the elimination of organic acids as their calcium salts. Conductivity measurements were also made which showed the extraction of non-sugars in the process of diffusion. This varied in the order of L.M.J. > D.J. > M.J. > C.J. > P.J., i.e. a continuous increase in the conductivity as the process of extraction progressed. Even at as low a Brix as 3·0, the conductivity of the last mill juice was $0{\cdot}34 \times 10^{-2}$ and that of primary juice at 18·0°Brix as $0{\cdot}21 \times 10^{-2}$. By taking conductivity as a direct measure of non-sugars, it may be seen that considerable quantities of non-sugars were extracted and/or passed into the system during diffusion.

Acknowledgments

Authors' thanks are due to Sri S. L. SAXENA, Director, National Sugar Institute, Kanpur, for his kind interest in the work.

Continuous sucrose nucleation

Observations of secondary particle breeding in sucrose/water/organic systems as related to a continuous sugar pan

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PART I

INTRODUCTION

THE development of a continuous sugar-boiling pan in the sugar industry is a major problem of long standing. DR VRIES[1], LUCE[2] and SILVER[3] all describe the state of development of continuous sugar processes as well as some of the problems encountered, while the system in use by the Verenigde Coöperatieve Suikerfabrieken G.A. has also been described[4]. Continuous sugar pans are particularly attractive for sugar refiners because of their centralization and large capacity together with the high state of automation of other unit operations. Savings to be expected include higher throughput per unit capital and operating costs as well as the possibility of improved product quality. BENNETT[5] has indicated the savings in steam costs to be expected in a continuous process.

Any continuous sucrose refining process must cope with the following items:

(*a*) operating costs should be reduced,

(*b*) better control should be achieved with reduced labour,

(*c*) product quality (ash, colour, purity) should be unimpaired or improved,

(*d*) crystal size distribution (CSD) should be uniform and controllable, i.e. mean size and narrowness of distribution should be acceptable,

(*e*) crystal habit and appearance should be attractive, and

(*f*) pan automation should fit in with existing automatic control.

Raw sucrose crystallization processes are geographically more dispersed and generally of lower capacity. However, there is an equal incentive to reduce unit costs through continuous processing. A similar list of items to cope with can be written

NOMENCLATURE

B°	nucleation rate, number per cm³ per min.
CV	coefficient of variation; standard deviation divided by mean, based on mass-weighted particle size.
G	linear crystal growth rate, microns/min.
i	exponent of growth rate in nucleation kinetics expression
j	exponent of solids concentration in nucleation kinetics expression
k_n	coefficient in nucleation kinetics expression
k_v	crystal volume shape factor, (volume)(length)$^{-3}$
L	crystal size, microns
M_t	solids concentration, g.cm^{-3}
$n(L)$	population distribution function, number per cm³-micron
n°	nucleus population density, B°/G, number per cm³-micron
S	coefficient of supersaturation, C/C_s
T	temperature, °K
ρ	crystal density, g.cm^{-3}
τ	crystallizer retention time, V/Q, hr.

[1] *Sugar y Azúcar*, 1957, **52**, (4), 27.
[2] *I.S.J.*, 1970, **72**, 131–133, 170–172.
[3] *Sugar y Azúcar*, 1970, **65**, (6), 36.
[4] *I.S.J.*, 1970, **72**, 221; *Sugar y Azúcar*, 1970, **65**, (10), 29.
[5] *Chem. Eng. Progress, Symposium Series*, 1969, **65**, (95).

for continuous raw sucrose processes; however, there is a greater emphasis on product quality (impurities must be removed later in expensive refinery steps). Continuous operation should be compatible with existing batch facilities as the dispersed state of the industry would make difficult the amortization of large sums for capital. Alternatively, improved product quality should pay for the new capital required. In raw sugar processing crystal size distribution and appearance are only important insofar as they affect final product purity.

