SUGAR BOILING
THE SYRUPS IN THE VACUUM PANS

by John Ziegler

In the sugar boiling process, it is most desirable to know the syrup concentration at all times so that its supersaturation may be held within certain limits. If it is carried too low, the crystallization rate suffers and above a maximum value, unwanted spontaneous grain formation takes place

One of the most practical means of measuring this important variable is by the temperature of the boiling syrup at a known absolute pressure or by reference to the temperature of water boiling at the same pressure. The so-called “Boiling Point Elevation” or “BPE” has long been used for this purpose. A considerable amount of care must be exercised in making the temperature measurements if they are to yield an accurate measure of supersaturation because the BPE range of interest covers only a few degrees Centigrade. The normal temperature gradients in vacuum pans make intolerable errors if the syrup temperature is taken even a short distance below the boiling surface. This poses some mechanical problems due to changing pan level but one widely used technique is to take the temperature of vapor leaving the pan as it will be at the surface temperature. More of measurement problems later.

In order to convert a BPE reading into the degree of supersaturation, one must know the sucrose solubility in the particular syrup at the boiling temperature and the BPE it produces at any concentration of total solids. This paper reports an investigation of the literature to see if reasonably accurate figures for the solubility and BPE of typical beet and cane syrups could be established over the range of values encountered in vacuum pan work. Not surprisingly, perfect agreement is lacking in the values reported by various investigators even on pure syrups, probably occasioned by experimental errors. Add to this the fact that the composition of the nonsucrose components present in lower purity syrups affects both values to some extent. However, by restricting the investigation to the normal temperatures, concentrations and purities of pan syrups, excluding those in crystallizers, dangerous extrapolation was avoided and fair average values established.

Bounding the Problem

In vacuum pans, syrups are generally boiled at some temperature between 65^{0}C and 85^{0}C with a good average in the 75^{0}C region. This fixes the operating pressure in the 4" to 9" Hg Abs range. Pans operated at a lower pressure suffer from poor overall massecuite circulation and high temperatures increase the probability of syrup degradation.

The only syrup concentrations of interest in pan operation lie above saturation and below the limit of the metastable zone where spontaneous nucleation takes place. This limit appears to be near 1.65 supersaturation on higher purity syrups and of the same order of magnitude on those of lower purity.

In normal vacuum pan work, there is no need to consider syrups of lower purity than they reach at pan drop. Beet syrups below 65 purity and cane syrups below 50 purity are only encountered in final crystallizer exhaustion of molasses.

Sucrose Solubility-Pure Syrups

There seems to be little disagreement between the many investigators of pure sucrose solubility, at least over the ranges of interest here. Brown and Nees (1), Charles (2), Grut (3), Thieme (4) and others are well within the tolerance presently required. Currently the solubilities of Vavrinecz (5) given in **Table 1** are those tentatively accepted by ICUMSA and seem to be a weighted average of previous tables.

Table 1. Solubility - Pure Sucrose.
(Tentative ICUMSA Standard)

Temperature (^{0}C)	**S/W** (g Sucrose /g water)
50	2.59
55	2.73
60	2.89
65	3.06
70	3.25
75	3.46
80	3.69
85	3.94
90	4.20

Sucrose Solubility
Impure Beet Syrups

The basis for **Table 2** covering these syrups was the well known Grut solubility **Table 3** since the values are in quite good agreement with those of other investigators. The Wiklund (6) relationship curves were plotted over the range of temperatures and purities of interest in pan work and it was found that the best average solubility coefficient was expressed by the equation: C = 0.20 N/W + 0.79 where C is the ratio of sucrose/water at saturation in the impure solution divided by the sucrose/water in a saturated solution of pure sucrose at the same temperature. N/W is the non-sucrose/water ratio in the impure solution. The Wiklund relationship is linear for solutions with N/W above 1.5 and serves as a valuable guide for plotting the solubilities of the lower purity pan syrups.

