Supersaturation profiles of L-sorbose water solutions in the cooling batch crystallization process

B. Wierzbowska,[a] J. Koralewska,[a] K. Piotrowski,[b] A. Matynia, [a] K. Wawrzyniecki [a]

[a] *Faculty of Chemistry, Wroclaw University of Technology , 50 – 370 Wroclaw, Poland*
[b] *Department of Chemical & Process Engineering, Silesian University of Technology , 44 – 101, Gliwice, Poland*

Abstract

L-sorbose, an intermediate product in L(+)-ascorbic acid synthesis, is effectively separated from postprocessing mixture (purification process) by multistage batch crystallization operations. However, water solutions of L-sorbose tend to form stable supersaturated systems, characterized by high values of maximum supercooling depending on saturation temperature (concentration) of initial solution and its cooling rate. This effect of undesirable accumulation of undischarged supersaturation makes some disturbances both in mass crystallization process yield and in crystal product quality (e.g. consequences of excess nucleation). The experimental results concerning time–distribution of supersaturation in the seeded water solutions of L-sorbose (55–70 mass % range) in a batch DT MSMPR crystallizer (linear cooling rate applied $(1.39 - 8.33)\cdot 10^{-3}$ K s^{-1}) are presented and discussed.

Keywords: L-sorbose purification, batch crystallization, supersaturation discharge, DT MSMPR crystallizer, linear cooling rate

1.Introduction

L-sorbose is a second, intermediate product in L(+)-ascorbic acid (vitamin C) synthesis according to Reichstein procedure (Boudrant, 1990; Davies *et al.*, 1991). This monosaccharide is a product of biochemical dehydrogenation of D-sorbitol by means of *Gluconobacter* (*Acetobacter*) *suboxydans* (Rosenberg *et al.*, 1993; Kim *et al.*, 1994; Bonomi *et al.*, 1993). D-sorbitol is a product of catalytic reduction of D-glucose (Kulchanek, 1970). L-sorbose ($C_6H_{12}O_6$, molar mass 180.16 kg $kmol^{-1}$) is a crystalline material (orthorhombic, bisphenoidal crystals, of 1650 kg m^{-3} density), about as sweet as sucrose. It is readily soluble in water but almost insoluble in alcohols (Šnajdman, 1973). An industrial scale crystal product should be composed of, according to the assumed technology yield, 97.0 – 98.8 mass % of L-sorbose. The required chemical purity results the most often from the subsequent batch mass (re)crystallization from its postprocessing water solutions. Investigations on stability of L-sorbose water solutions show that during their heating L-sorbose undergoes thermal decomposition, what manifests in form of solution colour change and also as the appearance of number of peaks of maximum absorption observed in ultraviolet radiation spectrum. Intensity of this process depends on solution's pH, length of heating period and the temperature level (Šnajdman, 1973). Character of ultraviolet absorption spectrum shows that L-sorbose in the acid solution decomposes into hydroxymethylfurfural followed by final formation of formic and levulinic acids. The lowest losses of L-sorbose were observed in the solutions of pH = ca. 3.

An characteristic property of the purification step is that water solutions of L-sorbose tend to form stable supersaturated liquid systems, characterized by relatively high values of maximum supercooling attainable: from ca. $\Delta T_{\max} = 10$ up till 50 K, depending both on saturation temperature of initial solution in a batch crystallizer (its initial concentration) and on cooling rate applied (Matynia *et al.*, 1990a; 2003). It reveals a direct influence both on mass crystallization process yield and on crystal product quality (crystal size distribution, their uniformity, shape and chemical purity) (Matynia *et al.*, 1997b; 2003).

The experimental results concerning time–distributions of supersaturation in the seeded water solutions of L-sorbose during batch mass crystallization process with adjusted cooling rate value providing linear decrease of a system temperature with the process time are presented. The tests were performed in a laboratory DT (*Draft Tube*) MSMPR (*Mixed Suspension Mixed Product Removal*) crystallizer. Laboratory test stand performance (temperature reduction regime) was controlled by means of PC computer system.

