THE EFFECT OF SEEDING ON SUCROSE CRYSTAL SIZE DISTRIBUTION AND CRISTALLIZATION KINETICS

UDC 664. 1.054 :66.012

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Abstract: *This research deals with kinetics of sucrose crystallization in impure solutions. Under laboratory conditions the cooling crystallization rate of sucrose was studied in the presence of different amounts of slurry. The Coulter Counter technique was applied for the determination of the particle size distribution in the slurry and the solutions. The obtained data made it possible to establish a relationship between the amounts of slurry and the quality of the crystal mass.*

Key words: *crystal size distribution, slurry, nonsucrose, sucrose crystal growth*

INTRODUCTION

The industrial crystallization of sucrose may be described as "crystal forming" in which large populations of crystals are produced. It is often required to produce such populations with certain distributions of size or shape and, in order to predict such distributions, it would be necessary to know the distribution of rates of crystallization in a population of crystals.

In sugar crystallization seeding has envolved during the last forty years from an almost uncontrolled collision of dust collected in the sugar house and introduced with air in the footings at very high supersaturation (>1,30) to rigorously controlled milled sugar crystals dispersed in isopropanol or another dispersant. Slurry, which is produced by wet ball-milling of sugar in alcohol is generally preferred as seed. In order to ensure a consistent crystal size, milling mass, milling time as well as crystal size of the sugar have to be kept constant (Schiweck, 1967). Fine crystal fragments suspended in low-viscous isopropanol, tend to form aglomerates due to van

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der Waals-forces. To separate the slurry particles, an addition of glycerine to increase viscosity and homogenization of the suspension in a well stirred vessel before seeding is recommended (Schliephake & Frankenfeld, 1987).

Successful seeding is commonly considered one important prerequisite for excellent centrifugation properties of the crystallization massecuite and white sugar quality. The groundwork for perfect crystal size distribution in crystallization is mostly made during the seeding period. The seeding under technical conditions remains a critical step which deserves optimization. Optimal seeding conditions followed by minimizing secondary nucleation throughout the crystallization cycle are needed.

The optimal quantity of seed crystals needs to be determined. It is possible to determine theoretically the mass of seed crystals if the yield of crystals as well as final size are known. This implies knowing the number of crystals per unit mass.

Assuming same diameters and constant number of crystals during crystallization, amount of slurry can be estimated by the d ^{3} rule (Witte, 1987):

$$V_{sl} ć 3 \cdot m_k [d_{sl} / d_k]^3 \quad (1)$$

V_{sl} – volume of slurry (dm^3)
m_k – mass of product crystallizate (kg)
d_{sl} - size of slurry particles (μm)
d_k – size of product crystallizate crystals (μm)

In the conditions of technical evaporating crystallization, more or less substantial conglomeration or dissolution of the added slurry crystals takes places because of inhomogeneous saturation levels. Secondary nucleation could occur in the metastable zone if the crystals are too far apart. This is explained by the fact that the path of sucrose diffusion from the site of supersaturation formation to the crystals surface depends on the volume between crystals.

In this paper, the results of reproducible cooling crystallization experiments with impure sucrose solutions are presented. The aim of this investigations was to determine the effect of slurry amounts on the crystal size distribution, crystal mass and linear growth rate in the laboratory tests by application the Coulter Counter method.

MATERIALS AND METHODS

Series of laboratory experiments were carried out on model solutions of sucrose with the purity about 90%. White sugar, molasses and destilled water were used. Sucrose model solutions were evaporated in laboratory evaporator until the content of dry substance was about 80 ºBx. When microscopic analysis proved that all the crystals were dissolved, saturation and seeding temperatures were determined according to content of the dry substance and sucrose.

The quality of solutions was estimated according to the methods published in the manual for laboratory control of the process of sugar factories production (Milić et al., 1992).

Slurry was prepared by wet-milling in ball mills, 2 l of iso-propanol were used per kg sugar having crystal size of 0,2 to 0,7 mm. Grinding took four hours. The slurry should be aged about four weeks before use. The water content of iso-propanol is an important factor. Before seeding of the model solutions, slurry was dispersed in glycerine and homogenized. Slurry was used in the amounts of 0,07, 0,09 1,7 to 2,9% w/w.

