

THE CRYSTALLIZATION OF HIGH GRADE MASSECUTE IN CRYSTALLIZERS

By E. E. A. ROUILLARD

Sugar Milling Research Institute

Abstract

It is shown that equations developed for predicting the mass transfer coefficient in agitated vessels can be applied to crystallizers. Calculations done with a mathematical model of a crystallizer based on this equation indicate that the main factors in high grade crystallization are the residence time, power input per unit volume and cooling rate. It is also shown that addition of molasses to crystallizers adversely affects the crystallization rate.

Introduction

The advantages of increasing the exhaustion of high grade massecuite by means of crystallizers has been pointed out by various authors. Lamusse et al⁷ reviewed previous work on this subject in 1962, and since then Grapa⁵, Parashar⁹ and Julienne⁶ have written about practical results obtained in the factory.

The potential purity drop in A massecuite is more than thirty points, of which between fifteen and twenty points are obtained in vacuum pans and the difference could be obtained by suitable crystallizer installations. In Table 1 are shown purity drops observed under South African conditions, and as can be seen the purity drop obtained in crystallizers were in general less than three points.

The study presented in this paper was undertaken to determine what are the factors that influence high grade crystallizer operation.

Estimation of mass transfer coefficients

The crystallization process is a mass transfer operation which takes place in two steps.

1. Diffusion of the sucrose molecule through the stagnant fluid surrounding the crystal.
2. Incorporation of the molecule into the crystal lattice.

Silin¹⁰ has pointed out that for high viscosity impure sugar solutions the first step is rate controlling, and that the second step can be neglected so that crystallization can be represented by the following equation:

$$\frac{S}{t} = k_f \cdot (C - C_{eq}) \cdot A \quad (1)$$

That is, the mass of sucrose crystallized per unit time is proportional to the product of the film mass transfer coefficient, concentration gradient and crystal surface area.

A correlation has been developed by Calderbank and Moo-Young² for calculating the film mass transfer coefficient in agitated vessels which is independent of the geometry of the agitation equipment.

$$k_f = 0,13 \left(\frac{\mu_n}{\rho_n^2} \cdot \frac{W}{V} \right)^{1/4} / \left(\frac{\mu_n}{\rho_n D} \right)^{2/3} \quad (2)$$

The accuracy of equation (2) for sugar crystallizers was verified by comparison with measured values obtained from equation (1). The data were obtained from the crystallizer installations shown in Table 2 and Fig. 1 and 2. It was necessary to take the average values from a number of observations because of variations in massecuite quality during the tests.

The weight of sucrose crystallized, S, was calculated from the difference in crystal content between the inlet and outlet, the crystal content being obtained from the relation

$$X = B_m (P_m - P_n) / (100 - P_n) \quad (3)$$

When molasses was being added to the crystallizer, the percentage added was calculated from

$$M = (B_{m_i} - B_{m_o}) / (B_{m_i} - B_{m_{ol}}) \quad (4)$$

and the crystal content at the outlet corrected by the equation

$$X^*_o = X_o \cdot (1 + M) \quad (5)$$

The crystal surface area at the outlet was obtained from a size analysis of the sugar produced, and the following equation derived from those suggested by Gillett⁴.

$$a_o = \frac{3,986 \cdot X_o}{L_o} \quad (6)$$

The crystal size at the crystallizer inlet was calculated from

$$L_i = \left(L_o^3 \frac{x_i}{x_o} \right)^{1/3} \quad (7)$$

TABLE I
Observed purity drops in A-massecuites

Factory	Massecuite			Drop in pan	Drop in receiver	Drop in pan + receiver	Pty crystallizer outlet	Pty drop in crystallizer	Total purity drop	Final temp.	Calculated potential purity drop	Pty. rise in fugals
	Pty	Bx	RS/Ash									
MV	85,89	91,67	1,3	15,76	3,18	23,23	59,19	3,47	26,7	36,2	31,68	2,29
	85,97	92,12	1,23									
SZ	85,78	91,88	1,52			19,45	63,62	2,71	22,12	57,6	25,12	
TS	83,75	91,69	1,47			19,66	62,61	1,48	21,14	44,7	30,69	
TS	87,23	92,32	0,98			17,39	67,6	2,24	19,6	39,5	30,20	3,02

TABLE 2
Details of crystallizer stations

Factory	Tonga		Sezela	Melville
Crystallizer type	Stork	Stork	Blanchard streamlined tubes	Blanchard round tubes
number	1	1	5	4
Volume, m ³	61,5	61,5	212	74
Cooling surface, m ²	360	360	265	120
Surface/volume	5,9	5,9	1,25	1,62
Installed power, kW	26	14,9	37,3	11,2
Installed Power/vol	0,42	0,24	0,18	0,15
Speed	1,8	1,0	1,0	0,75
Drive	Electric gearbox chain	Electric gearbox chain	Electric gearbox V belts worm gear	Electric gearbox V belts belt worm gear
Estimated mechanical efficiency	83	79	47	46

and the area at the inlet obtained the same way as a_0 , a being the average of a_j and a_0 .