The above discussion indicates that CSD, both magnitude and form (i.e. mean size and shape of distribution), is an important factor in the development of continuous raw or refined sucrose processes. RANDOLPH and LARSON[6] discuss the entire problem of manipulation of CSD and present a general algorithm relating crystal growth and nucleation rates with process configuration. These authors indicate the importance of the exponential population density distribution $n(L)$* in a data gathering and reference sense by means of equation (1).

$$n(L) = [\frac{B^{\circ}}{G}] \exp\{-L/G\tau\} \quad \ldots\ldots(1)$$

This exponential form is the expected distribution from a continuous mixed suspension, mixed product removal (MSMPR) crystallizer. A measure of the wideness of a distribution is the coefficient of variation (CV) defined as the standard deviation divided by the mean[7]. The exponential population distribution has a CV (mass basis) of 50%. If the weight density distribution function can be approximated by a normal distribution, the CV may be calculated[6] as follows:

$$\text{CV} \simeq \frac{L_{0\cdot84} - L_{0\cdot16}}{2L_{0\cdot50}} \quad \ldots\ldots(2)$$

Equation (2), easily computed from a cumulative screen analysis, is often used as a practical measure of wideness of particle distributions.

The MSMPR distribution is in general too wide to be acceptable for either raw or refined sucrose processing. HILL and ORCHARD[8] and RANDOLPH *et al.*[9] discuss the narrowing that can be expected in staged continuous processes with seeding of nuclei only in the first stage and with an equal product of growth rate times retention in all stages. In this case

$$\text{CV} = \frac{1}{(k+3)^{1/2}} \quad \ldots\ldots(3)$$

for the expected wideness of product from the k'th stage of a staged continuous process. Equation (3) indicates that staging *per se* is not a very efficient way to duplicate the 25–30% CV's that can be obtained in careful batch sugar boiling pans. RANDOLPH *et al.*[9] indicate the fortuitous narrowing of CSD that occurs in a continuous staged, classified process, but do not suggest any feasible way that such size classification can be achieved in a viscous massecuite.

The problem of narrow CSD has been attacked in the Fives Lille-Cail continuous process[8] with an apparatus that approaches plug flow, this being analogous to a process that is batchwise in time. In the limit an infinite number of unseeded stages is equivalent to the ideal plug flow configuration. Equation (3) indicates the asymptotic narrowness to be expected with many stages in series; a few stages, e.g. two or three, may not duplicate batch or plug flow processes yet may produce acceptably narrow products. Product narrowness is a moot point for the raw sucrose industry if dewatering of massecuite is acceptable and final product purity is improved. BENNETT[10] indicates that continuous crystallization machines of the FC type produce smaller CV than machines of the DTB type, often through elimination of oversize particles. The former crystallizer type is a likely machine for use in continuous sucrose processes. Staging, with seed source only in the first stage, narrows a distribution by growth of the fine crystals. Thus, a staged FC crystallizer would appear to have advantages in producing an acceptable product. However, it is unlikely that backmixed continuous processes with existing technology can compete with carefully controlled batch processes in the area of product narrowness. If proper amounts of crystals can be made in each size range, sucrose refiners can sidestep the problem of narrowness by sieving the final product.

An area closely related to product CV, and equally important, is mean product size. Particle size is a direct function of the number of seed relative to production; batch crystallizers with controlled seeding can, within limits, manipulate both these variables to change size. However, a continuous process with a stable seed source should be able to control product size within tighter limits.

Seeding of sucrose pans is directly related to the mechanisms of nucleation in the system. VANHOOK[11] discusses three regions of sucrose nucleation as a function of supersaturation driving forces.

(*a*) *Homogeneous Region* (S>1·3). New growth centres are formed by homogeneous nucleation as a function of supersaturation driving forces alone so that unseeded batch processes will nucleate under these conditions. Nucleation kinetics can be reasonably explained with the well-known homogeneous model deriving from Gibbs free energy considerations.

(*b*) *Secondary Region* (S=1·2–1·3). Spontaneous nucleation does not occur, but existing centres continue to grow and may induce further secondary nuclei (false grain). BENNETT[5] has shown that secondary nucleation occurs in backmixed crystallizers of the FC type.

