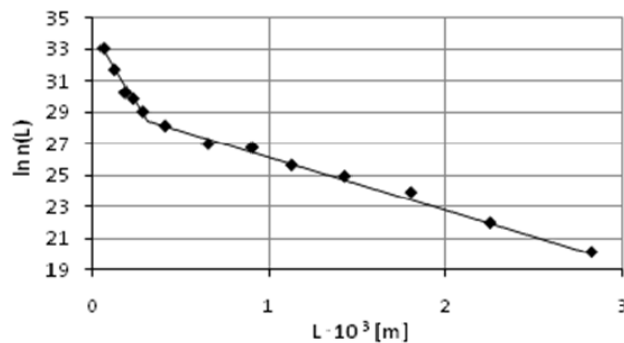


Figure 2: Exemplary caprolactam CSD produced in crystallizer with fines removal.

$$n(L < L_F) = n^o \exp\left(-\frac{rL}{G\tau}\right) \quad (2)$$

$$n(L > L_F) = n^o \exp\left[\frac{(1-r)L_F}{G\tau}\right] \exp\left(-\frac{L}{G\tau}\right) \quad (3)$$

nuclei population densities n^o , growth rates G and fines cut sizes L_F (the maximum fines sizes) were obtained. For the above parameters slurry density

$$M_t = M_{t1} + M_{t2} \quad (4)$$

can be calculated from the equations:

$$M_{t1} = f_v \rho_s \int_0^{L_F} n^o \exp\left(-\frac{rL}{G\tau}\right) L^3 dL \quad (5)$$

$$M_{t2} = f_v \rho_s \int_{L_F}^{\infty} n^o \exp\left[\frac{(1-r)L_F}{G\tau}\right] \exp\left(-\frac{L}{G\tau}\right) L^3 dL \quad (6)$$

where: f_v – a volumetric shape factor, ρ_s – crystal density.

Similarly, the concentration of crystals in slurry M_1 for size range $0-L_F$ can be expressed by equation (5), applying limits of integration from 0 to L . The concentration of crystals in slurry M_2 for size range L_F-L can be expressed by equation (6), applying limits of integration from L_F to L . Taking into account the equations, cumulative mass distributions $Q(L)$ were calculated from the relations:

$$Q(L) = \frac{M_1}{M_{t1} + M_{t2}} \quad 0 < L \leq L_F \quad (7)$$

$$Q(L) = \frac{M_1(L_F) + M_2}{M_{t1} + M_{t2}} \quad L > L_F \quad (8)$$

In Figure 3 exemplary calculated and experimental cumulative mass distributions of caprolactam crystal sizes in the crystallizer with fines removal are presented.

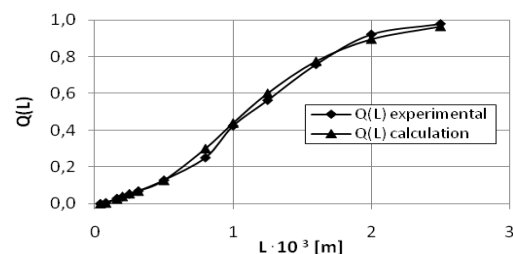


Figure 3: Exemplary calculated and experimental cumulative mass size distributions of caprolactam crystals in crystallizer with fines removal ($R = 0.9989$).

For the values expressing the operating conditions changed during the experiments, parameter n° assumed the form of this relation:

$$n^{\circ} = 5.5322 \cdot 10^8 \Delta t^{10.7963} M_t^{-1.2977} \varepsilon^{1.4767} r^{2.9488} \tau^{0.1016} \quad (R=0.946) \quad (9)$$

where Δt is the temperature difference between the crystallization temperature and the mean value of the crystallizer inlet and outlet temperatures of the cooling water directed to the draft-tube heat exchanger (during the experiments it was changed from 1.58 to 2.04 °C).