Crystallization by cooling was carried out in batch crystallizer with constant agitation speed, during the period of three hours according to the defined programme.

Particle size distributions were determined with off-line automated method, Coulter Counter (van der Poel et al., 1983).

For evaluation of particle size distribution the RRSB function was applied (ICUMSA, 2003).

The crystal growth rate was determined as mass growth rate R_G and linear growth rate L_G:

$$R_G = dm / (A \cdot dć) \quad (2)$$
$$L_G = d_{RRSB} / dć \quad (3)$$

R_G – mass growth rate (mg/($m^2 \cdot$ min)
m – crystal mass (mg)
A – crystal surface area (m^2)
ć – time (min)

L_G – linear growth rate (μm /min)
d_{RRSB} – characteristic size (μm)

Methods of analyses of the samples are presented in Table 1, and experimental conditions in Table 2.

Table 1.
Methods of analyses

Components	Methods	Instruments	
		Type	Producer
Dry substance	Refractometric	Refractometer DUR-S	Schmidt&Haensch
Sucrose	Polarimetric	Saccharomat	Schmidt&Haensch
Sucrose crystals	Particle size distribution	Coulter Counter, model ZM	Coulter Electronics GmbH
Sucrose crystals	Microscopic	AO Spencer	American Optical Company

Table 2.
Experiments characteristics

Experiments conditions	Experiment			
	A	B	C	D
Slurry quantity (%)	0,07	0,09	1,7	2,9
Seeding temperature (°C)	68	68	66	60
Final temperature (°C)	28	28	30	38
Cooling rate (°C/min)				
0-60min	0,17	0,17	0,15	0,10
61-120min	0,25	0,25	0,27	0,13
121-180min	0,25	0,25	0,18	0,13

RESULTS

Granulometric composition is determined by: number and mass distribution, mean crystal size d_{RRSB}, uniformity coefficient n, minimum and maximum size of crystal. In Table 3, granulometric composition of slurry are presented. Parameters of model solutions quality are shown in Table 4. Granulometric composition of sucrose crystal which were produced by seeding of model solutions with different slurry amounts are presented in Tables 5, 6, 7 and 8

Table 3.
Particles size distribution of slurry

Size range		Mean volume ($10^{-9}\cdot cm^3$)	Particles number ($10^4/cm^3$)	Number fractions (%)	Mass fractions (%)	Cumulative mass fractions retained (%)
d_1 (μm)	d_2 (μm)					
3,09	3,89	0,02	47,0	6,6	0,3	100,0
3,89	4,90	0,05	45,0	6,4	0,5	99,7
4,90	6,17	0,09	67,0	9,5	1,6	99,2
6,17	7,78	0,18	153,0	21,6	7,5	97,6
7,78	9,80	0,37	171,0	24,2	16,9	90,1
9,80	12,35	0,74	146,0	20,7	28,7	73,2
12,35	15,56	1,48	56,0	7,9	22,0	44,5
15,56	19,60	2,96	17,0	2,4	13,4	22,5
19,60	24,70	5,92	4,0	0,6	6,3	9,1
24,70	31,11	11,83	0,7	0,1	2,2	2,8
31,11	39,21	23,67	0,1	0	0,6	0,6

Table 4.
Parameters of model solutions quality

Characteristics of model solutions	Experiment			
	A	B	C	D
Dry substance (°Bx)	79,30	79,50	79,20	79,00
Purity (%)	90,30	90,60	90,50	90,41
Concentration of nonsucrose compounds (g/g H_2O)	0,37	0,36	0,36	0,36
Saturation temperature (°C)	75	76	75	74
Supersaturation at the point of seeding	1,10	1,12	1,13	1,20

Table 5.
Crystal size distribution in sucrose model solution, which is seeding by 0,07% w/w slurry