Crystallizer was fed with water solutions of L-sorbose of initial concentration adjusted to fit within the 55 – 70 mass % range (corresponded to saturation temperature range of T_{eq} = 324.5 – 368.5 K), cooled with linear cooling rate selected individually from $R_{\mathrm{T}} = (1.39 - 8.33)\cdot 10^{-3}$ K s^{-1} range.

2.Experimental stand and procedure

Experimental tests were performed in a laboratory–scale DT MSMPR crystallizer with propeller agitator for internal circulation of suspension (Fig. 1). It was a hermetic, glass–made cylindrical tank ($V_{\mathrm{t}} = 1$ dm^3, $D = 120$ mm, $H = 123$ mm) equipped with a cooling jacket (pipe–in–pipe type heat exchanger) embedded into a wall of circulation profile element (d = 57 mm, h = 53 mm) and connected with thermostat, where an ice load was applied to cool the heat acceptor – circulating water – down to a temperature T = 275 K. A second thermostat was applied to heat the entire crystallizer volume. Actual cooling rates were precisely adjusted by computer control system. In the tank axis, inside the circulation profile, a three–paddle propeller mixer (d_{m} = 55 mm) was installed. During all experiments the revolution number was kept constant (10 ±0.2 s^{-1}) providing stable and intensive enough circulation of solution (after nucleation–suspension) inside the crystallizer working volume. Circulations of heating and cooling media used in the stand are presented schematically in Fig. 1. The solutions of known compositions tested in the experiments, as biochemically active systems, were prepared just before their introduction into crystallizer using L-sorbose of the main component content above 98 mass % (suitable for biotechnological purposes, Fluka, Germany) and double distilled water.

Two test series were performed. In a first set of experiments concentration of L-sorbose in solution was: 55 (T_{eq} = 324.5 K), 60 (T_{eq} = 339.5 K), 65 (T_{eq} = 354.0 K) and 70 mass % (T_{eq} = 368.5 K) while constant cooling rate $R_{\mathrm{T}} = 8.33\cdot 10^{-3}$ K s^{-1} was applied. In a second set of tests an initial concentration of L-sorbose was assumed constant (55 mass %) while five various cooling rate values were successively applied, $R_T = (1.39, 2.78, 4.17, 5.56 \text{ and } 8.33)\cdot 10^{-3}$ K s^{-1} (i.e. 5÷30 K h^{-1}).