The concentration of sucrose existing in the mother liquor was obtained by dividing the weight of sucrose by the volume of the mother liquor.

$$C = \frac{B_n \cdot P_n \cdot \rho_n}{100(100 - X)} \quad (8)$$

The solubility of sucrose at saturation varies with the temperature, purity and reducing sugar/ash ratio of the solution.

A regression of the solubility coefficients (for purities between 70 and 40) of Charles quoted by Meade and Chen⁸ gave the following equation with a coefficient of multiple correlation of 0,98

$$c = 6,458 \cdot 10^{-10} \cdot T^{4,426} \cdot P_{neq}^{0,2578} \cdot (RS/A)^{-0,1464} \quad (9)$$

The solution of sucrose at saturation can also be expressed as

$$c = \frac{100 \cdot P_{neq} \cdot B_m (100 - P_m)}{(100 - P_{neq}) (100 - B_m)^2} \quad (10)$$

The solubility was calculated by solving equations (9) and (10) for c and P_{neq} .

Once the purity at saturation was known, it was possible to calculate the brix, crystal content and volume of mother liquor at saturation, and the concentration at saturation was calculated from equation (8).

The retention time was calculated from a heat balance around the crystallizers taking into account the heat lost to cooling water and atmosphere, heat input caused by stirring, and in certain cases heat lost or gained by addition of hot or cold molasses. The product of the mass rate of flow, specific heat and temperature drop of massecuite was equal to the heat losses, the mass rate of flow being the only unknown quantity. The retention time was then calculated by dividing the crystallizer volume by the volumetric flow rate. These figures agreed with massecuite volumes obtained from the pan floor. In the case of Melville where the massecuite level in the crystallizers varied, the retention time was calculated from pan floor volumes and crystallizer levels.

The variables of equation (2) were estimated as follows: The viscosity of the mother liquor was calculated from the equation:

