

Kinetics of Sucrose Crystallization

VII. Real Masseccutes¹

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A QUANTITATIVE specification of the melassigenic nature of sugar syrups is a matter of considerable interest and value to the sugar boiler. The older concept, which is based upon solubility behavior alone (6)², is obviously incomplete for it ignores the very significant factor of the finite and often limiting rate of crystallization which is encountered in practice. Although many workers have studied the rates of crystallization of sucrose from pure and natural syrups (reviewed in 5), they have, in general, omitted an exact, quantitative definition of the melassigenic property. A semi-empirical method has recently (5-f) been devised for assigning such a definite, numerical value to this factor for any given syrup. The objects of the present paper are:

- 1) to continue the study of the application of this method to natural syrups of different types,
- 2) to confirm, or not, the general behavior observed in previous experimental studies, and
- 3) by such evaluation of the melassigenic behavior as is possible, to provide the beginnings of a classification of syrups according to their crystallization rate inhibiting powers.

The melassigenic factor, therefore, is employed in this work with the specific implication of the rate inhibiting effect of the non-sucrose substances, or impurities, present. This kinetic interpretation includes the solubility factor as contained in the basic rate equation:

$$\text{Velocity} = k(a - a_{sat.})$$

The substitution of concentrations as molalities, or their equivalent, for activities, a , has been found to be satisfactory as a first approximation (5). It has also been observed that the specific reaction rate constant, k , is a simple semi-logarithmic function of the impurities present (5); and it is this behavior which forms the basis for the melassigenic rating suggested. Earlier workers, while recognizing that "the quantity and character of the non-sugars present in the syrups are, in the last analysis, the predominating factors in determining the rate at which sucrose will crystallize from them (4)", have been unsuccessful in providing data which lead to a ready evaluation of these factors.

¹Six previous papers in this series have been published (5)_g; of which 5-f bears the same subtitle as the present one.

²The numbers in parentheses refer to literature cited.

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The method of evaluation proposed in the present work may, besides yielding data which may have direct application to control practices in industry, provide information of value in the eventual determination of those impurities having the greatest crystallization inhibiting effect on sucrose. The elimination of these substances from syrups, or from cane and beet themselves, is conceivable (1). The definition also fulfills the condition prescribed by Hungerford (2) in being "A quantitative estimate of crystallizability— independent of operating conditions—measures crystallizability as a property of the syrup itself."

Table 1.—Source and composition of stock molasses.

Molasses	Source	Dry substance	True purity	Raffinose on D.S.
1. Refiner's Blackstrap	Revere Sugar Refinery	73.0%	41.92%	--
2. Puerto Rican Syrup	Unknown	74.2	62.5	--
3. Non-Steffen No. 1	Alma, Mich., 1946/47 Michigan Sugar Co.	83.5	63.45	0.0%
4. Non-Steffen No. 2	Clarksburg, Calif., 1946/47 Amer. Crystal Sugar Co.	83.4	64.1	--
5. Louisiana Blackstrap	New Iberia, La., 1946/47 Iberia Sugar Coop., Inc.	83.3	30.3	--
6. Steffen No. 1	Mason City, Ia., 1946/47 Amer. Crystal Sugar Co.	83.8	66.0	2.9
7. Non-Steffen No. 3	Chaska, Minn., 1946/47 Amer. Crystal Sugar Co.	83.2	63.1	1.6

Experimental

Massecutites were made up to 8 molal with respect to sucrose from the several cane and beet molasses described in table 1. This concentration happens to be a most convenient one for many natural syrups; but any other definite concentration yields the same results (5)—provided, of course, that it is supersaturated to a reasonable degree. The values given in the table are true dry substance and sucrose by double polarization; although refractive index solids, and single polarization sugar (in the case of beet products), give approximately the same, final melassigenic quotient. The rates of adjustment at 30 degrees C. were followed refractometrically after inoculating with a fixed amount of seed (6X Confectioner's to crystallizable sucrose=0.47). The saturation refractivities were taken after 24 hours; but it has been observed with many syrups that use of the 2-hour value does not alter the rate curves appreciably, unless the rate is extremely slow. In this case a higher sucrose concentration is advisable to accelerate the observations. A plot of the negative logarithm of the fractional refractive index change against the time is a straight line over most of the life of the run, and the slope of this curve is the specific reaction rate constant, k , in the integrated rate equation:

$$\ln \frac{n_0 - n_{\text{sat.}}}{n - n_{\text{sat.}}} = kt$$

The velocity constant is expressed most conveniently relative to that of a pure sucrose solution of the same molality. Absolute values of the growth