Size range		Crystal number (10^4/g)	Number fractions (%)	Crystal mass (mg/g)	Mass fractions (%)	Cumulative mass fractions retained (%)
d_1 (µm)	d_2 (µm)					
17,19	22,16	1,549	17,9	0,1	0,1	100,0
22,16	27,93	0,764	8,9	0,1	0,1	99,9
27,93	35,36	0,296	3,4	0,1	0,1	99,8
35,36	44,56	0,242	2,8	0,1	0,1	99,7
44,56	56,24	0,354	4,1	0,4	0,3	99,6
56,24	70,86	0,459	5,3	1,0	0,8	99,3
70,86	89,25	0,632	7,3	2,8	2,2	98,5
89,25	112,50	0,650	7,5	5,8	4,7	96,3
112,50	141,70	2,213	25,7	39,2	31,4	91,6
141,70	178,50	1,122	13,0	39,8	31,9	60,2
178,50	224,90	0,206	2,4	14,6	11,7	28,3
224,90	283,40	0,134	1,6	19,0	15,2	16,6
283,40	357,20	0,006	0,1	1,7	1,4	1,4

Table 6.
Crystal size distribution in sucrose model solution, which is seeding by 0,09% w/w slurry

Size range		Crystal number (10^4/g)	Number fractions (%)	Crystal mass (mg/g)	Mass fractions (%)	Cumulative mass fractions retained (%)
d_1 (µm)	d_2 (µm)					
17,19	22,16	0,748	7,5	0,1	0,1	100,0
22,16	27,93	0,247	2,5	0	0	99,9
27,93	35,36	0,314	3,2	0,1	0,1	99,9
35,36	44,56	0,511	5,1	0,3	0,3	99,8
44,56	56,24	0,655	6,6	0,7	0,8	99,5
56,24	70,86	1,047	10,6	2,3	2,4	98,7
70,86	89,25	2,288	23,0	10,1	10,7	96,3
89,25	112,50	2,103	21,2	18,7	19,8	85,6
112,50	141,70	1,286	13,0	22,8	24,1	65,8
141,70	178,50	0,488	4,9	17,3	18,3	41,7
178,50	224,90	0,159	1,6	11,3	12,0	23,4
224,90	283,40	0,762	0,8	10,8	11,4	11,4

Table 7.
Crystal size distribution in sucrose model solution, which is seeding by 1,7%w/w slurry

Size range		Crystal number (10^4/g)	Number fractions (%)	Crystal mass (mg/g)	Mass fractions (%)	Cumulative mass fractions retained (%)
d_1 (μm)	d_2 (μm)					
11,55	14,56	0,559	0,9	0	0	100,0
14,56	18,37	0,916	1,5	0	0	100,0
18,37	23,12	1,851	3,0	0,1	0,1	100,0
23,12	29,15	3,102	5,0	0,5	0,5	99,9
29,15	36,74	6,554	10,7	2,0	2,0	99,4
36,74	46,27	12,429	20,2	7,7	7,4	97,4
46,27	58,29	15,378	25,0	12,0	11,6	90,0
58,29	73,44	12,690	20,7	31,4	30,3	78,4
73,44	92,53	6,053	9,9	30,0	29,0	48,1
92,53	116,60	1,683	2,7	16,7	16,1	19,1
116,60	146,90	0,151	0,2	3,0	2,9	3,0
146,90	185,10	0,003	0	0,1	0,1	0,1

Table 8.
Crystal size distribution in sucrose model solution, which is seeding by 2,9%w/w slurry

Size range		Crystal number (10^4/g)	Number fractions (%)	Crystal mass (mg/g)	Mass fractions (%)	Cumulative mass fractions retained (%)
d_1 (μm)	d_2 (μm)					
11,55	14,56	17,940	13,4	0,3	0,5	100,0
14,56	18,37	19,374	14,5	0,7	1,2	99,5
18,37	23,12	20,079	15,1	1,5	2,6	98,3
23,12	29,15	20,494	15,3	3,2	5,6	95,7
29,15	36,74	17,998	13,5	5,6	9,7	90,1
36,74	46,27	17,414	13,0	10,7	18,6	80,4
46,27	58,29	14,167	10,6	17,5	30,3	61,8
58,29	73,44	4,915	3,7	12,2	21,1	31,5
73,44	92,53	1,126	0,8	5,6	9,7	10,4
92,53	116,60	0,033	0	0,3	0,5	0,7
116,60	146,90	0,002	0	0,0	0	0,2
146,90	185,10	0,002	0	0,1	0,2	0,2

DISCUSSION

The characteristics of particle size distribution of slurry were: mean particle size d_{RRSB} = 17 μm, uniformity coefficient n = 3,1 and number of particles larger than 3 μm = $0{,}7 \cdot 10^7$ /cm^3 . Granulometric composition of slurry implies that satisfactory ratio of sugar and iso-propanol was used, that is, the effect of milling is good. The largest numerical share from 66,4% consists of particles whose size ranges approximately from 6,17 μm to 12,35 μm. Experimental data, which are presented in Table 2 and Table 4, shows the reproducible conditions of cooling crystallization.