Table 2. Beet Syrup Solubility.
(g Sucrose / g water)

	Purity								
T^0C	**100**	**95**	**90**	**85**	**80**	**75**	**70**	**65**	**60**
65	3.06	3.04	3.01	3.00	3.05	3.17	3.30	3.62	4.07
70	3.25	3.20	3.16	3.16	3.21	3.33	3.57	3.94	4.50
75	3.46	3.40	3.37	3.38	3.44	3.63	3.90	4.35	5.05
80	3.69	3.63	3.61	3.62	3.70	3.93	4.29	4.82	5.72
85	3.94	3.88	3.85	3.86	3.94	4.23	4.70	5.32	6.38

Grut's 100 purity solubilities were slightly higher than the newer values given in **Table 1** so his values were dropped about 3% in the higher purity regions to get agreement.

Sucrose Solubility
Impure Cane Syrups

Table 3 solubility values are based on the data of Thieme (4) which are in close agreement. His high purity values were slightly lower than those of Vavrinecz in **Table 1** so a minor upward adjustment of their figures was made.

Table 3. Cane Syrup Solubility.
(g Sucrose / g water)

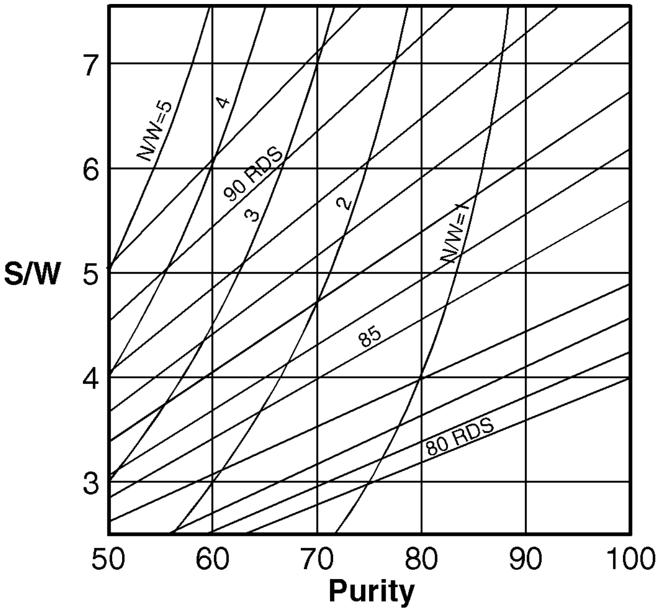
	Purity					
Temp	**100**	**90**	**80**	**70**	**60**	**50**
65	3.06	2.96	2.82	2.74	2.64	2.50
70	3.25	3.14	2.99	2.93	2.81	2.62
75	3.46	3.33	3.20	3.11	2.97	2.76
80	3.69	3.56	3.43	3.35	3.17	2.97
85	3.94	3.77	3.66	3.57	3.40	3.15

Solubility Chart Construction

A plot of solubility information can be useful in interpolating between points and in picturing changing syrup conditions during the course of the boiling process. The chart described here has proven most helpful in this regard. A basic chart is first constructed for any syrup and to it the temperature contours can be added showing saturation conditions for a specific syrup being processed. It need not have the impurity characteristics of the syrups of **Tables 2 and 3** but once its solubility data have been determined it is easily applied to the basic chart. Then a laboratory determination of massecuite or mother liquor concentrations and purities locates a point on the chart and calculation of syrup supersaturation, crystal yield and other important variables is greatly facilitated.

The basic chart of **Figure 1** plots sucrose/water ratio, S/W, against syrup purity over the range of interest in pan operation. Purity is given as the percent of total solids that are sucrose. The syrup concentration lines are then added as percent by weight of dry substance, refractometer dry substance or brix since it is usually given this dimension in lab reports rather than dry substance/water. They are located as follows: the 80 rds line crosses 100 purity at 80/20 or S/W = 4 and at 50 purity S/W = 2. At 100 purity and 86 rds the sucrose ratio would be 86/14 = 6.14 and at 50 purity it would be only half as great or S/W = 3.07 etc.