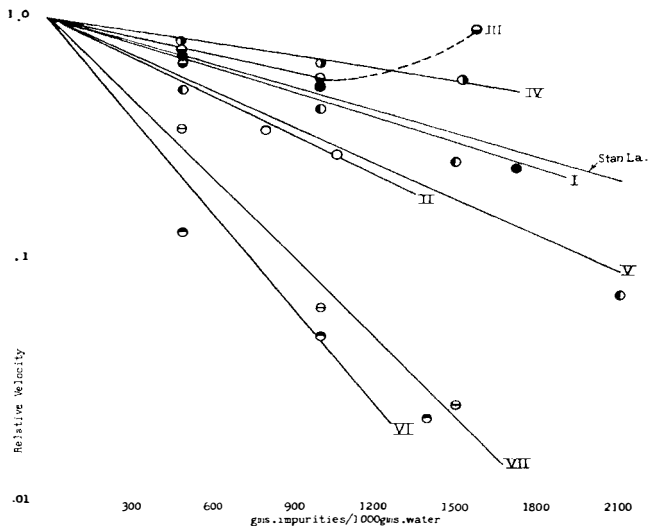


Figure 1. Melassigenic Curves

- - Sample I - Refiner's Blackstrap
- - " II - Puerto Rican Syrup
- ⊙ - " III - Non-Steffens #1
- ⊖ - " IV - Non-Steffens #2
- ⦿ - " V - Louisiana Blackstrap
- ⊕ - " VI - Steffens #1
- ⊗ - " VII - Non-Steffens #3

rate may readily be estimated from the previously determined value of $100 \text{ g/m}^2/\text{hr.}$ for pure sucrose at 8 molal. This value is almost exactly the same as Kucharenko's value (3).

Results and Discussion

For solutions of the same sucrose molality, identical crystallizing surface, etc., the activity theory of crystallization rate suggests:

$$\log(\text{Rel. Velocity}) = iI$$

The slope of the relative velocity versus the Impurity, I , (as g./1000 g. water) curve on semi-logarithmic coordinates, thus defines the coefficient i ,

which may be considered to be the melassigenic factor. Most of the syrups which have been examined to date confirm this equation in at least an approximate way. As a minimum, only one velocity determination is required, although at least three are utilized in each of the results represented in figure 1. With the exception of Syrup III, these curves fall into the general pattern demanded by the above expression. If the melassigenic rating suggested in an earlier paper (5-f) is extended to include these present data, the following table 2 is obtained.

Table 2.—Relative melassigenic nature of syrups—arbitrary i values.

Syrup	i
4. Non-Steffen	0.6
3. Non-Steffen	0.8
Standard Cane ^a	1.0
(Pure invert sugar	1.05)
1. Refiners' blackstrap	1.1
5. Louisiana blackstrap	1.7
Steffen No. 2 ^a	1.8
2. Puerto Rican syrup	1.9
Cane ^a	2.0
Non-Steffen No. 1 ^a	2.1
Louisiana Cane ^a	2.2
7. Non-Steffen	3.7
Steffen No. 1 ^a	4.1
Non-Steffen No. 2 ^a	4.6
6. Steffen	4.7

^aThis number refers to the designation employed in reference (5-f).

No particular classification is observed; but the range in values suggests that the melassigenic factor, i , may have some significance in representing the boiling and crystallizing behavior of massecuites. The abbreviated methods of the present paper also suggest the possibility of practical utility.

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