$$\mu = -1,469 + 5,4174 \log_e B_n + 0,3773 \log_e P_n - 0,06682 T \quad (11)$$

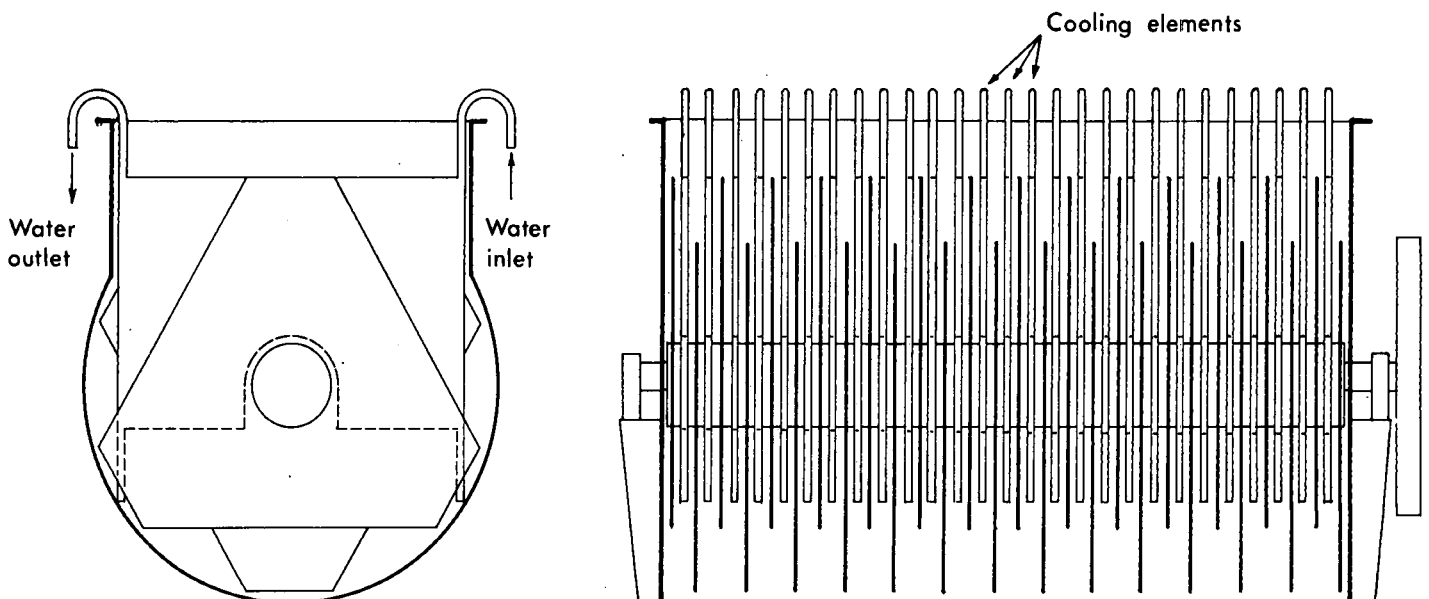


Figure 1: Stork rapid cooling crystallizer

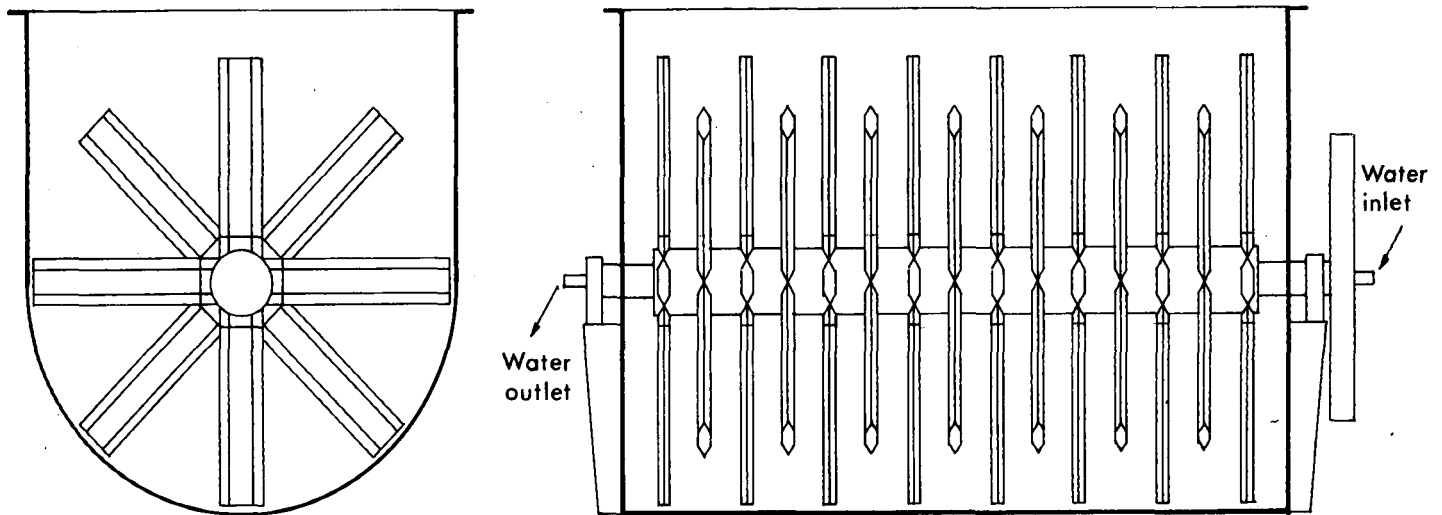


Figure 2: Blanchard type crystallizer with streamlined tubes.

which was obtained from a computer regression of measurements taken on 37 nutsch samples and has a coefficient of multiple correlation of 0,92. The density came from density tables. The exact value of the diffusion coefficient of impure sucrose solutions is not known, but Emmerich et al³ state that it may be 2,5 to 3,3 times greater than that of pure solutions having the same dry solids content. The larger value was used in these calculations, that is

$$D = 5,91 \times 10^{-15} \times T/\mu_n \quad (12)$$

The power was obtained from ammeter readings on the crystallizer drives, a correction being applied for the efficiency of the equipment as shown in Table 2.

The results obtained are given in Table 3 and are shown, together with the data of Calderbank and Moo-Young, in Fig. 3. The agreement is good and therefore equation (2) can be used with confidence for calculating the mass transfer coefficient in crystallizers.

Mathematical modelling of crystallizer

The following relationships must be established to describe the crystallization process in a continuous agitated crystallizer.

- A. Material balance of massecuite
 - (a) Water
 - (b) Crystalline sucrose
 - (c) Sucrose in solution
 - (d) Impurities
- B. Rate of crystallization
 - (a) Surface area of crystals
 - (b) Concentration gradient
 - (c) Retention time
 - (d) Mass transfer coefficient
 - 1. Density of mother liquor

- 2. Viscosity of mother liquor
- 3. Diffusion coefficient
- C. Heat balance
 - (a) Heat loss to surroundings
 - (b) Heat input from agitation
 - (c) Heat effect of molasses addition
 - (d) Heat loss to cooling water
 - 1. Rotating speed
 - 2. Thermal conductivity of massecuite
 - 3. Density of massecuite
 - 4. Specific heat of massecuite
 - 5. Viscosity of massecuite
- D. Power consumption

A flowchart of the model is given in Fig. 4. It consists of three loops for calculating by iteration the crystallization rate, heat transfer rate and power consumption.

To initialize the variables it is necessary to assume the quantity of sucrose crystallized and of molasses added, the brix and purity of the molasses, the outlet massecuite temperature and to set the limiting power.

The material balance is calculated from the brix and purity of the massecuite, nutsch and molasses and the assumed weight of sucrose crystallized.

The mass transfer coefficient, k, is calculated using equation (2), the crystal surface area from equation (6) and the concentration gradient from equations (8), (9) and (10). The sucrose crystallized is then obtained from equation (1) and compared with the assumed value.

The heat transfer coefficient for the heat loss to the cooling water is calculated using the equation obtained in a previous study for crystallizers with finned tubes¹¹. It is assumed that the influence of the massecuite properties on the heat transfer coefficient remains the same for other types of crystallizers.