Figure 1. Basic Solubility Chart



Nonsucrose/water lines are then added: for example, the N/W = 2 line would intersect the S/W = 6 line at a purity of 6/(6 + 2) = 75% and at S/W = 3 at a purity of 3/(3 + 2) = 60% and so on.

One may then superimpose temperature contours from experimentally derived information on any particular syrup. A typical plot using the figures from **Table 2** have been added on **Figure 2**. As expected, the lines slope upward with decreasing purity because of the increase in sucrose solubility caused by beet syrup impurities.

Figure 2. Beet Syrup Solubility

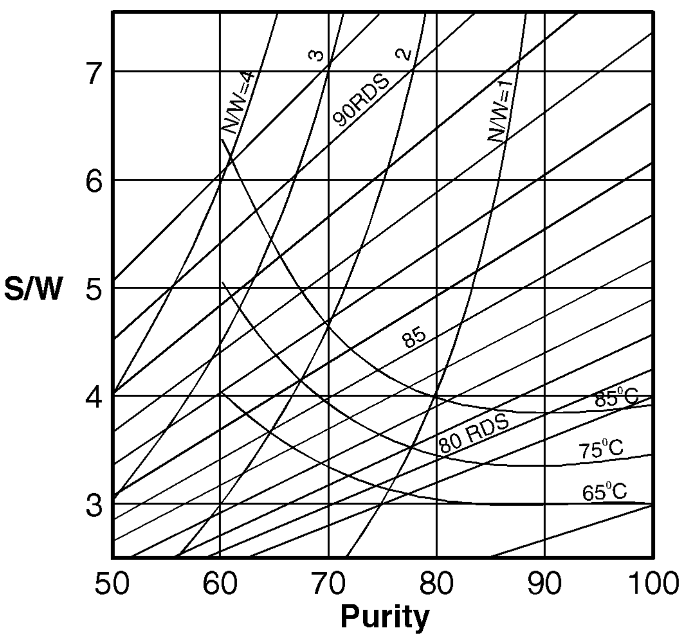
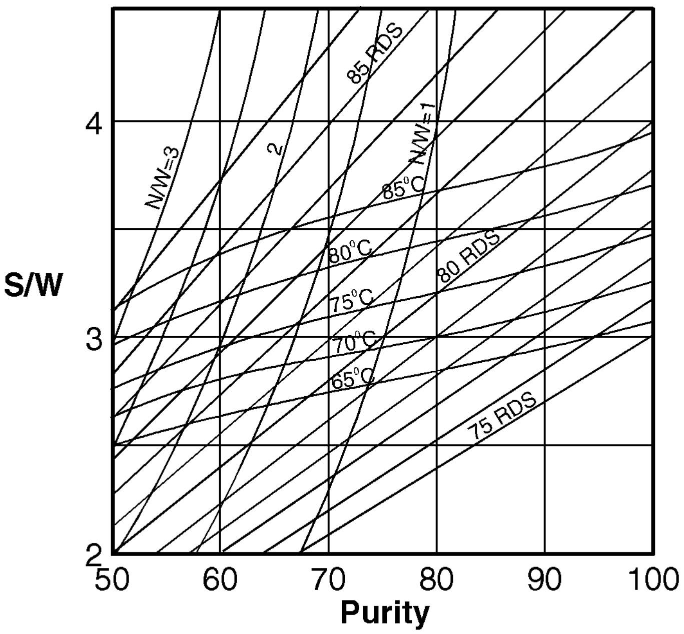


Figure 3 is a similar plot for typical cane syrups using the data of **Table 3** The "salting out" effect of cane impurities is readily apparent since sucrose solubilities decrease at lower purities.