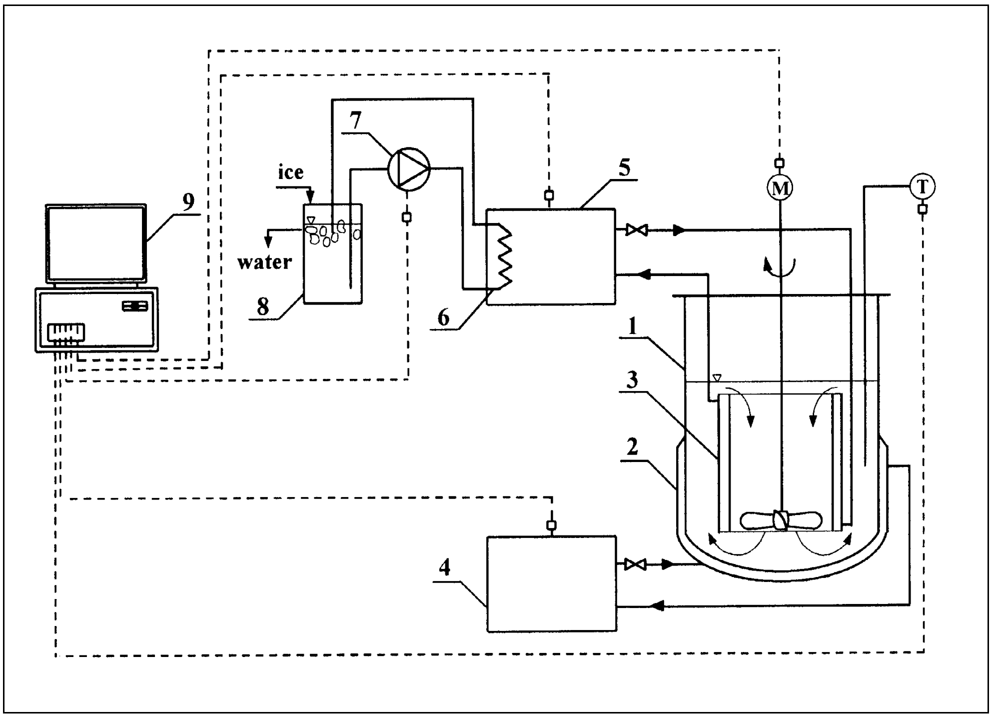

Fig. 1. Laboratory batch crystallizer – an experimental setup: (1) DT crystallizer with internal circulation of the medium, (2) heating jacket, (3) cooler, pipe–in–pipe type heat exchanger, (4) thermostat (heating), (5) thermostat (cooling), (6) cooling coil, (7) cooling medium pump, (8) cooling water tank: ice + water, (9) PC computer – integrated control system, (M) stirrer speed control, (T) temperature control.

An individual test procedure was as follows. The 0.7 kg of solution of known chemical composition, after introduction into the crystallizer, was heated till its actual temperature value was by ca. 5 K higher than the expected saturation temperature, T_{eq}. In this moment mixer action started (preventing temperature and concentration gradients occurrence). After ca. 15 min of the mixing the cooling process was included (constant cooling rate value, R_T, was assumed and stabilised electronically). When solution attained a temperature value by 1 K lower than the expected saturation temperature, T_{eq}, dozens of well shaped L-sorbose crystals (ca. 0.1 g of total mass, mean seed crystal size – 300 μm (Kubota *et al.*, 1978)) were introduced into the mixed system (heterogeneous/surface nucleation precursors – similarity to large–scale industrial process conditions) (Mersmann, 1995; Mullin, 1992)). While further cooling of this “thin suspension” a continuous observation of the system was realized till a moment of characteristic, spontaneous nucleation appearance (sudden turbidity in the bulk solution; liberated latent heat of spontaneous crystallization produces in result a clearly observable increase of temperature within the system under study, which is recorded by the computer measurement system – see Fig. 1).

This temperature in the system can be interpreted as the spontaneous crystallization temperature, T_{cr}. Cooling process was continued and finished when an assumed temperature of T_f = 283 K was attained. Crystal product was separated from mother liquor by centrifuge action, then the crystals were washed with cold water/ethanol and dried in T = 298 K without light. Exemplary image of L-sorbose crystals (Scanning Electron Microscope JEOL–5800LV) produced from solution of initial concentration 55 mass % of L-sorbose (T_{eq} = 324.5 K, T_{cr} = 299 K) cooled with $R_T = 8.33 \cdot 10^{-3}$ K s^{-1} is presented in Fig. 2, where some statistical parameters of crystal size distribution (Particle Size Analyzer COULTER LS–230) are also presented (Matynia *et al.*, 2003).