TABLE 3
Experimental Results

Factory	Number of observations	Agitation power kW	Av. Temperature massecuite °C	Heat transfer coefficient W.m. ⁻² .°K ⁻¹	Mass transfer coefficient m.s. ⁻¹ . 10 ⁹		Difference %
					Measured	Calculated	
TS (1,8)	42	18,9	51	27	17,3	11,8	- 31,9
TS (1,0)	26	10,1	48	22	8,77	9,26	+ 5,7
SZ (1,0)	11	8,2	61	21	9,35	9,98	+ 6,7
MV (0,75)	20	3,4	43	36	4,71	4,32	- 8,3

The influence of the geometry of the crystallizer is accounted for by including this variable in an experimentally determined constant. Each of the three crystallizer types studied has a different constant. The modified equation is

$$U = x \cdot (N \cdot r_{mf})^{0,216} \cdot y_{mf}^{0,9327} \cdot C_{p_{mf}}^{0,0673} \cdot \mu_{mf}^{-0,1487} \left(\frac{\mu_m}{\mu_{m_s}}\right)^{0,139} \quad (13)$$

The bulk, film and surface viscosities of massecuite are calculated using the equation of Awang and White¹

$$\log_{10} \left(\frac{\mu_m}{\mu_n}\right) = 1,65 \cdot X \cdot L^{0,15} (1 - CV/12) \quad (14)$$

The heat balance gives the change in the heat content of the massecuite, which is equal to the product of the mass rate of flow of massecuite, heat capacity and temperature change. The outlet temperature of massecuite thus obtained is compared with the assumed value.

The power consumption is obtained using the equation obtained in a previous study of crystallizers with finned tubes¹¹, modified in the same way as the heat transfer equations by incorporating the geometric parameters into the constant. This constant, determined experimentally differs for each type of crystallizer. The equation is expressed as follows:

$$W = y \cdot \mu_m^{1,152} \cdot N^{1,848} \cdot r_m^{-0,152} \quad (15)$$

The calculated power is compared with the power limit set by the design of the crystallizer. If less than the design power, the speed can be increased if desired so that maximum power is used. If greater, the speed can be either reduced or dilution molasses added. In the latter case the molasses can be either classified or unclassified. With classified molasses the difference in brix between the outlet nutsch and molasses is taken as -2,7 and the difference in purity as +0,9. With unclassified molasses the difference is -7,8 and +3,0 respectively.

The accuracy of the model was verified by comparing calculated and measured values of the outlet massecuite

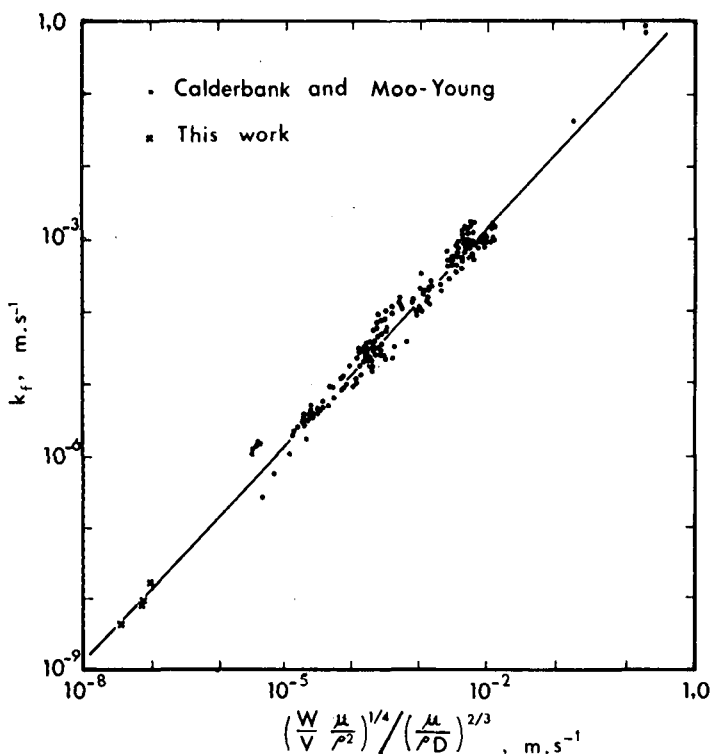


Figure 3: Comparison of measured and calculated mass transfer coefficients for agitated vessels.

temperature, molasses addition and purity drops. These are shown in Table 4.

