Seasonal and District Variations in the Rate of Crystallization of Sucrose From Beet-House Sirups

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The quantity of sugar which can be extracted from beets depends, theoretically, only on sugar content, losses, purity of purified juice, and the solubility of sugar in final molasses. Exhaustion of sugar in molasses to the limit of solubility, however, is never realized in practice because, at low purities, the rate of crystallization of sugar becomes vanishingly small. Qualitatively, mill operators recognize differences in crystallizability of sirups by differences in pan-boiling time, in pan yields, and particularly by differences in purity of final molasses. Unfortunately these estimates are strongly affected by variable operating conditions—variations in pan temperatures, variable amounts of grain, variable supersatiirations, and others. A quantitative estimate of erystallizability of sirups should be independent of operating conditions. It should measure erystallizability as a property of the sirup itself.

The rate of crystallization of sugar from pure sugar solutions has been measured by several investigators. Kucharenko's studies covered a wide range of supersaturations and temperatures and included a study of the effect of additions of a number of inorganic salts, as well as of invert sugar and caramel. Rates of crystallization of sugar from impure, naturally occurring juices have not been adequately studied.

Two methods have been developed or adapted by this laboratory for the measurement of rate of crystallization. The first of these has been described previously.[2]

This method, though laborious and time consuming, is the best available for the study of low-purity sirups when rates of crystallization of sugar from a sirup at a wide range of supersaturations and purities are desired. The second method, a modification of Kucharenko 's method, is best adapted to a study of high-purity sirups, particularly in cases where a comparison of several sirups under identical conditions of purity, temperature, and supersaturation is desired. The method has not been published. It is given in detail in the Appendix to this paper.

IN the first flow-purity) method, the sugar crystallized per unit time per unit surface is calculated from the rate of change of purity of mother liquor in the presence of a large, known number of crystals of known size. In the second (high-purity) method, the sugar crystallized per unit time per unit surface is calculated from the increase in length, width, and thickness of a few measured crystals in the presence of a large amount of sirup. Both methods require painstaking care, particularly in the determination of true sugar and of dry substance of mother liquors. The double acid method for sugar of Osborn and Zisch was used in most cases.[3] Some determinations of true sugar were made by the double enzyme method. Dry substance was determined by the method of Brown, Sharp and Nees.[4]

Supersaturations are calculated from solubility data, of R. J. Brown and from data of the author who used Brown's method.[5] Supersaturation coefficients as used in this paper are expressed as the quotient obtained by dividing the percentage dry substance of the sirup by the percentage dry substance in a saturated sirup of the same purity at the same temperature. Probably the most logical expression is one which expresses supersaturation in Terms of grains crystallizable sugar per liter of mother liquor. The calculation is involved. The usual coefficient of supersaturation is obtained by dividing the grams sugar per gram water in the sirup by the saturation number (g sugar per g water in a saturated solution) at the same temperature. In the latter case the solubility data of Hertzfeld for pure sugar is usually used and the assumption made that the saturation number is independent of purity. At moderately high purities this assumption is roughly justified, but not at low purities. The usual mode of expressing supersaturations gives very large coefficients of supersaturation at low purities for a given amount of crystallizable sugar compared to the coefficients corresponding to the same amount of crystallizable sugar at high purities. The supersaturation coefficients used in this paper correlate somewhat better with crystallizable sugar and are easier to calculate from solubility curves.

Figure 1 shows the rates of crystallization of sugar from a Brighton factory sirup at 40° 0. at purities ranging from 60 to 72 and at supersaturations ranging from 1.0 to 1.08 (corresponding to usual supersaturation coefficients of 1.47 at 72 purity and 1.70 at 60 purity). The curves cover a range of supersaturations well above those usually attained in factory operation. At purities above 65, rates of crystallization increase rapidly with supersaturation. At purities below 65, rates of crystallization increase much less rapidly with increased supersaturation. As molasses purity is approached,

