C SUGAR EXTRACTING IN HAKIM FARABI SUGAR REFINERY AND CRYSTAL STUDYING

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Abstract— Crystal and crystal formation since are the important Characteristics in the curing process of sugar factories. This project deals with: 1) studying the sucrose crystal determination and simulating cluster stricter by the SHELX, 2) Seed preparing technics of industrial sugar production, and 3) enhancement of C sugar production in the Hakim Farabi sugar refinery. The simulation takes the comprehensibility of image analysis. Rosin-Rammler and mathematical analysis determined the efficient seed. The data result from analysis indicated that RR could be an able model in sugar extraction and other crystallization processes.

Index Terms— SHELX, C sugar, Crystal Size Distribution, Supersaturation, Rosin-Rammler, uniformity coefficient.

INTRODUCTION

Crystal size distribution (CSD) is one of the most important parameters in sugar production. Objective is to grow crystals of uniform sizes or narrow CSD. Growth rate dispersion (GRD) causes a significant problem in the CSD of crystalline products, and gives a wide range of crystal product sizes. GRD can increase the amount of small, slow-growing crystals that it causes reduction of mean particle size [1]. GRD is due to difference in microscopic surface roughness which is caused by surface nuclei generated on the surface of the crystals [2].

Many equations are presented for quantitative and qualitative investigation of CSD such as Nukyama-Tansawa, Gates–Gaudin–Schuhmann (GGS), lognormal distribution, Rosin-Rammler (RR) models. RR equation is more suitable than Nukyama-Tansawa, since in RR two parameter are required whereas in Nuklyama-Tansawa equation four parameters (K_D, m, n, p) are needed [3]. RR model provides more accurate result for PSD analysis of agglomerated cork separation, than (GGS) model [4].

Driving force of crystallization process is Supersaturation (SS) and the speed of crystal growth is proportional to that. In literature the influence of saturation degree on crystal growth rate was studied [5, 6]. Khaddour et al studied the effect of initial SS on the sugar crystal growth and concluded that surface diffusion at low SS levels, and fast growth rates at the initial times of the growth process affect the following growth rate [7]. SS controlling is an important factor for investigating of growth kinetic and CSD [8] while monitoring of SS causes significant decrease in growth time [9]. However growth time decreases by increasing of SS but it may advance other undesired mechanisms (agglomeration, nucleation). Taking SS between solubility and nucleation curve (metastable zone) causes appropriate results. Inhomogeneity of the SS in the crystallizer is influenced by incomplete agitation and effect the CSD by local nucleation [10]. There must not be nucleation and breakage during the crystallization process and the batch should not be mixed with other batch crystals with a different history. Nuclei seed improving represents the most effective role in the crystallization progress that affects crystal growth and CSD [11, 12, 13, 14, 15, 16].

The CSD appears to be determined by the growth rate history of the crystals and the relative SS of the solution from which crystals are grown. The results from this study help use of RR model for comparing three types of sugar seeds nuclei in CH condition and fixed SS level to improve C sugar extraction in Hakim Farabi sugar refinery.

Experimental Section

Materials and equipment

Iranian Canesugar Corporation especially Hakim Farabi sugar refinery R&D center takes much force on sugar extraction. Crystallization process in this factory is based on the "three massecuites boiling system: A, B and C (as the final extracting stage). As it is shown in fig (1) the C crystallization process consists of three steps; seed magma preparation (C seed), continuous vacuum pan (CVP) and four times of cooling crystallizers respectively. At first the seed magma in the evaporative crystallizer are prepared then are fed by B liquor (purity=66.3, brix=84.5) and are heated under 75 ˚C in the CVP to be grown. Then the produced C massecuite is introduced into continuous cooling crystallizer since larger crystal size to be achieved.