(*c*) *Metastable Region* (S<1·2). In this region negligible homogeneous or secondary nucleation occurs, but

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* For the meanings of symbols see the key to nomenclature in the panel on p. 8.

[6] "*Theory of Particulate Processes*" (Academic Press, New York), 1971.

[7] POWERS: *I.S.J.*, 1948, **50**, 149.

[8] *Sucr. Belge.*, 1967, **87**, 200.

[9] *Amer. Inst. Chem. Eng. J.*, 1968, **14**, (5).

[10] *Chem. Eng. Progress*, 1962, **58**, 9.

[11] "Principles of Sugar Technology", Vol. 2, Ed. P. HONIG. (Elsevier, New York), 1959, pp. 113–148.

seed that is introduced will continue to grow. The existence of such a wide metastable region allows batch crystallizers to make sugar of exceptionally narrow CSD.

It becomes obvious that any continuous sucrose crystallization process must develop a stable continuous seed source and/or rely on secondary nucleation (false grain) mechanisms. The level of supersaturation driving forces encountered in typical continuous processes is such that some, if not all, growth centres will have to be added. Thus, development of a high quality continuous grain source is mandatory. The current practice of ball milling sucrose crystals in *iso*-propanol to make a seed innoculum may be adapted to continuous operation, but control of particle numbers and possible adverse effects of irregular seed shape on final crystal habit and purity have not been definitively investigated.

Scope of Present Work

The work reported in this paper describes a continuous secondary sucrose crystallization process that produces a fine-sized seed fondant of well-formed single crystals suitable as a seed source for a large-scale continuous process. Randolph[12] discovered that sucrose would breed copious quantities of secondary nuclei when a high concentration feed syrup (*ca.* 68°Brix) was continuously salted-out with lower molecular weight alcohols, ketones or mixtures of these. Low mass ratios of solvent:water (less than 2·0) were necessary to produce crystals of desirable single-crystal habit. Randolph and Crawford[13] and Crawford[14] studied this phenomenon and more carefully defined solvent type and condition required to produce acceptable numbers and quality of sucrose seed. Ziebold[15] continued this study and further maximized the yield of nuclei using a statistical experimental design of the significant variables.

That this process entails the mechanism of secondary nucleation is clearly shown by the fact that, after the feed streams are well mixed in the nucleator, considerable time (2 or 3 hours) elapses before breeding of secondary nuclei occurs. The appearance of these nuclei can be considerably speeded up by seeding the vessel initially with product-sized sugar. Kelly and Mak[16] describe an analogous technique for the homogeneous nucleation of sucrose using a salting-out process with ethanol or methyl cellosolve as the miscible organic agent. Excessive mass ratios (organic:water) of 25:1 to 120:1 were found to be necessary to promote homogeneous nuclei formation.

The present work continues process development of the salting-out secondary breeding process as a viable alternative for seed source in a commercial continuous sugar process. Specifically, conditions were sought which would produce sucrose nuclei densities of 10^6–10^7 nuclei/cm^3-micron with a population-weighted mean crystal size of 10–12 microns. A constraint on operating conditions was that the nuclei formed must be predominately of single-crystal habit.

Extensive calculations were then carried out to demonstrate the feasibility of using this technique for seeding large-scale continuous sugar processes. The purpose of these calculations was to demonstrate in a rigorous CSD simulation both the adequacy of such a nucleator as seed source as well as the concept of a continuous footing crystallizer[17] which would grow the crystals to an intermediate size for addition as partially developed grain in full-scale batch or continuous pans. The early period of grain development in current batch pans is particularly unproductive; such a technique would obviate this difficulty. In addition, increments of product quality might be expected using these well-formed seed, but such quality improvements could only be demonstrated in extensive pilot tests. The economic cost of this seeding technique can readily be deduced from these process calculations.