[3]"Sugar Analysis," Zerban and Brown, 3rd Ed., p. 465, 1941.
[4]"Sugar Analysis," Zerban and Brown, 3rd Ed., p. 39. 1941.
[5]Brown, R. J., et al, Ind. and Bug. Chem. 20, 945-8, 1928.
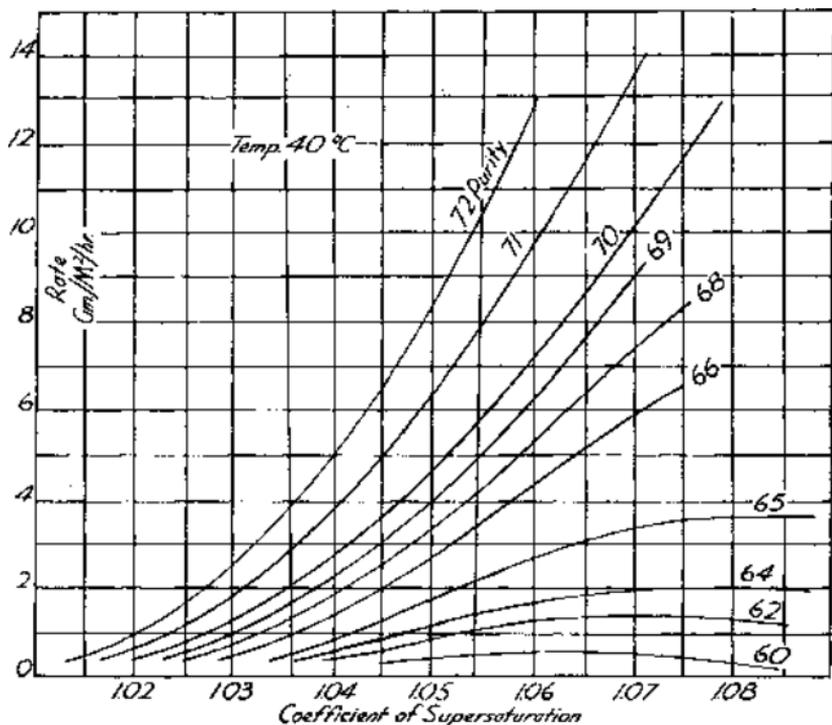
Figure 1.—Effect of supersaturation on crystallization rate at constant temperature (40° C) Rate expressed as grams sugar crystallized per hour per square meter of crystal area.

rates of crystallization approach a maximum at about 1.07 (corresponding to about 1.6 in the usual units). It has frequently been observed that at these low purities the rates of crystallization approach low, constant values, characteristic of the sirup, but nearly independent of moderate changes in supersaturation, purity, and temperature. The curves also show the extremely large increase in rate of crystallization with increase in purity.

Figure 2 shows the effect of temperature on rate of crystallization at constant supersaturation. The percentage dry substance is necessarily higher in the sirups at higher temperature than in those at the lower temperatures, both being at the same supersaturation, inasmuch as the solubility increases with temperature. The viscosity is likewise higher in the high-temperature tests, for, though viscosity diminishes with increasing temperature, it increases even more rapidly with increasing percentage dry substance. The rate of crystallization, however, increases steadily with temperature. Evidently the
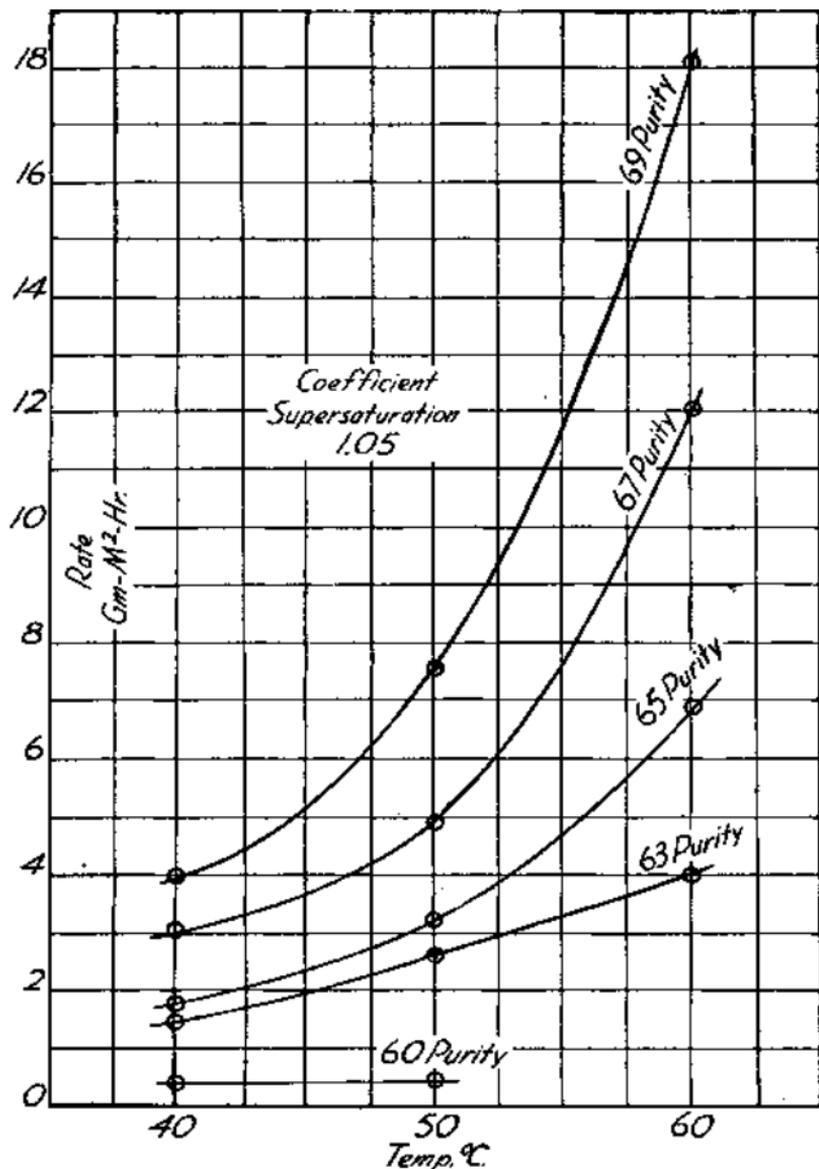
Figure 2.—Effect of temperature on crystallization rate at constant supersaturation. Rate expressed as grams sugar crystallized per hour per square meter of crystal area.