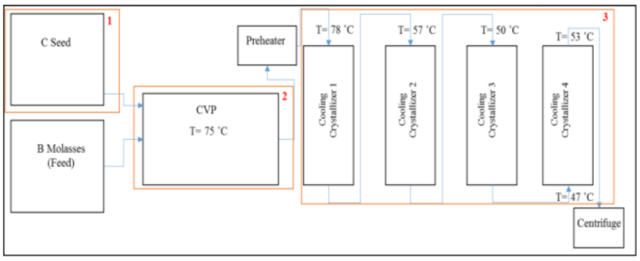


Figure (1): C step sugar crystallization in Hakim Farabi sugar refinery

All chemicals were of analytic grade and directly used as received. Sugar ($C_{12}H_{22}O_{11}$, ≥99.5%), were purchased from Merck. Isopropyl alcohol (>99.7%) was also purchased from Merck as a nonsolvent. Water used in these experiments was deionized and distilled. The crystallizer reactors was SIIC batch type vacuum pans. The Schmidt Haensch refractomoter was used measuring purity and brix. The 5 liter capacity nutsch filter is made in the factory. The HAVER EML 200 digital plus sieve was used crystal sieving. The microscope is the Nikon Eclipse 200 LED Binocular type.

Crystal size and size distribution

Crystals were grown in a batch of 45 m3 for white and 60 m3 for raw. In each analysis 100ml of massecuite was filtered through 30µm nutsch analyzer. Five times 1- 2 mg of samples were prepared to measure the crystal size. Sample crystals size was measured by calibrated microscopic fixed CCD camera. Best CSD emphasized on considering all crystals growth on desired size and minimizing content of fine grains.

Crystal uniformity

Nonuniform crystals reduce desired volume of crystals and causes filtration problems. Against uniform crystals result constant production rate, complete filtration and high crystal content. Crystals size uniformity have so significant role in growing rate. By optimizing the size uniformity, growth rates uniformity will be accessible. In other words GRD is decreased. In this study RR method applied investigating uniformity coefficient of produced crystals. RR equation, eq, 2;

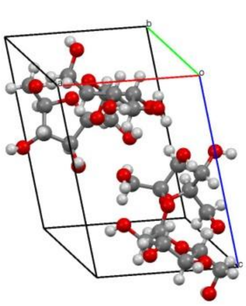
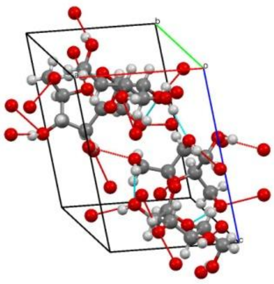
y=1-exp[-(d/d^')^n]   (2)

is introduced in MATLAB tool to calculate mean size, uniformity coefficient and to plot the uniformity diagram for comparing three seed nuclei types.

Results and Discussion

Sugar crystal simulation

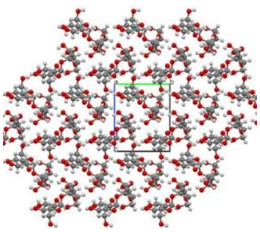
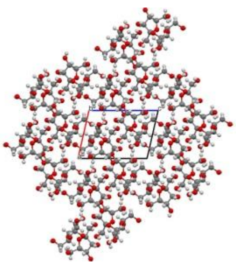
The sugar molecules arranged in the $P2_1$ (a=7.7, b=8.8, c=10.8, α=90.00, β=102.98, γ=90.00, cell volume=702.93) space group. Fig (2) shows the unit cell structure of the sucrose which modeled by the Shelx.

(a) (b)

Figure 2: Sucrose unit cell, a) simple structure, b) unit cell by H-bonds

Operational determination of three-dimensional cluster and nuclei structures is critical for studying structure–functions and for supporting CSD drug analysis. The great interest of cluster determination focused on secondary nucleation that may arise in the crystallization process. Basic information of the sucrose clusters are shown in the fig (3) .

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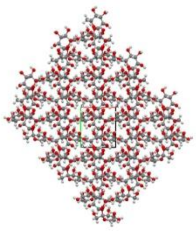


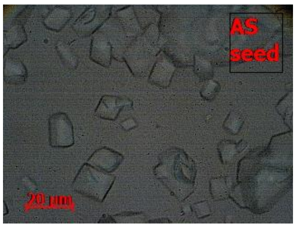
(c)

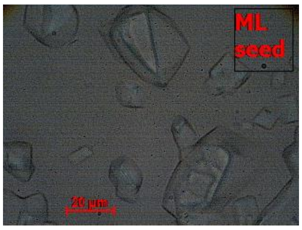
Figure 3: Sucrose cluster simulated by the SHELX program, a) Sucrose cluster along A, b) Sucrose cluster along B, c) Sucrose cluster along C.