Application of crystallizer model

The mathematical model was used firstly to show the relationship between retention time, agitation power and cooling without addition of molasses. Variations in power input and cooling rates were obtained by changing the speed of the crystallizer. The massecuite properties used in this exercise were as follows:

Brix massecuite	91,7
Purity massecuite	83,8

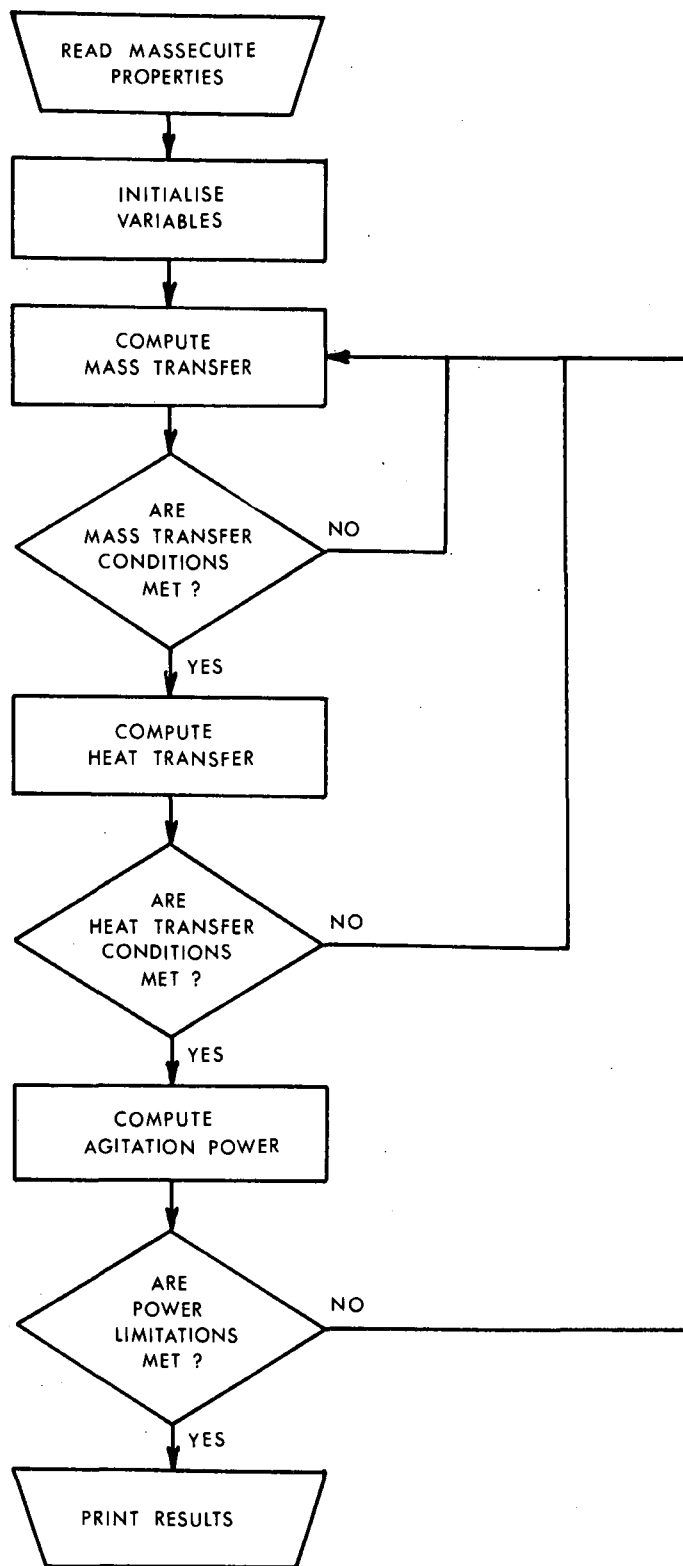


Figure 4: Flowchart of computer simulation.

Initial supersaturation	1,3
Crystal size	0,73
Coefficient of variation	0,27
Reducing sugar/ash	1,47
Initial massecuite temperature	57,5°C
Ambient temperature	30°C

The supersaturation is expressed as the ratio

$$\frac{\text{sugar / water}}{\text{sugar / water at equilibrium}}$$

for the same ratio non-sucrose/water, and the same temperature.

The calculated values were obtained by applying the model to a crystallizer with a cooling surface/volume ratio of 5,9 and cooling water at 20°C. The results are shown in Fig. 5.