impeding effect of increased viscosity is less than the accelerating effect of increased temperature. The temperature effect on rate of crystallization is greater at the higher purities.

The original purpose of our rate of crystallization studies was to study the effect of variation of factory processes (lime addition, use of carbon, etc.).

In a series of laboratory tests diffusion juice was treated with quantities of lime varying from 0.4 percent to more than 2.0 percent CaO on beets. The true purity of the purified juices showed, in general, the expected rise in purity with increased lime addition as shown in figure 3. The purity rise is not regular. In the tesit illustrated by the curve, as in all others, elimination appears to occur in a step-wise manner. From 0.9 percent to 1.1 percent CaO on beets the purity (true) remains constant at 93. Increasing the lime addition to 1.2 results in an abrupt rise in purity of about 0.3 and remains relatively unchanged with lime additions up to 1.5. Further purity rises usually occur on increasing the lime addition to 2.0 percent and in some cases, but not all, on increasing lime addition to as much as 4 percent on beets. Different diffusion juices showed this step-wise purity change, though not in the same degree, and not precisely at the same level of lime addition. The rate of crystallization of sugar from the sirups prepared with different lime additions, measured at identical purities, likewise showed differences.
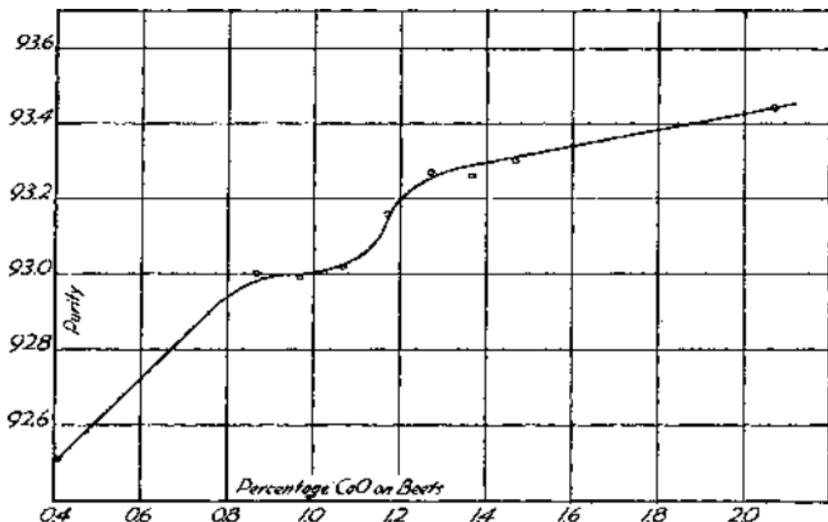
Figure 3.—Effect of variations in lime addition at first carbonation on purity of thin juice.

Tn Table 1 the crystallization rates at different lime additions are shown. The sirups were all reduced in purity by partial crystallization at 89 to 00 and adjusted to exactly 90 purity and 73.85 percent dry substance for the rate tests. These were made at 40° C. In every case high-lime addition was associated with diminished rates, though in most cases the differences were small. Rates are expressed in millimeters per hour increase in crystal length (direction of b-b axis). The most significant point brought out by these results is the consistency with which slower rates followed increased lime addition—not the magnitude of the difference.

Determinations of ash and of nitrogen in juices prepared from the same raw juice with varying quantities of lime indicate that the impurities eliminated by lime in excess of minimal quantities necessary for filtration are chiefly non-nitrogenous organic non-sugars. Some nitrogen, but practically no ash, is eliminated. The composition of the total impurities in juices prepared with high-lime addition is characterized by high-ash content. The percentage nitrogen on total impurities is usually slightly lower and the calculated percentage non-nitrogenous impurity other than raffinose is appreciably lower in juices prepared with high-lime additions.

