Studies in the Measurement and Evaluation of Crystallization Velocity

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The need for knowledge of the crystallizing qualities of the sugar-end liquors has long been recognized, for crystallization rates are important controlling factors in the economics of sugar production. Information relative to the crystallizing characteristics of liquors in process would greatly assist operators in maintaining maximum extraction. This project was initiated for the purpose of developing and testing a laboratory method at the factory level for estimating crystallization rates and to study the effect of nonsugars on crystallization rates.

Fundamentally the rate of growth of crystals in the mother liquor can be determined either by measurement of changes in crystal size or weight, or indirectly by the measurement of changes occuring in the mother liquor and calculating such changes as crystallization. Both methods are in common use. A method for control purposes, however, imposes the following limitations:

1. The method must be rapid enough to allow the use of the result while the liquor is still available.
2. The method must be simple enough to be performed by the ordinary laboratory technician.
3. The method should require a minimum of additional laboratory space and equipment.

Of the various procedures which were considered, those which involve the measurement of changes in the mother liquor seemed to offer the greatest possibility of succeeding at the factory level.

The refractometer offers a suitable means of observing changes in concentration of a supersaturated sample of liquor undergoing crystallization. The observed changes in concentration when made with respect to time can be used as a comparative indication of the crystallization rate of the liquor. This principle has been used by several investigators, among them Van Hook (1)[2]. Harris et. al. (2), and Rorabaugh and Norman (3).

Van Hook has proposed a procedure (1) for determining crystallization velocity and mellassigenic characteristics of liquors through the use of the refractometer. The method is reported to give values which compare favorably with the accepted data of Kucharenko. The method adopted for our own studies in crystallization is the Van Hook procedure modified and simplified into a possible control method. This modification, while it does not result in an estimate of the absolute crystallization

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velocity as is possible from the Van Hook Procedure, does provide suitable values to be used for comparative purposes.

The method is generally described as follows:

1. From single or double acid true purity determinations of liquors that are to be compared, calculated amounts of pure sucrose and water are added to the liquors to adjust purity and solids concentration to standardized values. Final adjustment of solids content can be made by water addition or by evaporation. The concentration should place the sample at a supersaturated level of between 1.1 and 1.2 when calculated as follows:

$$S = \frac{\text{Ratio of Sucrose to Water}}{\text{Ratio of Sucrose to Water in saturated solution at the same temperature and purity}}$$

Where S is the degree of supersaturation

2. Each sample is cooled to 20° C, and two to four 30 gram aliquots from each sample are weighed into test tubes. Each aliquot is seeded with stock fondant sugar, amounts ranging from 0.25% to 0.30% of total sucrose present with exactly the same quantity being used for each aliquot of each sample being compared.

3. The seed is thoroughly mixed into the syrup, which establishes zero time. The aliquots are kept sealed at 20° C. until the final time is reached, which may be taken from 30 to 120 minutes, depending on purity, supersaturation, and the amount of seed used. Experience will show the minimum time required to demonstrate significant differences between samples for the conditions chosen. No crystals have been observed to settle out for crystallization periods up to two hours; therefore, it is not necessary to agitate the slurry after the initial mixing of seed and syrup.

At the end of the designated time a thick smear of the seeded syrup is placed between the prisms of the refractometer and the reading made directly.

4. The calculations are made from the following formula:

$$\text{Crystallization Rate} = \frac{C_o - C}{T} \times 1000$$

Where: C_o = Original concentration, grams total solids per 100 grams water.

C = Final concentration, grams total solids per 100 grams of water.

T = Total time in minutes.

[2] Numbers in parentheses refer to literature cited.

The results will be the average milligrams of sugar crystallized per 100 grams water per minute.
The results from the aliquots are averaged to give the sample value.

For true comparisons between samples, the factors of starting purity, starting total solids concentration, amount of seed, time, and temperature must be maintained accurately constant.

The Bausch and Lomb Precision Refractometer is satisfactory for the purpose of this method. However, some experience is required to make an accurate concentration determination by direct reading method. The test temperature of 20° C. was chosen to correspond to the normal refractometer operating temperature coincident with thermostating the seeded aliquots in the refractometer water bath.