In the laboratory tests the amount of slurry varies from 0,07% to 2,9% w/w. According to d^3 rule the amount of 0,15% w/w is estimated.

Table 9.
Characteristics of crystal size distribution

Experiment	A	B	C	D
Mean crystal size (µm)	190	165	90	64
Uniformity coefficient	4,5	4,3	4,5	3,5
Size range (µm)	17,19–357,20	17,19–283,40	11,55-185,1	11,55-233,20
Crystal number (1/g)	86 261	99 229	613 717	1 335 455
Maximum mass distribution				
Frequency (%)	31,9	24.1	30,3	30,3
Size (µm)	160,1	127,1	65,9	52,3

Table 10.
Characteristics of crystal number and mass distribution

Experiment	A	B	C	D
Crystal size < 14 µm				
Number contribution (%)	33,0	18,3	41,4	84,8
Mass contribution (%)	0,3	0,5	10,0	38,1
Crystal size 44 – 112 µm				
Number contribution (%)	24,3	61,4	58,3	15,2
Mass contribution (%)	8,0	33,7	87,0	61,7
Crystal size > 112 µm				
Number contribution (%)	42,7	20,3	0,3	0
Mass contribution (%)	91,7	65,8	3,0	0,2

This calculation assumes the final characteristics of crystallizate: crystal main size of 100 µm and crystal content of 10%. It can be concluded that the crystal contents of 10% are achieved in experiments A, B i C which are seeded by slurry amount from 0,07 to 1,7%. Lower slurry amounts initiates lower number of crystals that have larger size and mass. This effect is presented in Table 9. Carriers of mass are larger crystals, which is shown in Table 10. In this experiments the values of crystal uniformity coefficient are about 4,5, that present good results. In experiment A, that was seeding with 0,07% w/w of slurry, the secondary nucleation was occured, although the seeding point of supersaturation was in the metastable zone.

In experiment D crystallization have given results of lower quality, because of the application of too great amount of slurry 2,9%. Bigger quantity initiates growth of larger number of crystals that have smaller size and mass and lower uniformity coefficient.

In Table 11 the results of crystal growth rate are presented. The mass crystal growth rate and linear crystal growth rate become lower with increasing the amount of slurry.

Table 11.
Mass growth rates and linear growth rates of sucrose crystals

Experiment	A	B	C	D
Linear growth rate (µm/min)	1,06	0,92	0,50	0,36
Mass growth rate (mg/m^{2}min)	907	758	278	275

CONCLUSION

This paper deals with the results of the application of Coulter Counter method for the investigation sucrose crystallization kinetics in sucrose model solutions in presence of nonsucrose compounds. Cooling crystallization was carried out in laboratory scale in reproducible conditions. The solutions purity was varied in very narrow range from 90,30% to 90,60%. Dry substance of solution were ranged from 79,00 °Bx to 79,50 °Bx. The supersaturation at the point seeding was in metastable zone in all experiments. Initation of the growth of sucrose crystals in model solutions was done by seeding with different amounts of slurry from 0,07% to 2,9% w/w.

Investigating the effect of seeding on the kinetics of sucrose crystallization the following can be concluded:

- The most favorable characteristics of crystal mass were achieved in solutions that were seeded with 0,07% to 1,7% w/w of slurry.
- According d^3 rule, the teoretical estimated amount of slurry was 0,15% w/w. Slurry amount of 0,09% w/w is the most similar to the teoretical value.
- The amount of slurry had strong influence on the crystal size distribution, mean size, uniformity coefficient and secondary nucleation.
- The values of crystal mass and linear growth rate depended on the applied amounts of slurry.
- The Coulter Counter method can be applied for the determination of the crystal size distribution, crystal mass and linear growth rate.

ACKNOWLEDGMENTS

This research work is the part of project number 20066 - head Dr Jasna Mastilović. This project is supported by Ministry of the Science and Technological Development, Republic of Serbia.

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