Higher, relative, ash content increases the solubility of sugar in sirups, hence in the tests shown in table 1, obtained at the same purity and percentage dry substance, the supersaturations of the sirups prepared with high-lime additions were slightly lower. Highly accurate solubility determinations could not be made with the small quantities of sirups available, but some fairly good tests were made. The saturation dry substance of a 90 purity beet-house (non-Steffen) sirup at 40° C. is, according to R. J. Brown, 71.70 percent. The sirups prepared with 1 percent CaO in the tests reported in this paper showed exactly this solubility. Those prepared with higher-lime additions showed progressively higher, saturation, dry substances up to 71.95 at 2 percent CaO. The changed solubility may be calculated to account for at least 30 percent of the changes in rale found—in some cases more. The remainder of the rate change appears to be the direct effect of changed composition of impurities.

In the experiments discussed above, the raffinose content was not changed by the treatment. In concentrations below 0.5 percent on sucrose the effect of raffinose on crystallization is small, though real. Small deviations cause too little effect to measure. As raffinose concentrations are raised to 1 percent or more, the effect on rate of crystallization becomes marked. The full effect of raffinose on crystallization rate can only be measured by measuring the rate of growth of the sucrose crystal in three dimensions. The vertical rate of increase on the alpha pinacoids (the large flat surfaces of the crystal) is most quickly and most seriously affected by increasing raffinose

Table 1.—Effect of variations in lime addition at firsf carbonation on crystallization rates from sirups, prepared from various beets, at constant purity, concentration and temperature. Crystallisation rate expressed in millimeters per hour increase in length of b-b crystal axis.

Percentage CaO on Beets	Rate mm./hr.	Percentage CaO on Beets	Rate mm./hr.
Juice A		*Juice F*	
1.00	0.070	1.07	0.070
2.00	.052	1.07a	.067
Juice B			
1.25	.067	*Juice L*	
1.75	.061	*Ft. Morgan*	
2.00	.060	0.60	.045
		.90	.029
Juice C			
1.00	.060		
1.35	.055	*Juice M*	
1.75	.043	0.60	.047
		.90	.044
Juice D		1.50	.041
1.07	.057		
1.07a	.062		
1.57	.041		

"a" 0.1 Percent CaO to 2d Carb.

concentration. Rate of growth of the crystal on the c- pinacoid is next, while rate of growth on the end prisms (prolongation of b- axis) is last and least affected by increasing raffinose concentrations. The changed relative growth rate of crystal faces results in the typical distorted crystal produced from sirups containing more than 1 per-cent raffinose on sucrose. At 40° C. the rate of growth of sucrose crystals from 90 purity sirups was reduced 50 percent on the a-

pinacoids, and about 30 percent on the a-b prisms by increasing the raffinose concentration from 0.44 percent to 1.03 percent on dry substance. The tests were made at 1.04 supersaturation. At lower supersaturations the decrease in relative rate of growth, on the a-pinacoids is oven more marked. Under the conditions of the above test the time required to produce a crystal of a given weight is nearly 60 percent greater in the presence of 1.03 percent raffinose than in the presence of 0.44 percent. The time of boiling pans of such sirups will not. of course, be increased, by this amount, since in practice much of the diminished crystallization rate of the sirup will be overcome by increased supersaturations built up in the more slowly crystallizing massecuite.

Treatment of beet-house juices with large quantities of activated carbon improves crystallization rates. Sirups of 75 purity were treated with 32 percent carbon on impurities, equivalent to about 5 pounds per ton of beets. Improvement in crystallization rates of from 30 percent to 50 percent were found. Use of smaller amounts of carbon gave quite different results. Four percent carbon on impurities, equivalent to nearly *2* pounds per ton of beets, caused improvements in crystallization rales barely large enough to measure. The effect of still smaller quantities could not be detected.

It is evident that only very drastic changes in juice treatment cause appreciable changes in the rate of crystallization of sugar from sirups. Much greater differences in rate are found between sirups produced by the same process but from different beets.

Figure 4 shows the rates of crystallization of several sirups made under essentially the same factory conditions but from different beets. The rates are measured at 70 purity, 40° C. and at a supersaturation of 1.06 (equivalent to 1.33 in the usual units). Sirup No. 1 was produced at Lyman, Nebraska, in 1933, sirup Nos. 3 and 6 were made at Brighton, Colorado, in 1933 and 1928, respectively. The other sirups were produced at Brush, Colorado, at different periods in the 1934 campaign.

In this figure rates of crystallization ranging from 3 to 9 grams per square meter per hour are shown for sirups at the same purity, supersaturation, and temperahire. Further data on rates of crystallization of sirups from different factory districts were obtained in 1937. The sirups were taken near the end of the campaign and do not necessarily represent the average sirup produced. In this series, the rate of measurements were made at 75 purity, 1.05 supersaturation (corresponding to 1.24 in the usual units), and at 40° C.