Distinguishing between cluster and nuclei regime is firstly based on the size and then based on the growth activation free energy values.

Nuclei Seed and Seed Preparation

Nowadays crystal seed injection is common method of industrial nucleation in sugar crystallization process. Tree types of seeds were prepared fig (4):





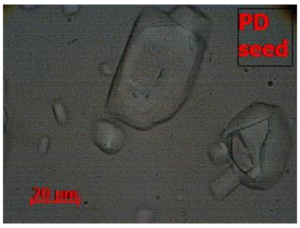


Figure (4): Microscopic image analysis of nuclei seeds (AS, ML, and PD)

Agitating saturated solution AS: Amount of sugar crystals were sieved by 850, 700, 650, 500, 355 and 250 µm size during 45 min. Then 900 g of sieved sugar crystals around about five batches are collected and dissolved in 360 ml distilled water at 70 C0. This solute was added in 2000 ml stirred isopropyl alcohol. 1650 ml other isopropyl alcohol added five minutes later. After 30 min stirring, slurry was dried and filtered by 50 µm sieve and solved in isopropyl alcohol. Produced slurry named AS.

Wet milling filtered crystals ML: In this way sugar crystals in order to reform in seed size are affected by physical force in presence of organic solvent. Solvent should not be sugar solver such as isopropyl alcohol, ethanol. At first amount of crystals are sieved. Then 1 kg of sieved sugar product by 650-800 µm size sieve are collected. Then collected sugar is washed by saturated isopropyl alcohol for 15 min to remove fine particles. 2200 ml of isopropyl alcohol decanted in ball mill in the running state. Then 1 kg of 650- 800 µm sieved sugar added it. After 4 hours running produced slurry was dried and filtered by 50µm sieve. Finally this product seeds was spread in isopropyl alcohol to produce seed slurry named ML in this study.

Powdered crystals: In sugar refinery after centrifuging and drying step sugar crystals elevated for warping. In this step grain and small crystals are separated and because of low weight are dispersed in the factory environment. Yet no application introduced for this grains. Amount of this particles collected and are washed by isopropyl alcohol. Then they were dried for 3 hours and filtered by 50µm sieve. Amount of needed powdered directly used in nucleation.

Common History seed (CHs) and crystal growth

Tanneberger et al [20] studied the effect of variation of SS on the growth rate of potash alum crystals. They observed that in secondary step of the two steps change in SS, growth rate increase and decrease with increasing and decreasing of SS respectively, but not with the previous value, after returning to the first SS. CHs crystal growth rate was studied in the batch crystallizer. Therefore in constant low SS, and fixed temperature and fixed vapor pressure the crystals GRD will be proportional to the seeds that introduced in the solution.

Crystallizer is fed by pure sugar solution brix (BX) 63.35, purity 98.92, and temperature 70 ˚C SS controlled for pure solution by sugar concentration that directly depends on sugar solubility and for syrup by Viklund-Vavricenz solubility coefficient (SC) related on sugar concentration and amount of nonsugar per water (NS/W) in syrup. Vapor pressure fixed on the vacuum 100 - 120 kPa abs. Amount of seed introduced to crystallizer represented by equation that related on required crystal size, eq. 3:

G_s=C_y*(S_s/C_s)^3*1587*1000 (3)

where Gs represents gram of seed needed per cubic meter of massecuite. Cy is the required crystal size Ss and Cs are the seed size and required crystal size respectively. By improving CSD decreasing crystals damage in filtration, descent of polymorphs creation and facilitate drying process can be achieved. The sugar with narrow size distribution gives more qualitative and quantitative efficiency in industrial production. CSD can be studied by achieved comparing information about sugar seeds quality. CSD behavior during crystallization progress gives information about history of crystals growth. In a way that keeps a defined CSD curve means uniform growth related to the size of crystals were occurred. CSD presented along four times on Log-normal CSD. A mass log-normal CSD demonstrates that the number distribution is consequently log-normal with the same numeral standard deviation and same geometric distribution [17].