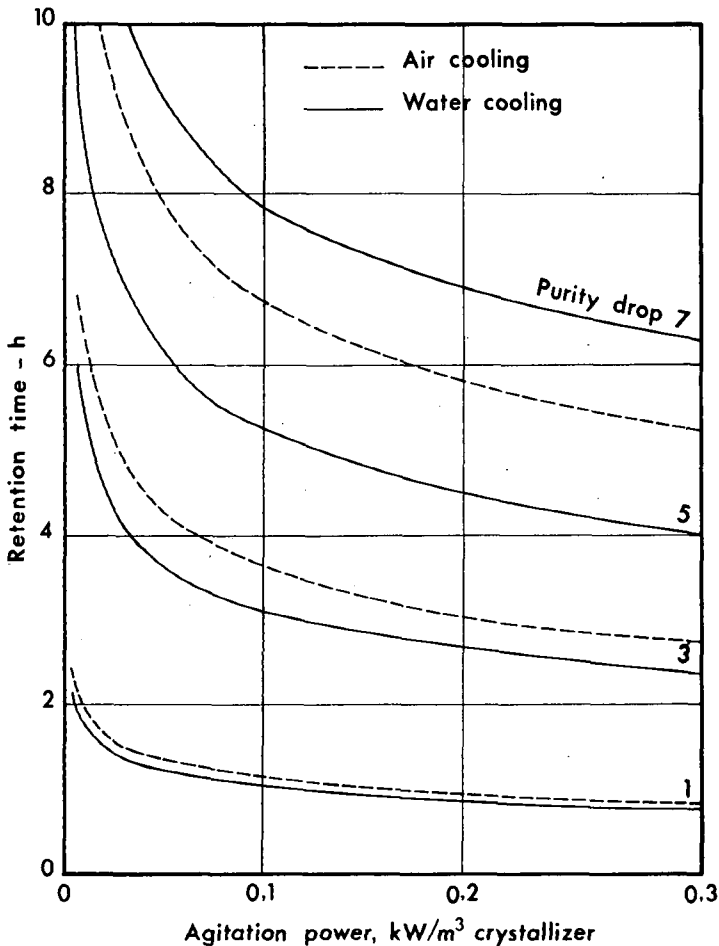


Figure 5: Purity drop of high grade massecuite as a function of retention time and power input.

TABLE 4
 Verification of accuracy of model

Factory		TS	TS	SZ	MV
No. of crystallizers		1	1	5	4
Speed, rpm		1,8	1,0	1,0	0,75
Purity drop	Measured	1,3	1,9	2,5	3,2
	Calculated	1,4	2,2	2,1	3,0
Outlet massecuite temperature °C	Measured	44,7	39,5	57,6	36,2
	Calculated	43,4	40,1	56,9	36,4
Percent molasses added	Measured	10,7	6,9	-	6,3
	Calculated	13,5	8,8	-	5,7

It is seen that purity drop is a function mainly of retention time. The process can be speeded up by agitation and cooling particularly for the higher purity drops, but there is a limit as to what can be achieved in doing so.

It must be remembered, however, that the values shown in Fig. 5 are not absolute since initial massecuite properties such as temperature, supersaturation, crystal size and reducing sugar/ash ratios will affect the purity drop.

Since the main variables in crystallizer operation are the retention time and agitation power, it was possible to use the model to determine the economic power input. This was done by adding the cost of the agitation equipment to that of the crystallizer shells. In Fig. 6 are shown crystallizer costs as a function of power input for different purity drops.

Based on the cost data available to us, it appears that the economic power input is around 0,11 kW/m³ which corresponds to a 7 kW motor on a 50 m³ crystallizer with efficient power transmission such as hydraulic or chain drive and about 12 kW if worm and gear reduction is used.

At this power input the retention time required is about 3,5 hours for a purity drop of 3 points, 6 hours for 5 points and 8 hours for 7 points, and the costs are R1 800, R3 000 and R4 500 respectively per m³/h of massecuite. Thus the cost to a 300 tch factory would be about R150 000 for an A-massecuite crystallizer installation giving 5 points of purity drop.

Another use for the crystallizer model is optimization of existing equipment. This is demonstrated by the optimization of a rapid cooling crystallizer, and is illustrated in Fig. 7.

Equation (2) shows that the mass transfer coefficient increases with the power input per unit volume, and from equation (15) it is seen that the power input increases with the crystallizer speed. Therefore, it should be possible to obtain a greater purity drop from an existing installation by speeding up the crystallizers. However, one constraint that must be kept in mind is that the torque on the shaft must not exceed a certain maximum value which depends upon the design of the equipment.

The crystallizer studied has a volume of 61,5m³ and processes 28,5 m³/h of massecuite. The same massecuite properties as those used in the previous study were assumed. It is seen in Fig. 7 that as the speed is increased there is a rapid rise

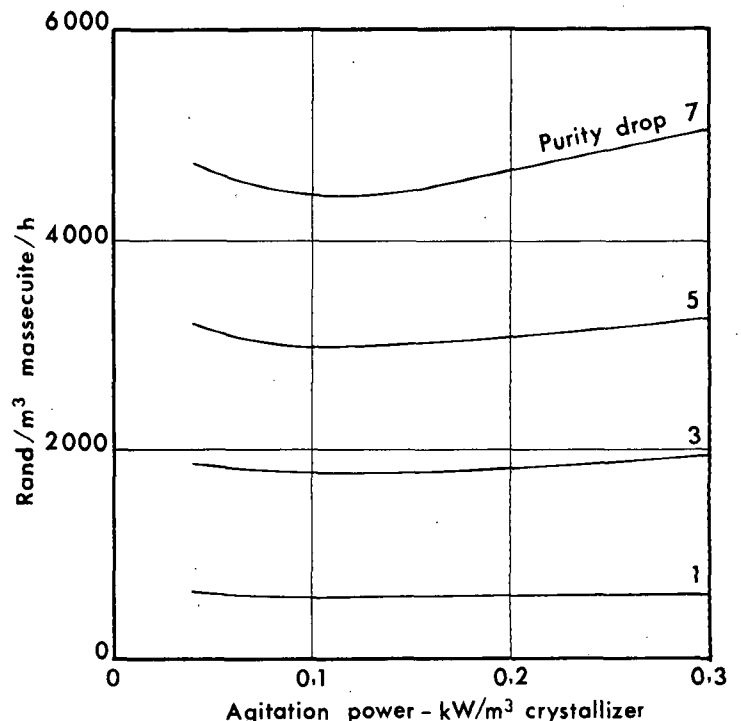


Figure 6: Cost of crystallizers for high grade massecuite.

in the mass of sugar crystallized. This is represented by line AB. At point B the maximum torque of the crystallizer is reached. Beyond this point measures must be taken to limit the torque either by addition of molasses to reduce the massecuite viscosity, or by the removal of some of the cooling elements to reduce the load on the shaft.