Sirups from the four northern Colorado factories showed nearly the same crystallization rates, 21 g/sq. meter/hr. The sirup from Brush in eastern Colorado and that from Fort Lupton, Colorado, a factory with a somewhat mixed district, showed rates about 25 per-
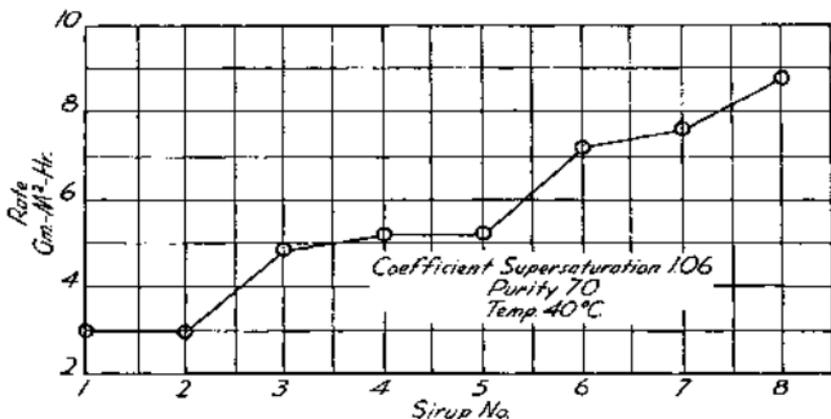
Figure 4.—Comparison of crystallization rates at constant purity, supersaturation and temperature from sirups of various seasons and districts. Rate expressed as grams sugar crystallized per hour per square meter of crystal area.

cent smaller, 16.5, The raffinose content was nearly the same in all Colorado sirups, 4.5 percent to 5.0 percent on impurities. The sirup from Hardin, Montana, showed a rate of crystallization significantly better than that of the best Colorado sirup (23.0). Its raffinose content, however, was only 1.8 percent on impurities, which perhaps accounts for the difference.

These measurements were made at exactly 75-percent purity. Rates fall off nearly 4 g per square meter per hour for each percentage reduction in purity between 75 and 70 purity.

The differences in crystallization rates between the sirups from northern Colorado and those from Brush and Fort Lupton are large enough to affect materially the sugar-end operations. Even greater differences are shown in the crystallization rates of sirups taken at different periods of the same campaign at the same factory.

Table 2.—Rate of crystallization of sugar from beet sirup from various districts at constant purity, supersaturation and temperature.

Factory	Percentage raffinose on impurities	Rate of crystallization g/sq. meter/hr
Great Western		
Brush, Colo.	4.7	16.7
Port Lupton, Colo.	4.7	16.3
Windsor, Colo.	4.4	20.8
Eaton, Colo.	5.0	21.7
Greeley, Colo.	4.9	21.4
Brighton, Colo.	4.7	21.2
Holly		
Hardin, Mont.		
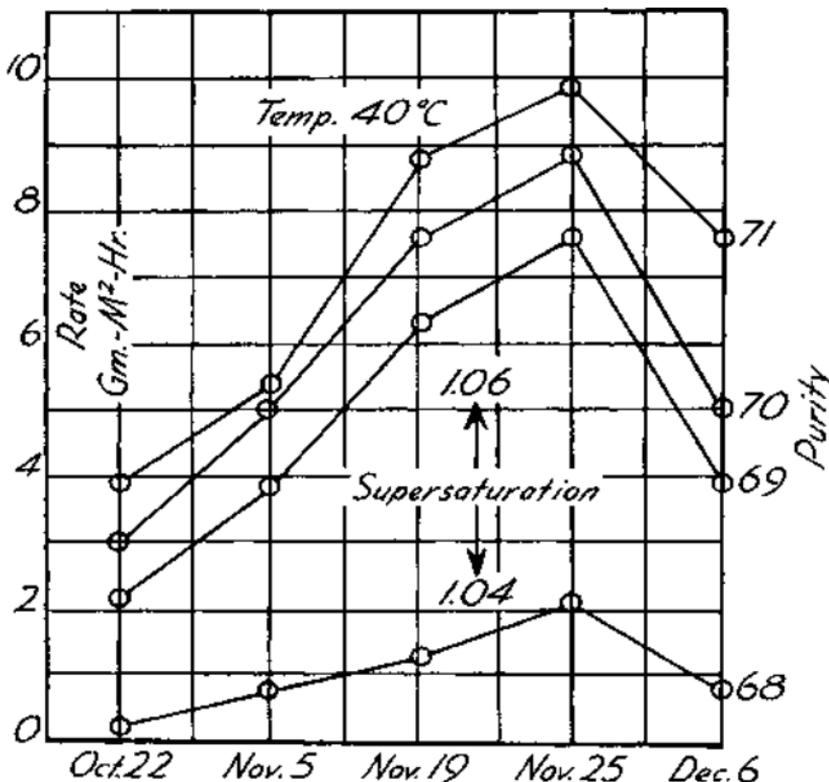
Figure 5.—Seasonal variation in crystallization rates from sirups from a single factory. Rate expressed as grams sugar crystallized per hour per square meter of crystal area.