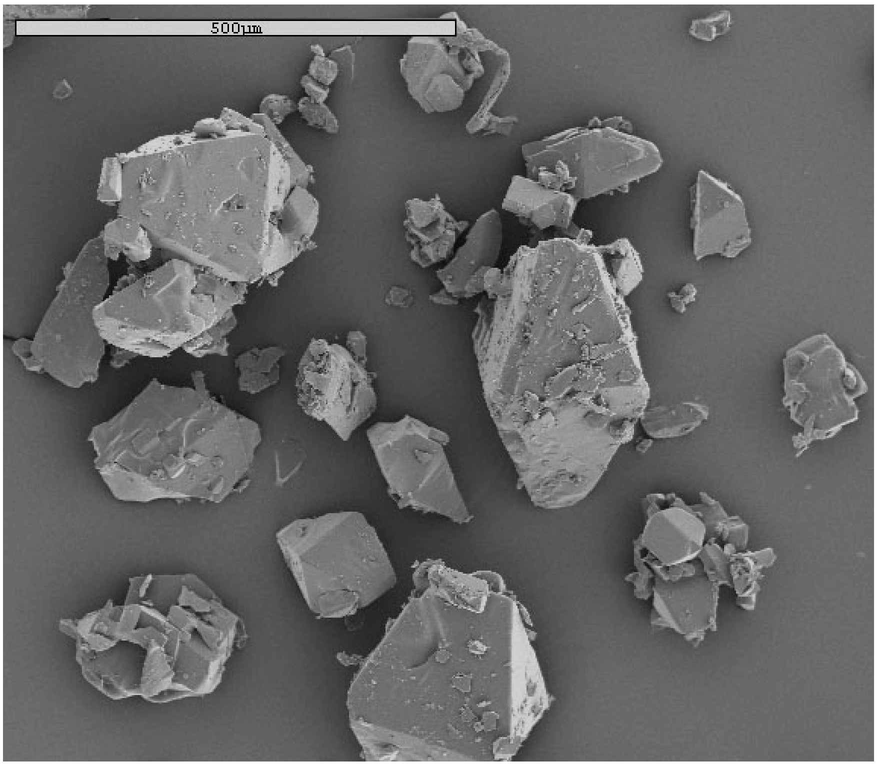

Fig. 2. Scanning electron microscope images of L-sorbose crystals produced in a DT MSMPR batch crystallizer (V_w = 0.6 dm^3): L_m = 282 µm, L_{50} = 261 µm, CV = 51.7%, k_v = 0.52 (test No. 1 – see Table 1). Magnification 100x.

During cooling of selected solution/suspension with an assumed cooling rate from spontaneous nucleation temperature (T_{cr}) to a final process temperature (T_f) samples of the solution (of approx. $2 \cdot 10^{-3}$ dm^3 volume) were withdrawn every Δ5 K temperature change by the use of injection system equipped with a special filter. Concentration of L-sorbose (c_{LS}) was determined analytically.

Supersaturation Δc in a cooled solution in a selected temperature point, T, was then calculated with Eq. (1):

$$\Delta c = c_{LS}(T) - c_{eq}(T) \tag{1}$$

or alternatively presented in a form of relative supersaturation, σ, Eq. (2):

$$\sigma = \frac{\Delta c}{c_{\mathrm{eq}}(T)} \tag{2}$$

where solubility concentration of L-sorbose in water, $c_{\mathrm{eq}}(T)$, can be estimated on the basis of experimental data presented by Šnajdman (1973) and Matynia *et. al* (1997a) as empirical Eq. (3):

$$c_{\mathrm{eq}} = 0.323T - 49.80 \tag{3}$$

Batch crystallization time, τ_{cr}, is calculated with Eq. (4):

$$\tau_{\mathrm{cr}} = \frac{T_{\mathrm{cr}} - T_{\mathrm{f}}}{R_{\mathrm{T}}} \tag{4}$$

3. Results

Experimental data and calculation results are presented in Figs. 3 and 4 (relative supersaturation values, σ, Eq. (2)), while selected numerical data are shown in Tables 1 and 2 (direct Δc values (Eq. (1)). Spontaneous nucleation temperature, T_{cr}, is marked in Figs. 3 and 4 in a form of filled points.

Table 1. Changes in supersaturation value in water solutions of L-sorbose during their cooling from T_{cr} down to T_{f} in a batch DT MSMPR crystallizer – influence of solubility temperature, T_{eq}.

Batch solution of:		Supersaturation in temperature:						
c_{LS} mass %	T_{eq} K	T_{cr} K	Δc_{max} mass %	σ_{max} –	T_{f} K	τ_{cr} s	Δc_{f} mass %	σ_{f} –
55	324.5	299	8.2	0.175	283	1920	5.0	0.120
60	339.5	318	7.1	0.134	283	4200	4.5	0.108
65	354.0	336	6.3	0.107	283	6360	3.9	0.094
70	368.5	353	5.8	0.090	283	8400	3.1	0.075

Assumed linear cooling rate $R_{\mathrm{T}} = 8.33 \cdot 10^{-3}$ K s^{-1}.