Synopsis of Experimental Studies

Research work was carried out over a period of nine months to answer the questions posed and achieve the goals set in the previous section. Specifically, the accomplishments of this study were as follows:

(1) A laboratory bench-scale salting-out MSMPR crystallizer was modified and operated to produce sugar crystals from a sucrose/water/solvent system. The solvent used was either a 50:50 methanol/*iso*-propanol mixture or "Vanzol A-1"-denatured ethanol [100 parts by volume of 190 proof alcohol, 1 part of methyl isobutyl ketone, 1 part of ethyl acetate, 1 part of a hydrocarbon solvent (Stoddard's)].

2. Preliminary crystallizer runs were made to solve initial difficulties with the system and to make necessary modifications. A standard run was established with set conditions to compare with Crawford's data[14]. Laboratory technique, which is very important, was also developed.

3. Optimization of chosen process conditions was carried out with the objective of finding conditions which would produce a crystal-size distribution with a nuclei density approaching 10^7 per/cm^3-micron with a characteristic population-weighted size of 10 microns.

Thus, the primary objective of the research was to produce a sucrose seed-crystal fondant with the salting-out process having superior single crystal form and with a high nuclei population density. Exploratory runs were executed to map out regions worthwhile to study in depth. This phase was guided by a Plackett-Burman, one-level statistical analysis design[18] to find a likely region in which to carry out more detailed kinetic studies. Independent variables of the salting-out nucleator that were explored were as follows:

(*a*) system temperature (5°C–27°C),

[12] Unpublished work on sucrose nucleation research carried out at the Dept. of Chemical Engineering, The University of Florida, Gainsville, Fla., 1966.
[13] US Patent 3,695,932; *I.S.J.*, 1973, **75**, 325.
[14] "The Continuous Nucleation of Sucrose" (Master's Thesis, The University of Arizona), 1970.
[15] "Continuous Sucrose Crystallization", (Master's Thesis, The University of Arizona), 1973.
[16] *I.S.J.*, 1972, **74**, 133–136.
[17] Petri: Private communication, 1971.
[18] Isaacson: *Chem. Engr.*, 29th June 1970.

(*b*) feed concentration (68°–75°Brix),

(*c*) solvent type (50:50 methanol/*iso*-propanol *vs.* "Vanzol A-1").

(*d*) surfactants [methylamine HCl and "Fluorocarbon FC-96" (3M Co.)]

(*e*) holding time (1–3 hours).

The goal was to find combinations of these variables to produce high population densities of small seed. This seed might then be used directly in a full-scale process or as a seed source for a footing crystallizer used to grow the seed to an intermediate size before seeding a vacuum pan. Eight exploratory runs at high and low level values of the above variables were made after the "shakedown" runs. An added constraint, verified by photomicrographs, was that the crystal habit should be of a single-crystal form. Key variables were selected and evaluated in a further kinetic study in an attempt to optimize the number and quality of seed produced. All CSD determinations were made using the Model "T" Multi-Channel Coulter Counter calibrated with ragweed pollen.

Synopsis of Computer Simulations

The kinetics developed were used in an extensive computer simulation of continuous seeded sucrose processes. A computer simulation of a three-stage process comprised of a nucleator (with optimized kinetic conditions) staged in series to a seed ripener and a forced circulation continuous crystallizer was implemented to study the feasibility of this system used as seed source in a continuous crystallizer. CSD values were calculated using the rigorous Mark I CSD simulator[19]. Auxiliary computations were made to determine the feasibility of recovering solvent from the nucleator by flash evaporation in the ripener.