Addition of unclassified molasses is represented by line BC and classified molasses by line BD. It is seen that in both cases it results in a reduction of the sucrose crystallized. Removal of part of the cooling elements is represented by line BE, and causes a slight increase in sucrose crystallized up to a speed of about 2,5 rpm beyond which there is a gradual drop.

The crystallization obtained for different operating conditions at 1,8 rpm is given in Table 5. It is seen that addition of molasses results in a lower concentration gradient, shorter retention time and smaller crystal surface area per unit volume of massecuite, with the net result that less sucrose is crystallized.

Discussion

Although this mathematical model gives a reasonable picture of the crystallization process that takes place in high grade crystallizers, it has its limitations and shortcomings, the most important of which will be discussed here.

In the equation for the mass transfer coefficient there are two points which must be considered. The first is the power input per unit volume. This parameter has the advantage that it is independent of the geometry of the agitation equipment. However, it assumes that agitation is uniform throughout the volume of the crystallizer and that there are no stagnant areas. The second point is the diffusion coefficient. The value of the diffusion coefficient for impure sucrose solutions is, according to Emmerich et al³, between 2,5 and 3,3 times that of pure sucrose. The larger value was used in this study, as it gives a better correlation between the calculated and measured values of the mass transfer coefficient, but it is not known how this variable is affected by the purity of massecuite.

The surface area available for crystallization plays an important part in the rate of crystallization. For example in Table 5 if the crystal size was smaller by 10% there would be an increase of 7% in the mass of sucrose crystallized. The equation used to calculate the crystal area assumes that all

surfaces are available and effective. This may not be the case when crystal elongation occurs. It is also assumed in these calculations that no new nuclei are formed in the crystallizer.

The concentration gradient is calculated from solubility figures that take into consideration the purity, temperature and reducing sugar/ash ratio. Based on this data the reducing

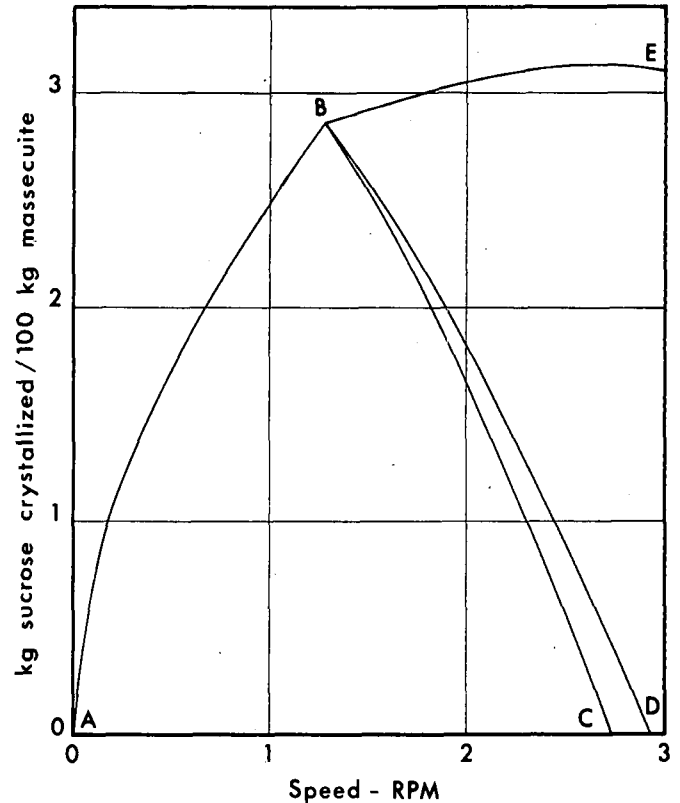


Figure 7: Optimization of 61,5m³ crystallizer processing 28,5 m³/h massecuite

- AB Power and torque increase
- BC Torque constant, Addition of unclassified molasses
- BD Torque constant, Addition of classified molasses
- BE Torque constant, Reduction of cooling surface.