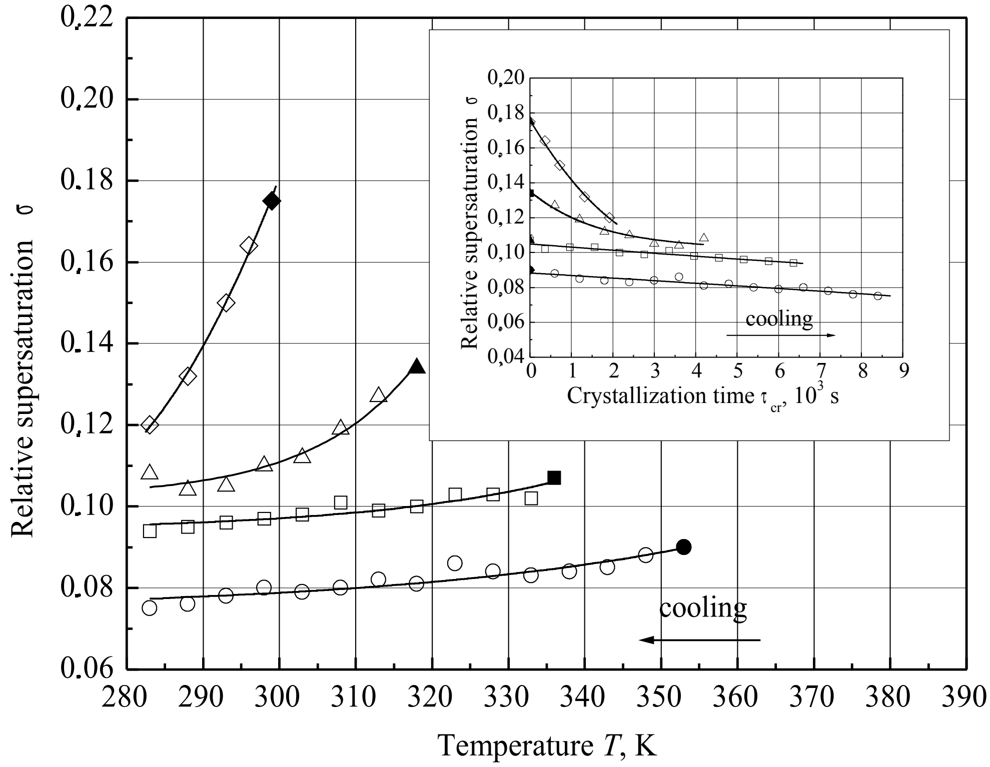

Fig. 3. Temporal profiles of relative supersaturation in water solutions of L-sorbose of various initial concentrations (55 (◊), 60 (Δ), 65 (□) and 70 (○) mass %) during their linear cooling (R_T = $8.33 \cdot 10^{-3}$ K s^{-1}) in a batch crystallizer starting from spontaneous nucleation temperature, T_{cr}, down to a final temperature, T_f = 283 K.

Table 2. Changes in supersaturation value in water solutions of L-sorbose during their cooling from T_{cr} to T_f in a batch crystallizer – influence of linear cooling rate, R_T.

$R_T \cdot 10^3$ K s^{-1}	τ_{cr} s	Supersaturation in temperature:					
		T_{cr} K	Δc_{max} mass %	σ_{max} –	T_f K	Δc_f mass %	σ_f –
1.39	20160	311	4.3	0.085	283	0.3	0.007
2.78	8640	307	5.6	0.113	283	0.8	0.019
4.17	5280	305	6.3	0.129	283	2.3	0.055
5.56	3600	303	6.9	0.143	283	3.3	0.079
8.33	1920	299	8.2	0.175	283	5.0	0.120

Initial concentration of L-sorbose in its water solution: 55 mass % (T_{eq} = 324.5 K).