Figure 5 shows the seasonal variation in crystallization rates of sirups produced at the Brush factory. These data were obtained in connection with a factory test of the use of very small amounts of carbon. Each sample of sirup accurately represents the house production for a 2-week period. A quarter pound of carbon per ton of beets was used in alternate periods. As may be seen by the graph, the seasonal variation completely obscured whatever effect carbon may have had. Crystallization rates increased regularly from October 22 to November 25, then fell off in the period ending December 6. The decreased rates of crystallization found in the final period are probably the result of a combination of causes: Deterioration of beets in piles, accumulation of deleterious substances in the sugar end, and possibly, some diversion of beets from other districts at the end of campaign.

The results shown in figure 5 *were* obtained with particular care. The solubility of sugar in each sirup was actually measured, hence the supersaturations are known to be correct. These results show the futility of basing estimates of the value of a process change on the operation of a sugar end when successive periods of operation must be compared. The most drastic modification of the purification process affects crystallization insignificantly compared to these enormous seasonal effects. The molasses purities during this test, though varying in the expected direction, did not show as great differences as figure 4 might indicate. The reason is that when slowly crystallizing sirups are encountered, supersaturations are carried higher, hence sugar is crystallized from them at higher supersaturations than from better sirups. Obviously, overcoming slow rates of crystallization by increasing supersaturation has its limitations. At very low purities, 63 and below, increasing the supersaturation has little effect. Moreover, the high dry-substance content accompanying high supersaturations increases enormously the viscosity of the mother liquor. Massecuites become difficult to centrifuge and raw sugar of low purity inevitably results.

Because rates of crystallization increase rapidly with purity, the effects of slow-crystallizing sirups are usually not serious in first boilings. Except in those houses where facilities for intermediate boiling are limited, the full effect of slow-crystallizing sirup is not seriously felt until the final, low-raw massecuite is reached.

In Table 3 is shown a comparison of behaviors of two sirups in the crystallizer calculated from rate data. One of these sirups is a good Brighton sirup, the second is a poor Brush sirup. The calculation is based on the following conditions:

15 million crystals per liter; 1.075 percent supersaturation at all times; (.Mother liquor I). !S. = approximately 87.0 percent at 65 purity).

It has been found that after raw pans have been dropped to crystallizer at 65° to 70° C. crystallization proceeds so rapidly that the supersaturation of the mother liquor is not maintained at the final raw-pan supersaturation, but falls off to a minimum of from 1.02 to 1.05 in about 11 hours despite continued cooling. Easily crystallizing sirups sometimes reach a purity as low as 63, while slowly crystallizing sirups may not have been reduced as low as 65 purity during this period. In this calculation, it is assumed that the sirup is 64 purity at the end of 11 hours and that the temperature is 46.5° C, corresponding to a supersaturation of 1.075. The time necessary to reduce the mother-liquor purity from 64 to 59 and to intermediate purities has been calculated. To obtain 60 purity molasses, mother-liquor purity must usually be reduced to 59.

Table 3.—Comparative performances of a "-good" and "poor"' sirup In the crystallizcr.
Calculated hours required to reach a given purity of mother liquor at a
given cooling rate.

| Purity | Rate Gm./M²/hr. | | Time Hours | | Temp. |
	Good	Poor	Good	Poor	°C
64	4.0	2.0	0.	0.	46.5
63			1.0	2.0	42.5
62	2.0	1.0	2.3	5.7	37.5
61	1.5	0.4	4.8	15.1	34.0
60	0.5	0.2	12.3	34.0	30.0
59	0.3	0.1	24.8	82.0	30.0

As shown by table 3 the purity of mother liquor is reduced to 59 purity in 25 hours in one case and in 82 hours in the second. In this calculation optimum supersaturation is assumed, hence the time required for these crystallizers must be regarded as minimum. Brighton produced molasses of about 60.5 purity from the good sirup. Brush produced molasses of more than 62 purily from the poor one. The hours in crystallizer at both houses was about 50.

The chemical differences in composition of impurities of beet juices which cause one sirup to be better than another are not known. The very slowly crystallizing sirups usually contain more ash. High raffinose, also, is often associated-with difficultly crystallizable sirups. The effect of other constituents is less well established. We have seen that sirups, such as those prepared with low-lime additions, which contain more of the non-nitrogenous organic constituents, show better crystallization rates than those sirups which contain less. This indicates that the non-nitrogenous organic substances have less effect than ash on crystallization rates, but does not prove that they are without effect. Even less is known regarding the effect of nitrogenous compounds. The nitrogen content of impurities in the juices studied does not vary greatly. No correlation between nitrogen content and crystallization rate has been found in these limited experiments.