Figure 3. Cane Syrup Solubility



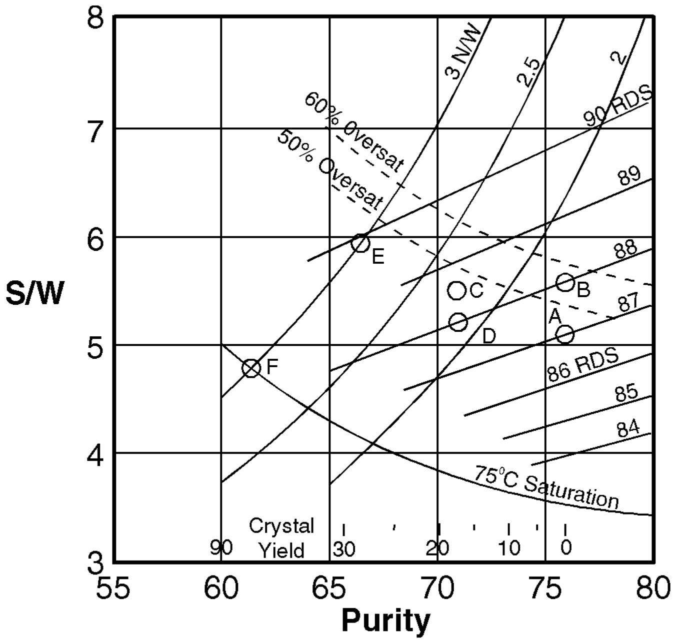
Supersaturation

Many ratios have been used in the literature to describe the condition of syrups with more or less material in solution than would exist if it were just saturated. This has caused considerable confusion. In this paper a straightforward ratio will be used, namely, the total solids to water content of the syrup divided by the total solids to water content in a saturated solution at the same temperature and purity. Numerically the same value is obtained if one takes the sucrose to water content divided by the sucrose to water that would be present in a saturated solution at the same temperature and purity.

An example will make this doubly clear. An 80 purity cane syrup at 75^{0}C from **Table 3** would be saturated when S/W = 3.20. Take out water until S/W = 4.80 and its supersaturation would be 4.80/3.20 = 1.50 or 50% oversaturated. Add water until S/W is 2.40 and the supersaturation would be 2.40/3.20 = 0.75 or 25% undersaturated.

The same syrup at saturation would have 3.20/0.8 = 4.00 g total solids per g water and if concentrated until it had 4.80/0.8 = 6.00 g total solids per g water would likewise be 6.00/4.00 = 1.50 supersaturation.

Figure 4. Solubility Chart Example



Using Solubility Charts

The type of solubility charts presented here can be used to plot syrup conditions during the entire course of a strike and the subsequent crystallization process although the latter is beyond the scope of the present paper.

Consider a typical low raw beet strike boiled at 75^{0}C and fed with 76 purity machine syrup throughout. The chart of **Figure 4** shows only the contours of interest during the boiling cycle.

A graining syrup charge is brought into the pan and, as it is concentrated, the S/W increases until a proof sample shows it to be 87 rds, point A. From the chart, S/W is 5.08 and since saturation at 75^{0}C is 3.58, the syrup is at 5.08/3.58 supersaturation; 1.42 is a safe point to introduce seed but it is delayed until the concentration reaches 88 rds. S/W is then 5.57 or 1.56

supersaturation which is approaching the upper safe limit so syrup feed is started to prevent further increase. Point B of **Figure 4**.

Microscope checks show the grain in and growing nicely as would be expected with no sign of new nuclei. After a time the massecuite "comes together" and a lab check shows the mother liquor to be 88.5 rds and 71 purity, point C. S/W from the chart is 5.50 and saturation is 3.83 so the syrup is at 1.44 supersaturation. From the purity drop from 76 to 71, the crystal yield can be calculated as the percent of total solids present.

$$V = \frac{(\text{Massecuite purity} - \text{syrup purity}) \times 100}{(100 - \text{Syrup Purity})}$$

Crystal yield is then (76 - 71)/(100 - 71) x 100 or 17.2% which represents a good boiling consistency so syrup feed is adjusted to maintain this crystal/liquor ratio. The increasing crystal surface area causes a slow fall in supersaturation as pan level increases.