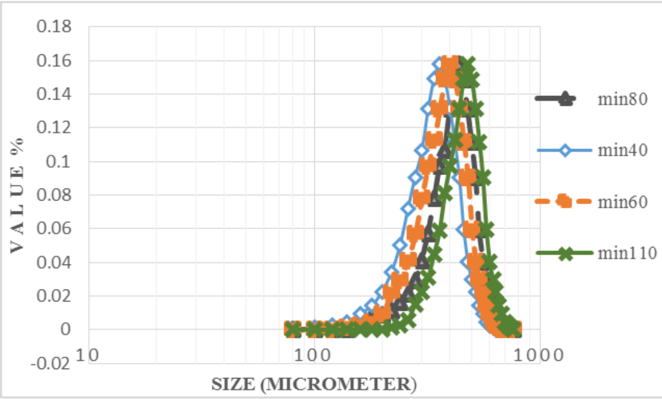


Figure (5): Crystal Size Distributions of crystal growth nucleated by solute seed slurry

Fig (5) shows that CSD follow a regular progress with crystal size increasing meaning that CSD have same geometrics. This type of growth progress shows that no breakages, nucleation or dissolutions were happened during the crystallization. In same condition of crystallization, common growth rate history is feasible. Cumulative CSD fig (6) shows that the distribution curve during the crystallization stage was shifted to the larger sizes with the same slop. Also the growth of crystals in the metastable level SS with the time is intelligible whereas the crystals have their initial uniformity without any breakages, dissolutions or nucleation.

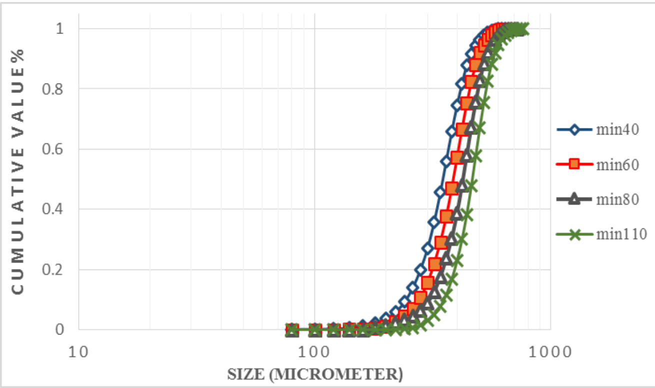


Figure (6): Cumulative Crystal Size Distributions of crystal growth nucleated by solute seed slurry

Nuclei seeds comparison

Nucleation to sugar crystallization was handled by seeds in 25 sets of runs for seeds comparison in white sugar solution. Each set contained three runs for three seeds. 25 other sets of runs acted for seed comparison in raw sugar solution. CSD can be studied by RR equation. An advanced model of RR equation introduced to MATLAB software to show a retained against the crystal size.

Full seeding system is important in industrial sugar production. Therefore it is required to know crystals behavior in sugar crystallization progress. Crystal percent retained in definite size demonstrates the quality of CSD that the narrow size distribution indicates large slop.

For raw sugar production such as white sugar solution the CSD of crystals were determined and RR distribution plots were drawn. Difference between two types of solution (white & raw) is the amount of nonsugar component such as carbohydrate (mono, oligo and poly, saccharides) and inorganic salt and components (K, Na, Mg salts). These components affect the crystal growth and shape. Therefore these components affect the GRD and so CSD [17, 18]. Fig(7) indicates, AS crystals represents the largest slope and ML crystals follow a slope lower than AS and higher than PD. High slope represents crystals were grew with high uniformity and have narrow crystal size distribution.