The total time requirement for this procedure will vary with the characteristics of the original liquor which requires purity and concentration adjustment, and the length of the crystallization period. Starting with molasses of known purity and concentration and using granular sugar to adjust purity, about two hours are required to prepare the material for crystallization. To obtain significant concentration changes in one hour or less, the purity of the samples should not be less than about 85 percent true purity. It is believed that at the factory level the total time for the determination can be reduced to about two hours.

Application of Method

This procedure was used by Central Laboratory to compare crystallization rates of liquors from The Amalgamated Sugar Company's factories during the 1956-57 campaign. In this case, weekly molasses composites were adjusted to 85 purity, and 74.1 RDS. The seeding ratio was 0.3 percent seed on sucrose present and crystallization was allowed to proceed for 60 minutes at 20° C.

The results for all factories operating over 100 days (on storage beets after about the first 30 days) showed a steady decline in crystallization rate as the processing period progressed. Also, observed results for straight house operations consistently showed higher velocities than their adjacent Steffens house operations. Figure 1 is typical of these data.

The level of certain impurities in the liquor was followed along with the crystallizing quality tests, and it was of particular interest to note that the decline in crystallization rate was accompanied by a general rise in raffinose content. This is also demonstrated in Figure 1.

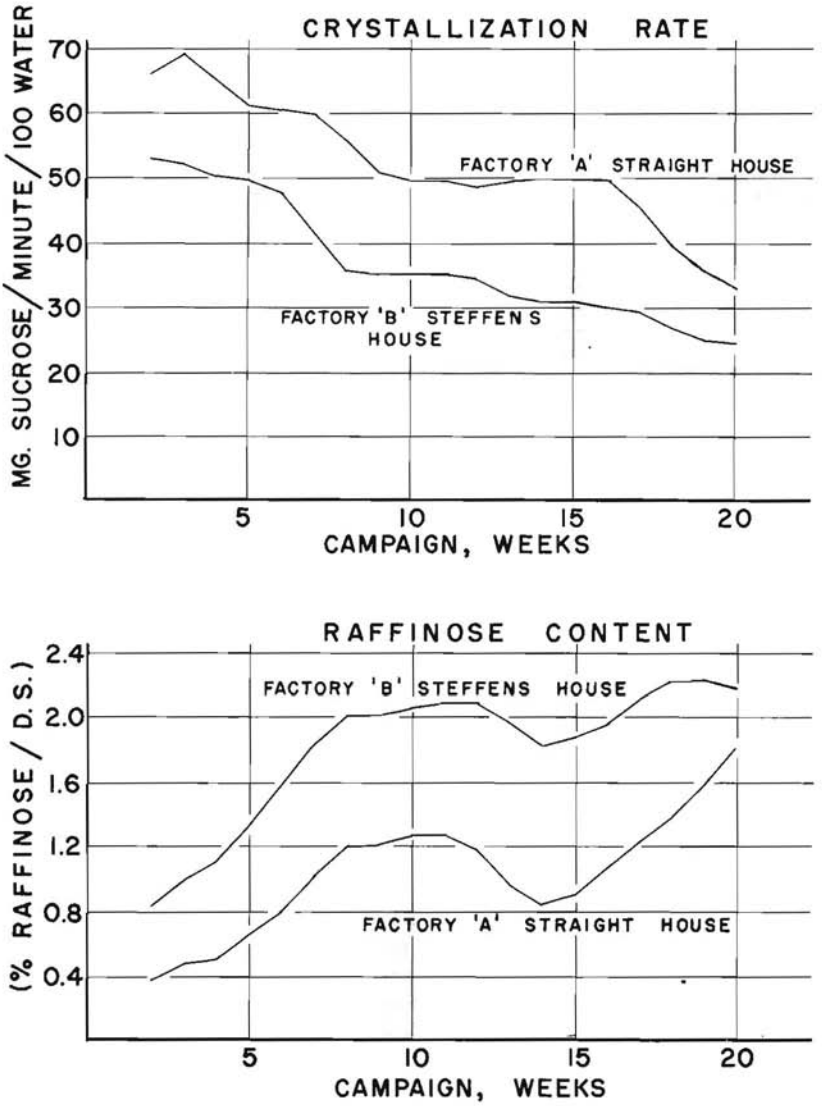

Figure 1.—Crystallization rate and raffinose content of adjacent Steffens house and straight house factories.