When the pan is full, the liquor is still 71 purity but a check shows it to be only 88 rds, Point D. The S/W is 5.20 and, dividing this by 3.83 at saturation, gives a supersaturation of 1.36 so it should be safe to stop feed and brix up the massecuite without having to feed any water to slow the operation.

When the pan is dropped, the liquor tests 66.5 purity and 89.9 rds, Point E. so S/W = 5.93 and N/W = 3.00 from the chart. The supersaturation is 1.41 and, from the purity drop, the crystal yield is 28.3% of total solids. The massecuite can be easily evaluated.

In the syrup phase, the solids amount to 5.93 + 3.00 = 8.93 g dry substance per g water. Since this accounts for 71.7% of all the solids including the crystals, the total solids are 8.93/0.717 = 12.45 g/g water. The massecuite is thus 12.45/13.45 = 92.6 rds so at drop its make-up is
3.52 S as crystals
5.93 S
3.00 N
1.00 W

After dropping, the N/W remains unchanged but crystals continue to grow toward the saturation point F on the N/W = 3.00 line. Cooling will of course further reduce the final S/W.

Other useful solubility charts can be constructed for solving syrup problems. Note the added contours on **Figure 4** for higher supersaturation values and the scale of crystal yield which, would only apply to pans of 76 purity material. Not only do charts such as these simplify syrup calculations; they have proved most valuable in plotting strategic pan manipulations and for giving operating personnel a better picture of the sugar boiling operation.

Boiling Point Elevation of Syrups

Laboratory analyses of syrup conditions in vacuum pans require more time than is allowable if optimum conditions are to be maintained continuously. The primary consideration is, of course, syrup supersaturation which must be kept below the upper safe limit at all times to prevent new grain formation but be maintained at as high a level as possible to force crystallization within the constraint imposed by massecuite consistency and its effect on the circulation of pan contents. A continuous indication or record of supersaturation is of invaluable assistance in pan operation and BPE, although indirect, provides a practical means of following this important variable.

In the literature, there is a great deal of experimental data on BPE of various syrups but much of it is of little value because of errors in the determinations. This is completely understandable due to the problems associated with making accurate measurements of the two temperatures. If done in vacuum pans, the erratic circulation and ebulition patterns that are inherent in such equipment make the equilibrium boiling point determination most difficult. The rather viscous syrups involved militate against accurate measurement in even the most carefully designed laboratory equipment.

But by plotting and replotting the available data to eliminate obvious typographical errors, a pattern does emerge that is probably close enough to the truth for practical purposes. After all, there is no such thing as a typical beet or cane syrup, at least in the lower purity regions, and the object here is to develop good average values that can be used by those seriously engaged in improving their pan operation. The final criterion on a particular syrup is the boiling point elevation that can be tolerated without new grain formation.

The best information on the boiling point elevation of beet sugar solutions appears to be that of Vavrinecz (7) as it checks quite well with the values reported by Spengler, Boettcher, Werner (8). The latest determinations on cane syrups are those of Batterham and Norgate (9) and, although their figures are slightly higher at the pure syrup end, a minor adjustment has been made here to bring them into agreement.

At a given boiling temperature and syrup purity, the BPE appears to increase almost linearly with the dry substance/water content of the syrup. Thus it is convenient to apply a factor Kds, for the BPE per gram dry substance per gram water. For example, a 100 purity syrup with S/W = 4 at 82^{0}C exhibits 8^{0}C BPE so its Kds = 2.0^{0}C/g/g.

Operating temperature has a very minor effect on BPE. Taking the mid operating temperature of pans as 75^{0}C, Kds increases about 0.6% per ^{0}C above this point and decreases a like amount below. So over the range of 65^{0}C to 85^{0}C being considered here, the change is only plus or minus 6% from that at the mean level.