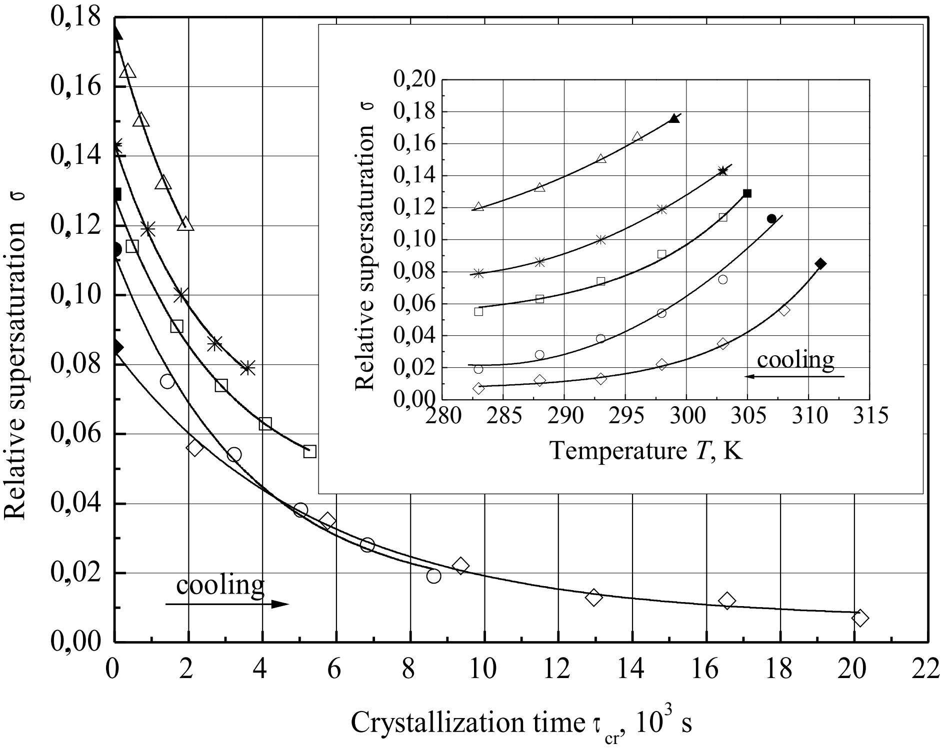

Fig. 4. Relative supersaturation in water solutions of L-sorbose (55 mass %, T_{eq} = 324.5 K) as a function of batch crystallization time or process temperature (internal figure) for various cooling rates of solution/suspension from spontaneous nucleation temperature, T_{cr}, down to a final process temperature, T_f = 283 K. Cooling rates applied: R_T = (1.39 (◊), 2.78 (○), 4.17 (□), 5.56 (✳), 8.33 (Δ))·10^{-3} K s^{-1}.

Application of more concentrated solutions of L-sorbose results in a desirable decrease of both supersaturation values – maximum one and its final value. It is visible while comparing extreme cases from Table 1 and Fig. 3. For c_{LS} = 55 mass % σ_{max} = 0.175 and σ_f = 0.120, while for c_{LS} = 70 mass % it is: σ_{max} = 0.090 and σ_f = 0.075. The highest difference between σ_{max} and σ_f is reported for more diluted solutions (for c_{LS} = 55 mass % σ_{max}/σ_f = 1.46 while for c_{LS} = 70 mass % σ_{max}/σ_f = 1.2 – see Fig. 3). Both variables inform directly or indirectly about process yield (σ_f) and product quality (σ_{max}). They can be also modified by appropriate change of cooling rate – see Table 2 and Fig. 4. The greatest desirable effects can be obtained using as low as possible cooling rate, providing smooth discharge of generated supersaturation as it comes. For R_T = 1.39·10^{-3} K s^{-1} it was obtained: σ_{max} = 0.085 and σ_f = 0.007. Contrary, for R_T = 8.33·10^{-3} K s^{-1} σ_{max} = 0.175 and σ_f = 0.120. The largest difference between σ_{max} and σ_f is for the lowest cooling rate applied in the experiments (R_T = 1.39·10^{-3} K s^{-1}): σ_{max}/σ_f = 12.14. For the largest cooling rate applied (R_T = 8.33·10^{-3} K s^{-1}) value of this indicator is considerably lower (σ_{max}/σ_f = 1.46).