3. Crystallizer design procedure

The procedure developed for designing the new type crystallizer for suspension melt crystallization includes the calculations of:

1. Nuclei population densities n° from equation (9) after assuming input data (based on the values used in the experiments) such as: Δt , M_t , ε , r , τ .
2. M_{t1} , M_{t2} , G by solving the system of equations (4) to (6) for the assumed value of fines cut size L_F .
3. The concentration of crystals in slurry M_1 for size range $0-L_F$, from equation (5), applying limits of integration from 0 to L_F , and the concentration of crystals in slurry M_2 for size range L_F-L , from equation (6), applying limits of integration from L_F to L .
4. Cumulative mass distributions $Q(L)$ by solving the system of equations (7) and (8), and then L_{50} (median crystal size), L_{16} , L_{84} – crystal size with respectively 50%, 16% and 84% of oversize fraction, taking $Q(L)$ equal to 0.16, 0.50, 0.84, and the approximate value of coefficient of variation CV (Rojkowski and Synowiec, 1991) from:

$$CV = \frac{L_{84} - L_{16}}{2L_{50}} \quad (10)$$

5. The ratio between the mass flow rate of the crystals removed from the crystallizer as fines and the mass flow rate of the crystal product

$$\phi = \frac{\dot{m}_{s1}}{\dot{m}_s} = \frac{\dot{V}_F M_{t1}}{\dot{V}_P (M_{t1} + M_{t2})} \quad (11)$$

which (by applying equation (1)) can be written as

$$\phi = \frac{(r-1)M_{t1}}{M_{t1} + M_{t2}} \quad (12)$$

6. The mass and heat flows of the streams shown in the flow diagram of the crystallizer (Figure 4) as well as the mass fraction of water in the mass streams and their temperatures, by solving a system of mass and heat balance equations, assuming such input data as: the crystal product flow rate, crystallization temperature t_c , the mass fraction of water in the feed stream of caprolactam, the effect of the mass fraction of water on melting temperature for the caprolactam-water system, the difference between the equilibrium temperatures and the temperatures of the individual streams, the effective distribution coefficient based on the experimental data, and the values of Φ , r , M_T .

7. The settling velocity of crystals with cut sizes, using the Stokes type correlation with correction parameter p

$$u = \left(\frac{L_F}{p} \right)^2 \frac{g(\rho_s - \rho_l)}{18\eta} \quad (13)$$

where: ρ_s , ρ_l are respectively solid and liquid density, η – viscosity. Parameter p can be calculated from the equation

$$p = 0.3891M_{f1}^{0.1685} \varepsilon^{0.1} \quad (R=0.987) \quad (14)$$

which was derived on the basis of the experimental data.

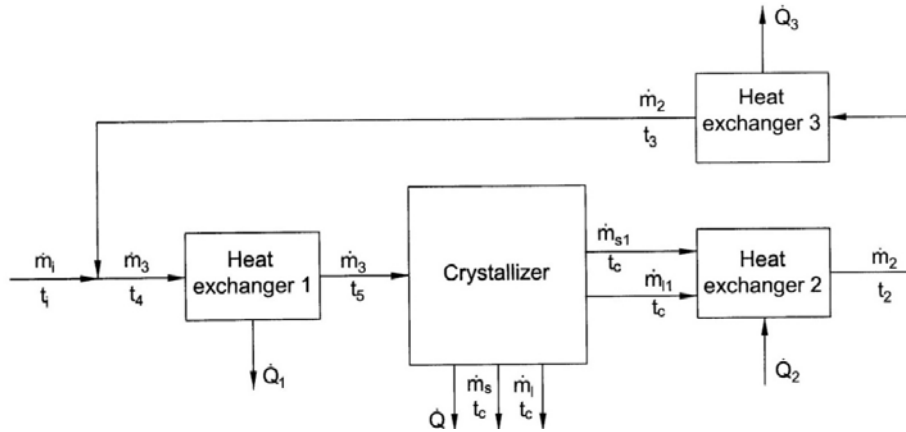


Figure 4: Flow diagram of crystallizer with fines removal for suspension melt crystallization; mass flow rate of: \dot{m}_i - feed, \dot{m}_s - crystal product, \dot{m}_l - mother liquor, \dot{m}_{s1} - crystals in fines stream, \dot{m}_{l1} - mother liquor in fines stream; \dot{Q} - flow of heat removed from crystallizer, \dot{Q}_2 - flow of heat used for melting fines, \dot{Q}_1 , \dot{Q}_3 - flows of heat removed from circulation stream.