This lead to further studies involving raffinose in which a sample of liquor from one factory, having a low raffinose content, was adjusted to the raffinose level of a sample from another factory which was higher, and the crystallization rates then compared. Table 1 shows the results of several of such tests.

Table 1.—Comparison of Crystallization Rates of Liquors from Different Factories and the Same Liquors with Equalized Raffinose Content.

Test	Factory A (Original)	Factory B (Original)	Factory A (Adjusted)
1. Raffinose, % on RDS	0.85	2.15	2.15
Crystallization Rate*	65	33	26
2. Raffinose, % on RDS	1.03	2.25	2.25
Crystallization Rate*	58	23	21
3. Raffinose, % on RDS	1.24	2.21	2.25
Crystallization Rate*	63	23	29

*mg. sucrose/100 water/minute

This procedure was also used to compare the individual effect of various impurities on the crystallization rate of sucrose solutions. The impurities were added in the amount of 0.5 grams per 100 grams of sucrose to make a supersaturated solution of 70.6 percent solids. Crystallization rates of these solutions were compared with the crystallization rate of a pure sucrose solution at the same total solids concentration. These results are shown graphically in Figure 2. The order of magnitude of the melassigenic effects exhibited here compares favorably with the work of others (3) except in the case of betaine.

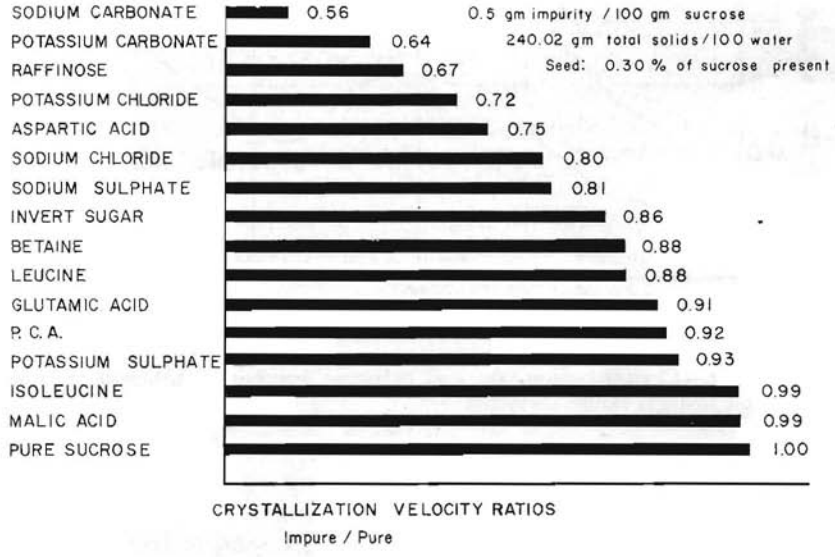

Figure 2.—Velocity ratios of crystallization for pure and impure sucrose solutions.

Summary

A method for determining crystallization rates of beet sugar house syrups and the effect of specific impurities on crystallization rate is presented.

The essential procedure involves a determination of true purity of the syrup, adjustment of purity and solids concentration to standardized values; and finally, determination of comparative crystallization rates of the standardized syrups by use of a refractometer. The time required for the procedure is approximately two hours under ideal conditions.

Crystallization rates of weekly molasses samples for the 1956-57 campaign indicates a decreasing crystallization potential as campaign progresses and correlates highly with increasing raffinose content.

The effect of specific impurities on crystallization rate has been determined and agrees, with minor exceptions, with other investigations.

Experiences in the use of this refractometer procedure indicate that it has good possibilities of succeeding as a factory control method. Further refinements are under consideration which, it is hoped, will make the method even more acceptable for this purpose.

Literature Cited

(1) VAN HOOK, A. 1953. Subject No. 12. Evaluation of the crystallizing qualities of beet and cane factory juices. Report, with Appendix. National Committee, ICUMSA.

(2) HARRIS, W. A., NORMAN, L. W., TURNER, J. L., HANEY, H. F., and COTTON, R. H. 1952. Methanol insoluble material in sorgo and beet juices. Ind. Eng. Chem. 44:2412-17.

(3) RORABAUGH, GUY and NORMAN, LLOYD W. 1956. The effect of various impurities on the crystallization of sucrose. Jour. of the Amer. Soc. Sugar Beet Tech. IX (3) :238-252.