4.Conclusions

On the basis of experimental results it can be concluded, that technological recommendations concerning purification process of L-sorbose by multistage batch crystallization process should include hints to carry out the process with possibly highest concentration of L-sorbose in initial solution while applying a possibly lowest cooling rate. These process conditions effect in the lowest values of both maximum supersaturation (effective restriction of unnecessary excess primary nucleation, influencing disadvantageously crystal product properties) and final (residue) supersaturation (growth of general process yield). The experimental data presented can be also used in design works concerning improvement or optimization of L-sorbose purification technology.

Acknowledgement

This work was supported by the Ministry of Science and Higher Education of Poland under grant No. 3T09B 122 27.

Symbols

CV – coefficient of variation, %
c_{eq} – solubility concentration of L-sorbose in water solution, mass %
c_{LS} – concentration of L-sorbose in water solution, mass %
Δc – supersaturation, defined by Eq. (1), mass %
Δc_f – undischarged supersaturation of L-sorbose in water solution in a final process temperature, T_f (final supersaturation), mass %
Δc_{max} – critical, maximal supersaturation of L-sorbose in water solution, mass %
D – crystallizer diameter, m
d – draft tube (DT) diameter, m
d_m – propeller mixer diameter, m
H – crystallizer height, m
h – draft tube (DT) height, m
k_v – volumetric shape factor of crystal
L_m – mean size of crystals in a population tested, m
L_{50} – median size of crystals (for undersize mass fraction equals to 50 mass %) in a population tested, m
R_T – (linear) cooling rate, K s^{-1}
T – temperature, K
T_{cr} – temperature of spontaneous nucleation of L-sorbose, K
T_{eq} – solubility temperature of L-sorbose water solution, K
T_f – final temperature of batch crystallization process, K
ΔT_{max} – critical, maximal value of supercooling in the solution (maximum allowable supercooling), defined as $T_{eq} - T_{cr}$, K
V_t – total volume of crystallizer, m^3
V_w – working volume of crystallizer, m^3

Greek letters
τ_{cr} – batch crystallization time, defined by Eq. (4), s
σ – relative supersaturation, defined by Eq. (2)
σ_{max} – maximal relative supersaturation
σ_{f} – final (undischarged) relative supersaturation

Abbreviations
DT – Draft Tube crystallizer
MSMPR – Mixed Suspension Mixed Product Removal crystallizer

References

Bonomi, A., Augusto, E.F.P., Barbosa, N.S., Mattos, M.N., Magossi, L.R. and Santos, A.L., (1993) *J. Biotechnol.*, 31, 39–59.

Boudrant, J., (1990) *Enzyme Microb. Technol.*, 12, 322–329.

Davies, M.B., Austin, J. and Partridge, D.A., *Vitamin C: Its Chemistry and Biochemstry*, The Royal Society of Chemistry, Cambridge (1991).

Kim, W.–K., Chun, U.–H., Park, Y.–M., Kim, CH.–H., Choi, E.–S. and Rhee, S.–K., (1994) *Process Biochem*., 29, 277–283.

Kubota, N., Karasawa, H. and Kawakami, T., (1978) *J. Chem. Eng. Japan*, 11, 290–295.

Kulchanek, M., (1970) *Adv. Appl. Microbiol*., 12, 11–30.

Matynia, A., Wierzbowska, B. and Bechtold, Z., (1997a) *Przem. Chem.*, 76, 275–276.

Matynia, A., Wierzbowska, B. and Bechtold, Z., (1997b) *Przem. Chem.*, 76, 443–444.

Matynia, A., Wierzbowska, B. and Bechtold, Z., (2003) *Pol. J. Appl. Chem.*, 47, 31–44.

Mullin, J. W., *Crystallization,* Butterworths – Heinemann, Oxford (1993).

Myerson, A.S., *Handbook of Industrial Crystallization*, Butterworths – Heinemann, Boston (1993).

Rosenberg, M., Švitel, J., Rosenbergova, I. and Šturdik, E., (1993) *Acta Biotechnol*., 35, 269–274.

Šnajdman, L.O., *Proizvodstvo Vitaminov*, Piščevaja Promyšlennost, Moskva (1973).