8. The diameter of the crystallizer

$$D = \left(\frac{4\dot{m}_{l1}}{\pi\rho_l u} \right)^{1/2} \quad (15)$$

9. The heat exchange surface area in the crystallizer

$$F = \frac{\dot{Q}}{k\Delta t} \quad (16)$$

where k is an overall heat transfer coefficient based on the experimental data.

It is assumed that the industrial-scale crystallizer will be additionally cooled down by a cooling jacket mounted on its wall. For this reason, extra scrapers will be introduced to prevent incrustation on the wall, and heat exchanger surface area F will be the sum of the cooling jacket heat exchanger surface area and the draft-tube heat exchanger surface area. The diameter of the draft-tube heat exchanger can be calculated exploiting the geometrical similarity between the diameter of the draft-tube heat exchanger in the laboratory crystallizer and in its industrial version. Knowing the above values the height of the draft-tube heat exchanger and the height of the cooling jacket mounted on the crystallizer wall can be calculated.

10. The distance between the bottom crystallizer and the draft-tube heat exchanger, the distance between the cone baffle and the draft-tube heat exchanger, the height of the cone baffle, the distance between the cone baffle and the cover plate of the crystallizer, exploiting the geometrical similarity between the laboratory crystallizer and its industrial version, and the total height of the crystallizer. Using the sizes volume (V_m) of the crystallizer mixing zone and the volume (V_s) of the crystallizer settling zone the total volume (V) of the crystallizer is calculated.

11 Mean residence time τ of the product crystal slurry in the crystallizer mixing zone

$$\tau = \frac{V_m}{\frac{\dot{m}_s}{\rho_s} + \frac{\dot{m}_l}{\rho_l}} \quad (17)$$

If the obtained value is not equal to τ assumed in point 1 of the design procedure, all the calculations should be repeated for a new value of τ . The iteration ends when the difference between the assumed value and the calculated value of τ is acceptable from the point of view of the adopted accuracy of the calculations.

12. The stirrer speed using specific power input ε and assumed agitator sizes

$$\omega = \left(\frac{\varepsilon V_m}{Ne \rho_{sus} d_{os}^5} \right)^{1/3} \quad (18)$$

where: Ne – the Newton number, d_{os} – the diameter of the outside scrapers, ρ_{sus} – suspension density.

13. The overall heat transfer coefficients for the cooling jacket heat exchanger surface and the draft-tube heat exchanger surface, using the equations from heat transfer theory and the obtained crystallizer sizes. The heat transfer coefficients on the scraped side can be calculated from the equation (Kozioł and Konieczny, 1978) chosen on the basis of the experimental data

$$Nu = 1.39 Re_m^{0.5} Pr^{0.3} Z^{0.5} \quad (19)$$

where: Nu - the Nusselt number, Re_m – the Reynolds number for the mixing process, Pr – the Prandtl number, Z – the number of scrapers.

Using the calculated overall heat transfer coefficients, the cooling jacket heat exchanger surface area and the draft-tube heat exchanger surfaces area, the mean value of the overall heat transfer coefficient can be calculated. If the obtained value is not equal to k assumed in point 9 of the design procedure, all the calculations should be repeated for a new value of k . The iteration ends when the difference between the two values of k is less than the assumed difference.

4. Conclusion

The presented crystallizer design procedure enables one to calculate the most important data such as: the caprolactam CSD, the crystallizer sizes and the energy consumption by the suspension melt crystallization of caprolactam in the new type continuous crystallizer with fines removal. The design method has been verified by calculations performed for an industrial-scale crystallizer with an efficiency of 0.278 kg caprolactam/s. The design method relations can also be used to simulate the effect of fines removal and crystallizer operating conditions on the above data critical for the implementation of the crystallizer in industry.

References

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