Theoretical Considerations

MSMPR technique

The apparatus used in this research work could ideally be considered an MSMPR (mixed suspension mixed product removal) crystallizer. This unit is a continuously-fed mixed-magma crystallizer of volume V which produces crystals dispersed in mother liquor, in this case by salting-out with a miscible organic compound. Supersaturation thus generated causes both crystal growth and secondary nucleation. The feed rate, composition, and temperature as well as the crystallizer volume and temperature remain constant. Randolph and Larson[6] present the crystal population balance in an MSMPR crystallizer and derive equation (1) for the expected number distribution of the crystal product.

$$n(L) = [\frac{B^\circ}{G}] \exp(-L/G\tau) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

In this equation, n is the population density which has dimentions of number/length-volume. The intercept at $L = 0$, given as B°/G, is defined as the population density of the embryo-size crystals. The characterizing dimension of the crystal is given the symbol L and the rate at which this dimension grows is termed the growth rate G. The drawdown time τ is the crystallizer volume divided by the suspension output, i.e. $\tau = V/Q$.

Some of the assumptions that must hold in order that equation (1) be valid are:

(1) McCabe's ΔL law[20], i.e. $G \neq f(L)$,

(2) the feed to the crystallizer contains no seed ($n_i = 0$),

(3) the population density of the crystallizer product is the same inside the crystallizer, i.e. no classification and perfect mixing, and

(4) the suspension volume remains constant in time.

The nucleation rate B° is related to the nuclei density and the growth rate by the following equation:

$$B^\circ = n^\circ G \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Nuclei densities can be determined for various experimental runs by plotting $\ln(n)$ against L and determining the intercept at $L = 0$. The population-weighted characteristic size ($G\tau$) can be found from the slope of the line; B° is obtained from equation (4). Slurry density M_t is given by the equation[6]

$$M_t = 6k_v\rho n^\circ (G\tau)^4 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Here, M_t is the solids concentration, k_v is the crystal shape factor which relates the cube of the characteristic size dimension of the particle to its volume, and ρ is the crystal density.

Equations (1), (4) and (5) can be used to analyse the CSD of the MSMPR crystallizer. It should be noted that each parameter of equation (1) can be related to the kinetics of the system and the imposed system constraints. The growth rate G is determined by the kinetics of growth and τ, the holding time, which is known in any operating system. These two quantities, however, cannot be fixed independently. Generally, one fixes the mass and energy flows and the kinetics of growth and nucleation inherent to the crystal system determine the growth rate which exists. The adjustable controls in the sucrose system include the syrup feed concentration, the rate of energy input or removal, and the feed rate.

Crystal nucleation kinetics

In the sugar/water/solvent system, secondary nucleation is likely, owing to collision breeding. Nuclei result from the collision of seed crystals with solid surfaces which, in the case of a stirred crystallizer, may be other crystals, impeller blades, or crystallizer surfaces.

According to Youngquist and Randolph[21] no fundamental theory for prediction or correlation of secondary nucleation exists; most experimental data have been obtained using MSMPR crystallizers. Data are frequently correlated using a power-law model of the form:

$$B^\circ = k_n G^i M_t^j \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

[19] Nuttall: "Computer Simulation of Steady-State and Dynamic Crystallizers" (Ph.D. Dissertation, The University of Arizona), 1971.

[20] McCabe and Smith: "Unit Operations of Chemical Engineering" (McGraw-Hill Book Co., New York), 1967.

[21] *Amer. Inst. Chem. Eng. J.*, 1972, **18**, (2).

The mechanism of secondary nucleation (or self-nucleation) has also been studied by CLONTZ and MCCABE[22] and by RANDOLPH and CISE[23]. Their findings have indicated that contact secondary nucleation plays an important rôle in operating crystallizers. This phenomenon may be important in sucrose/water/organic systems owing to the reduced viscosity of the massecuite.

Crystal growth kinetics

In addition to secondary kinetics of the form of equation (6), a growth rate kinetics relationship is necessary for complete simulation of a seeded crystallization process. The following linear equation was obtained using the data that BENNETT[5] presented on the sucrose/water system in a continuous FC unit.

$$S = (G + 5{\cdot}36)/(4{\cdot}66) \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

In Equation (7) S is the coefficient of supersaturation and G is the growth rate in microns per minute.

Crystal modifiers

Trace chemical additives are often used to suppress or promote nucleation and/or promote better crystal growth and habit. Such additives are usually considered proprietary information by industrial companies and therefore few published data exist on this subject. These additives are usually quite specific in their effect on nucleation, and inhibit as well as accelerate nucleation.