The conclusion to be drawn from this study of crystallization rates is that the problem of improvement in this quality is a problem connected with the improvement of beets rather than one of modifications of factory operation.

APPENDIX

Determination of Rates of Crystallization of Sucrose

Apparatus.—1. Crystallizer tube (see figure 6). 2. Constant-temperature bath having a clear space of at least 12" x 15" x 12" deep, controlled to 0.05° C. Suitable hinged holders for 6 crystallizer tubes are mounted in the bath at a height sufficient to keep the tubes immersed to within 1 to 1/2 inch of the top. A crank shaft is mounted on the top of the bath to which tube pistons may be quickly attached. Length of stroke, 2 inches. Speed, 7.5 r.p.m.

Preparation of Sirup.—Concentrate a quantity of the juice to be tested by evaporation under reduced pressure. Determine accurately the true purity of the sirup (double acid or enzyme true sugar and accurate dry substance by oven drying). Adjust the purity to the desired purity by addition of the calculated amount of pure sugar. Adjust the dry substance to give the desired supersaturation by evaporation or addition of weighed quantities of water. Heat to dissolve added sugar and mix thoroughly. Place 300 to 400 grams in a weighed stoppered flask. During the adjustment the dry substance will usually have changed. Determine the dry substance again, add accurately the amount of water necessary to bring the dry substance exactly to the desired value. Stopper tightly and suspend in a water bath at a temperature at least 10° higher than the saturation temperature.

Preparation of Second Crystals. — Select from a commercial coarse sugar (Confectioner's A) a number of unbroken, clean crystals. Suspend them in a saturated sugar solution. With constant shaking, warm to a temperature a few degrees above saturation temperature (to dissolve surface dust). After 10 to 20 minutes, cool to a temperature about 10° below saturation temperature, keeping the crystals moving by rotating the flask. (This operation is most easily performed by using the crystallizer tubes.) After 1 hour drain the sirup off through a screen and carefully wipe the crystals with clean cloths (a painstaking task). The crystals should be clean and possess sharp, true edges. Crystals weighing 10 to 15 milligrams are convenient. Using a microscope with moveable stage and, preferably, a calibrated eye-piece scale, measure each crystal with a precision of .01 to .02 mm. in the following directions: With the crystal lying on the a-pinacoid, measure its length between the 2 end prism intersections (b). With the crystal in the same position, measure the width of the crystal along the edge of the easily focused "right" prism (c). (The **"left"** prism is usually truncated, top and bottom.) Support the crystal between 2 pieces of a microscope slide placed on another slide and measure the thickness of the crystal (a), perpendicular to the a-pinacoid.
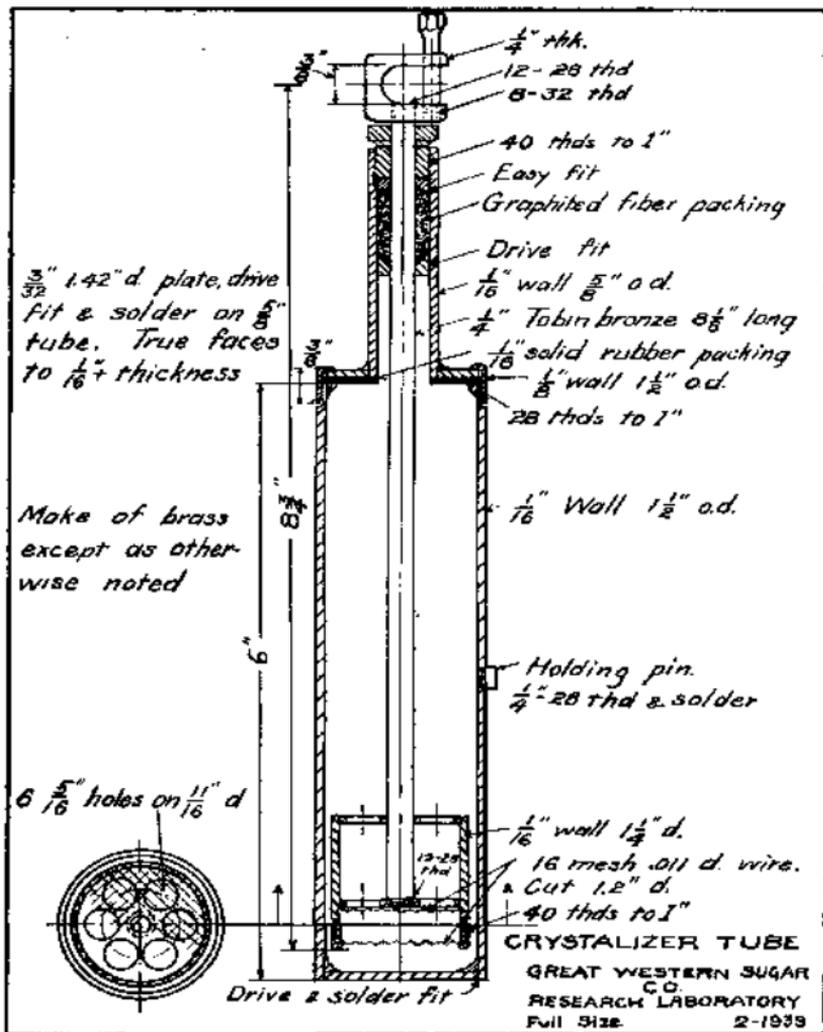
Figure 6.—Design of crystallizer tube used in determination of crystallization rates.