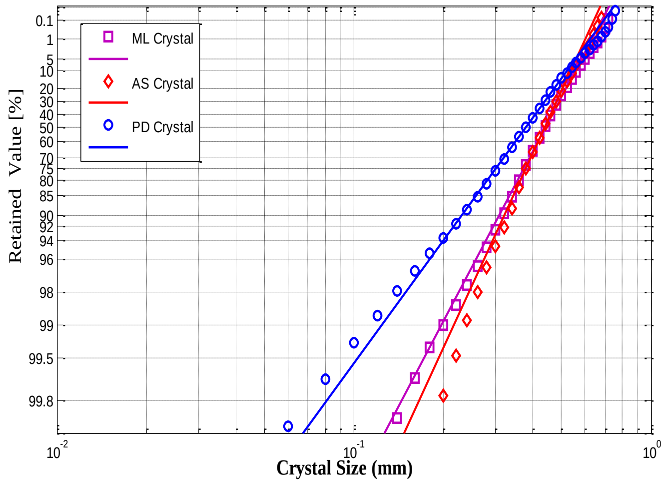
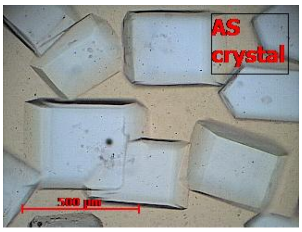
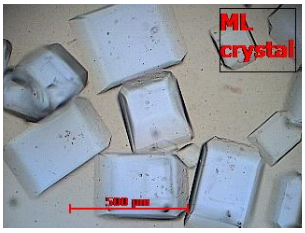


Fig (7): RR Diagram of sugar crystals seeded in raw sugar solution

Crystal uniformity

White sugar crystals: Crystal size uniformity coefficient has more important role in crystal content, sugar extraction, crystal filtration, drying and savage. Note that law uniformity coefficient cause solving of molasses film of small crystals and tight film around the large crystals and sucrose loss. Otherwise high uniformity facilitate centrifuging operation and also time and energy savage. However the high uniformity coefficient causes controllable filtering and desired molasses film on crystals to comfortable saving. RR represents the uniformity coefficient of crystals investigating the CSD.





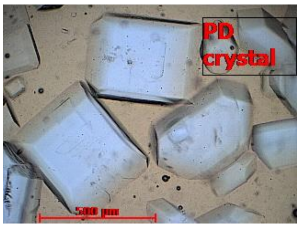


Figure (8): Image analysis of produced sugar crystals (AS, ML, and PD)

Raw sugar Crystals: In this case as it shown in table (2) such as white sugar crystals the AS crystals get best result but PD crystals get undesired uniformity coefficient 3.39±0.04 not as for white sugar solution 4.39±0.04. It can be because of carbohydrate and inorganic component influence on the crystal lattice. These results are sensible in the presented crystals image fig (8).

Table (1): Uniformity Coefficient (UC) for crystals resulted from seeded raw sugar solution

NUCLEI / SEED	AS	ML	PD
D'(MM)	0.466±0.005	0.0473±0.006	0.418±0.009
UC	6.00±0.02	5.25±0.02	3.38±0.04

Investigating crystallization process in final sugar production stage by RR model

The CSD of sugar is one of the most important parameters that controls the extraction and crystallization process. Series of experiments have been carried out to investigate the effect of CSD and crystals uniformity on the sugar extraction. The RR distribution model was used investigating CSD for the crystals recovered within the outlet of each crystallizer respectively. The cumulative and RR distribution model of crystals are depicted in fig (9), (10).

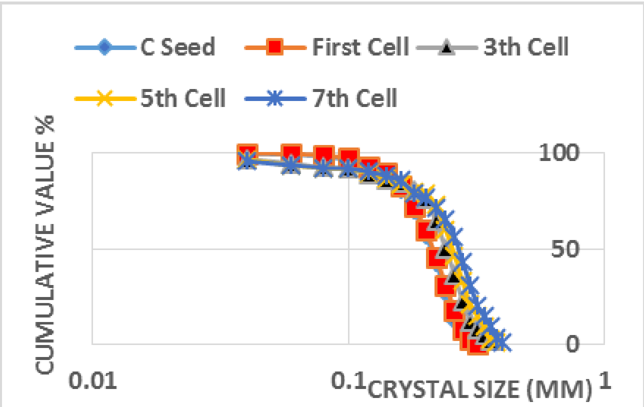


Figure (9): Cumulative log-normal CSD during the C crystallization in the CVP.

During CVP quality of the CSD decreases and the fine crystals are increasing during crystallization stage. Furthermore the uniformity coefficient (n) during CVP crystallization are decreasing and the fine crystals are increasing. Also the CSD broadens with passing the CVP during the crystallization. These results suggest that the fine size of the crystals in the CVP stage is decaying the common history of crystals growing.