TABLE 5

Optimization of a rapid cooling crystallizer of 61 m³
Speed 1,8 rpm massecuite volume 27,5 m³/h

Operating Conditions	Outlet Massecuite conditions		Molasses added (%)	Retention time (h)	Concentration gradient (kg/m ³)	Crystal area (m ² /kg)	Mass transfer coefficient (m/s x 10 ⁶)	Purity drop	sucrose crystallized (kg/100 kg)
	Temp °C	Viscosity molasses (Pas)							
Unclassified molasses Cooling water 20°C	45,7	2,62	7,07	2,02	82,3	2,80	1,20	1,32	2,03
Classified molasses Cooling water 20°C	45,7	2,66	7,76	2,01	88,3	2,80	1,19	1,69	2,15
Classified Molasses No cooling	56,7	1,94	2,97	2,11	75,0	2,81	1,45	1,94	2,34
18% of elements removed No cooling	56,7	1,93	-	2,18	85,1	2,83	1,46	2,38	2,76
33% of elements removed Cooling water 20°C	47,7	2,53	-	2,18	109,4	2,84	1,23	2,61	3,00

sugar/ash ratio has a strong influence on the crystallization rate. In Table 5 if the reducing sugar/ash ratio was reduced from 1,47 to 0,97 the mass of sucrose crystallized would decrease by 20%.

In this model it is also assumed that no short circuiting of massecuite occurs across the crystallizer, for this should not take place with proper agitation.

The equations used to calculate the heat transfer coefficient and power consumption are based on those developed for crystallizers with finned tubes. It is assumed that the effect of the physical properties of massecuite for this crystallizer also applies to other types of crystallizers, but it may be worthwhile to ascertain this point by further investigation.

In existing equipment, maximum purity drop can be obtained by utilizing all the power available. This can be done by increasing the speed, or in Blanchard crystallizers by means of baffles to increase the shear, but care must be taken that the power requirements do not become such that addition of molasses is required. In new installations maximum power input can be ensured by means of hydraulic motor drive with constant torque.

Conclusions

This study indicates that crystallization is mainly time dependent, but to a certain extent can be speeded up by agitation and cooling.

The addition of molasses decreases the crystallization rate and should be avoided.

Acknowledgements

The author expresses his thanks to Dr. W. S. Graham and Mr. T. Traicos of Tongaat, Mr. T. Currie of Melville and Mr. B. Stuart formerly of Sezela for their assistance and advice, and the laboratory staff of the SMRI who did most of the analytical work.

Nomenclature

The symbols used in the text are listed below.

A	crystal surface area	m ²
B	brix	
C	soluble sucrose concentration	kg m ⁻³
CV	coefficient of variation	
Cp	heat capacity	J kg ⁻¹ K ⁻¹
c	solubility of sucrose, gm/100 gm water	
D	diffusion coefficient	m ² s ⁻¹
k	film mass transfer coefficient	m s ⁻¹
L	length of crystal	mm
M	molasses fraction	

N	rotational speed	s ⁻¹
P	purity	
RS/A	reducing sugar/ash ratio	
S	mass of sucrose crystallized	kg
T	absolute temperature	K
t	time	s
U	overall heat transfer coefficient	Wm ⁻² K ⁻¹
V	volume	m ³
W	power	W
X	crystal content	
X*	crystal content corrected for molasses addition	
x	constant (equation 13)	
y	constant (equation 15)	
<i>Greek</i>		
γ	thermal conductivity	Wm ⁻¹ K ⁻¹
μ	viscosity (dynamic)	Pas
ρ	density	kg m ⁻³
<i>Subscripts</i>		
eq	equilibrium value	
f	film	
i	initial value	
m	massecuite	
mol	molasses	
n	nutsch	
o	exit value	
s	measured at heat transfer surface temperature	

REFERENCES

1. Awang, M. and White, E.T. (1976) "Effect of crystal on the viscosity of massecuite". QSSCT Proc 43: 263-270
2. Calderbank, P.H. and Moo-Young, M.B. (1960) "The continuous phase heat and mass transfer properties of dispersions". Chem. Eng. Sci. 16: 39-44
3. Emmerich, A., Finke, D., Panitz, N. and Rieck, H. (1976) "Investigations of diffusion in pure and technical sucrose solutions". Zucker 29: 302-307.
4. Gillett, E.C. (1948) "Low grade sugar crystallization". California and Hawaiian Sugar Refining Corporation.
5. Grapa, E.A. and Alba, A.C. (1963) "A-massecuite crystallizer cooling." Philipp. Sug. Ass. Proc 11: 83-85.
6. Jullienne, L.M.S.A. (1976) "A-massecuite exhaustion and low purity C-massecuite at Melville". SASTA Proc 15: 194-197
7. Lamusse, J.P., Wiehe, H.F. and Randabel, M. (1962) "The use of crystallizers for the cooling of high grade strikes in raw sugar manufacture". ISSCT Proc 11: 885-893
8. Meade, G.P. and Chen, J.C.P. (1977) "Cane sugar handbook". Wiley, New York.
9. Parashar, D.R. (1973) "The behaviour of high grade massecuite during cooling". Sugar News (Bombay) 4: 7-8
10. Silin, P.M. (1958) "Technology of beet sugar production and refining". Pishchepromizdat, Moscow
11. Rouillard, E.E.A. (1977) "Cooling and reheating C-massecuite with extended surface elements". ISSCT Proc 16: (In press).