Operation.—Place 1 to 5 measured seed crystals in the screen compartment attached to the piston of the crystallizer tube, figure 6. Shake the prepared sirup thoroughly and cool to a temperature just below saturation temperature. Remove the stopper and quickly fill the crystallizer tube to within 1 inch of the top, Quickly fasten on the cap which carries the crystal basket, place in the constant-temperature bath and attach piston to the crank shaft. Total operation should require less than 3 minutes. Record the time to the nearest minute, taken when the piston is attached.

After 10 to 20 hours, remove the crystals and wipe them with a clean cloth. Record time. Measure the crystals as before,

Calculation of Results.—The formulae which follow are calculated from the known axial ratios and inter-axial angles.

Axial ratios: a: b : c :: 1.295 : 1.000 : 0.8782
    Inclination of a-axis—103°30'.

The measurements taken are: Length (b)—measured along (a-a') axis.

Width (c)—measured along (c-c') axis.
Thickness (a)—measured perpendicular to the plane of the (b-b') and (c-c') axes.

For simplicity, the crystal is assumed to be bounded only by 2 a-pinacoids, 2 c-pinacoids and by 4 (a-b) prisms (110). Other small prism forms are neglected.

By geometry:
    Volume—$1.028 \ a \ b \ c - 0.420 \ a^2 \ c$.
Surface—$2.057 \ (a + c) + 0.976 \ a \ c - 0.840 \ a^2$.

Assuming a fixed crystal habit, 2 axial ratios in length of crystal (b-b') and 1 axial ratio in thickness and width (a-a') and (c-c'), the rate of growth in grams per square meter per hour may be determined by the rate of increase of length alone:

1. Rate (g/M²/hr.) = $600 \ \dfrac{db}{dt}$, approximately, where $\dfrac{db}{dt}$ = rate of increase of crystal length in mm. per hour.

Equation (1) suffices where seed crystals are nearly alike in form and size and where only a comparison of 2 sirups is needed. The absolute value of rates given by equation (1) is high because seed crystals selected from commercial sugars have large pinacoid faces, hence a small rate of growth on them results in a disproportionately large weight increase. An approximation somewhat better, though mathematically indefensible, is given by:

2.   Rate $(g/M^2/hr.) = 200 \left(\dfrac{da}{dt} + \dfrac{db}{dt} + \dfrac{dc}{dt} \right)$.   In this equation

$\dfrac{da}{dt}$, $\dfrac{db}{dt}$ and $\dfrac{dc}{dt}$ are, respectively, the rates of growth in thickness,

length, and width in mm. per hour.

If the calculation of rate is based on crystal form in which the three dimensions of the crystal are assumed proportional to their respective rates of increase, the result is theoretically correct, because the form is the one actually developing in the sirup.

3.   Rate $(g/M^2/hr.) = \dfrac{9492\ (2.45\ m - 1)\ n\ \dfrac{da}{dt}}{m\ (n - 1) + 0.475\ n - 0.408}$

$\dfrac{da}{dt} = $ rate of increase in cm/hr.

$$m = \dfrac{db}{dt} \Big/ \dfrac{da}{dt}, \qquad n = \dfrac{dc}{dt} \Big/ \dfrac{da}{dt}$$

NOTE: $\dfrac{da}{dt}, \dfrac{db}{dt}, \dfrac{dc}{dt}$ are rates of increase in cm. per hour,

not mm/hr.)

The time (T) required to produce a crystal of a given weight W (in grams) under the conditions assumed in equation (3) is:

4. $T = \dfrac{0.856\ W^{\frac{1}{3}}}{[\ (m - 0.408)\ n\ ]^{\frac{1}{3}}\ \dfrac{da}{dt}}$

Equation (4) gives an inverse expression of rate of crystal growth without reference to surface area. By it the time required to produce a crystal of a form natural to the sirup in question under the conditions of the experiment is found.