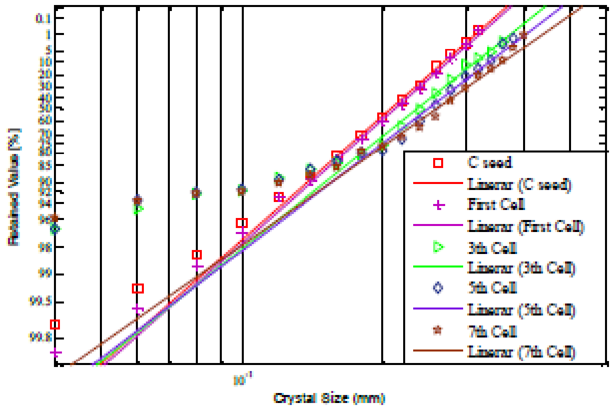


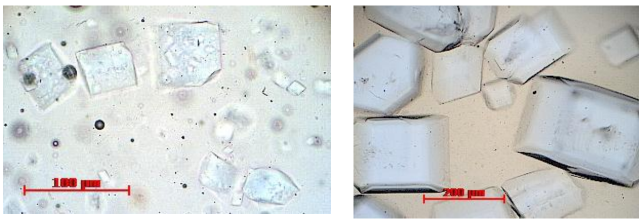
Fig (10): RR model of CSD during the C crystallization in CVP.

Size uniformity coefficient has more important role incrystal content, sugar extraction, crystal filtration, drying and savage. Crystal fineness (K) and uniformity coefficient (n) are examined from view of their ability on the size characterizing. Note that law uniformity coefficient causes solving of molasses film of small crystals and tight film around the large crystals and also sucrose loss. The characteristic parameters of CSD such as crystal fineness (K) and uniformity coefficient

(n) are also presented in Table (2). In all of the crystallization processes K value increased during crystallization. When the crystals grow with the related history of their size the CSD will keep n constant, where the larger the value of n indicates, the narrower CSD [2-5].

In the CVP the mean crystal size was decreasing and the size variation was increasing. And the n value is decreasing through the CVP and the sizes are losing their uniformity against the C seed crystals. The possible explanation is addition of amount of small crystals with the B liquor that create greater competition for solute as the general and the small added crystals grow to become in desired size. The results are in agreement with in the crystals were shown in fig (11).

The mathematical analyzing of crystals presents a numerical view of crystals growth. In the CHS growing of crystals the numerical standard deviation of the crystal size was constant during crystal growth. Also the Coefficient of Variation (CV) of crystals will be constant during the crystallization process if crystals grow in CHS condition [20]. High amount of CV indicates less amounts of uniformity. By controlling of the CSD and other relative parameters, narrow crystal size is feasible. Low amount of CV causes effective purging otherwise different dimension crystals lose some sugar during purging (separation step).



(a) (b)

Figure (11): Microscopic images of sugar crystals B liquor crystals(a), CVP crystals (b)

Table (2): mathematical evaluation of crystal growth; coefficient of variation and crystal mean size during Cvp sugar extraction process

CVP Steps	**CV**	**Mean Size**
Seed Magma	35.14	213.48
First Cell	36.21	235.34
3th Cell	37.56	238.68
5th Cell	38.62	239.81
7th Cell	39.74	238.46

Conclusion

Sugar extraction was studied by RR technique, mathematical model, and growth habit of crystals (GRD and CHs). C sugar process fixed in the analytical condition of CHs. Three types of seeds were compared of CSD and Uniformity Coefficient. The AS seed introduced to C sugar extraction and the secondary nucleation and image analysis improved by the SHELX crystal simulation. RR and lognormal distribution can be applied for investigating CSD in crystallization process and these results give the best crystallographic way of online monitoring of crystal growth technique.

Appendices

1) Solubility Coefficient (SC):

SC=-0.06265*NS/W+0.982+(0.018) exp (-2.1*NS/W)

2) Brix (BX):

The sugar content (%w/w) in pure solution and dissolved solid content in impure solution.

3) Purity:

The true purity is the sucrose content such as the brix. The dissolved solids consist of sugar plus nonsucrose components (colorants, ash, and invert). Apparent purity is expressed as polarization divided by refractometer brix, multiplied by 100.

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