Two surface-active agents, methylamine hydrochloride and "Fluorocarbon FC-96" (3M Company), were chosen for study, mainly because they accelerated nucleation in the KNO_3 system[6].

Other types of surfactants that affect crystallization in the sucrose system are discussed by VANHOOK[11]. It was pointed out that most impurities impede the crystallization velocity (growth rate) of sucrose. If an additive (e.g. an impurity or an electrolyte) can be found that will slow down the growth rate of the sucrose system, and if this surfactant can be readily dissolved in aqueous-alcohol mixtures, then a smaller crystal size in the sucrose seed nucleator may be achieved, with the net effect that higher supersaturation and more nuclei are created.

NICOL and FARMER[24] have recently studied the effects of lysine and glycine on the nucleation and crystallization of sucrose. They found that the nucleation rate of sucrose was increased by glycine because the impurity acted as a centre for heterogeneous primary nucleation.

CRAWFORD[14] tested the effect of the surfactant "Aliquat 26" (trimethyl tallow ammonium chloride) on sucrose crystal growth and nucleation. It was suggested that the surfactant may have changed the system kinetics but no conclusive evidence was given.

(to be continued)

[22] *Paper read at 62nd Annual Meeting Amer. Inst. Chem. Eng.*, 1969.
[23] *Amer. Inst. Chem. Eng. J.*, 1972, **18**, (4).
[24] *Sucr. Belge.*, 1972, **91**, 55–59.

Correspondence

To the Editor,
The International Sugar Journal.

Dear Sir,

SOME NOTES CONCERNING "THE POTENTIAL OF A SCREW PRESS TANDEM" by S. G. Smart[1]

The writer would like to make some comments concerning the above-mentioned paper:

(1) It is well known that the rather poor performance of a three-roller mill(ing tandem) is due to:

(*a*) the incapability of a mill to achieve under normal working conditions a better liquid to solids (i.e. juice to natural fibre) ratio than roundabout 0·9:1. This ratio is attained when the bone-bry fibre content of the bagasse is 42%. Making allowance for the presence of Brix-free water in the fibre of cane and bagasse, the corresponding natural fibre content is calculated as 52·5% and the juice content as 47·5%.

(*b*) the incomplete mixing of the imbibition liquid with the residual juice present in the bagasse fed into a mill[2].

(2) For a new type of sqeezing apparatus to show a better performance than a three-roller mill it must either achieve a lower juice:solids ratio or a better mixing efficiency or, preferably, both.

(3) As to the moisture content of bagasse as discharged by a screw press Mr Smart states that a screw press is "capable of giving a much lower moisture figure". However the M%PB data given in his Table I, presumably obtained under normal working conditions, fluctuate between 57·17 and 49·25%. Such results could have been obtained also by a good mill.

(4) The extent to which the imbibition liquid mixes with the residual juice is reflected in the "mixing efficiency", the "stage efficiency" or the "mixing coefficient" figure.

DOUWES DEKKER (*l.c.*) defined the mixing coefficient as the fractional figure n denoting the proportion of the residual juice which has mixed homogeneously with all imbibition liquid before the excess of this mixture is removed by the next squeeze. By studying the results of a milling tandem he found that n was probably in the order of 0·25 to 0·40.

BUCHANAN[3] stated that stage efficiencies are rather low. The lowest one he found was under 25%; "this could be interpreted as only one quarter of the residual juice actually mixing with the imbibition juice at each stage before expressing".

Mr. SMART compares the actual Brix of press juice with the Brix which would have been obtained if complete mixing of imbibition liquid with residual

[1] *I.S.J.*, 1973, **75**, 371–375.
[2] DOUWES DEKKER: *Proc. 10th Congr. I.S.S.C.T.*, 1959, 86.
[3] *Proc. 39th Ann. Congr. S. African Sugar Tech. Assoc.*, 1965, 34.