For a constant boiling temperature and dry substance content, the BPE increases with falling purity. This is understandable because in both beet and cane syrups, the average molecular weight of impurities is considerably less than that of sucrose; cane syrups with their higher proportion of invert sugars have a smaller effect on BPE than beet syrups at the same purity. Curves of Kds for the two syrup types are plotted in **Figure 5** and the coordinates are given in **Table 4** which also has values for a more convenient factor, Ks which is the BPE per gram sucrose per gram water obtained by multiplying Kds by 100 purity. It is included because saturation data and curves are in terms of S/W.

Table 4. BPE Factors - Beet and Cane syrups at 75^{0}C. Kds values are BPE, ^{0}C per g Dry Substance per g water. Kds values are BPE, ^{0}C per g Sucrose per g water.

	Beet		Cane	
Purity	**K_{ds}**	**K_S**	**K_{ds}**	**K_S**
100	1.90	1.90	1.90	1.90
95	1.95	2.05		
90	2.03	2.26	1.96	2.18
85	2.13	2.51		
80	2.25	2.81	2.02	2.53
75	2.37	3.16		
70	2.52	3.60	2.08	2.97
60			2.14	3.57
50			2.20	4.40

BPE Chart Construction

Assuming that information on sucrose solubility and boiling point elevation presented here is reasonably accurate, it becomes an easy matter to calculate and construct charts of supersaturation versus BPE for any syrup being boiled in a vacuum pan.

For example: 90 purity beet syrup at 75^{0}C is saturated when S/W = 3.37 from **Table 2** and from **Table 4** Ks = 2.26 so the BPE at saturation would be (3.37) (2.26) = 7.62^{0}C. At a higher boiling temperature, say 85^{0}C, the same syrup is saturated when S/W = 3.85 and Ks would be 6% higher because of the additional 1^{0}C above 75^{0}C so the BPE will be (3.85) (2.26) (1.06) = 9.24^{0}C. And at 65^{0}C when saturation is at S/W = 3.01, it would be (3.01) (2.26) (0.94) = 6.38^{0}C.

By following this method, the chart of **Figure 6** is quickly plotted giving the boiling point elevation of saturated beet sugar solutions over the range of temperatures under consideration; the similar plot of **Figure 7** gives the same information for cane syrups for the purities of interest.

Figure 5. BPE Factor, Syrups 75^{0}C

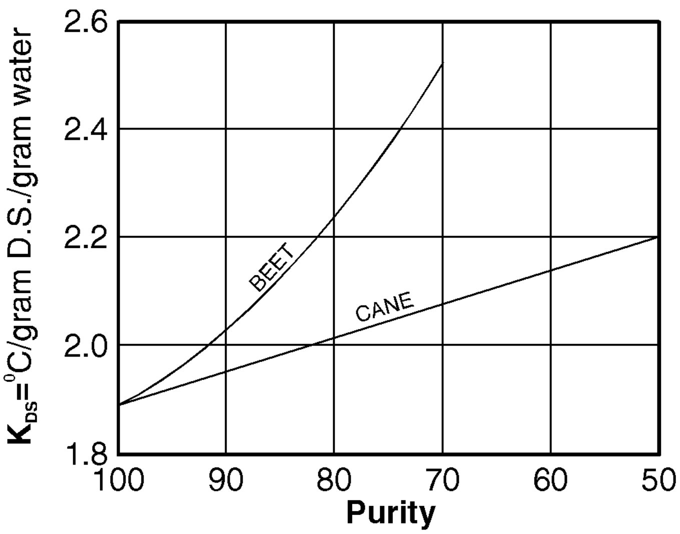


Table 5. BPE Saturated Beet Syrups.
Values are BPE in ^{0}C.

	Syrup Temperature (^{0}C)		
Purity	**65**	**75**	**85**
100	5.48	6.57	7.92
95	5.87	6.97	8.42
90	6.38	7.62	9.24
85	7.08	8.48	10.27
80	8.05	9.67	11.24
75	9.41	11.47	14.17
70	11.15	14.04	17.95

In practical sugar boiling. syrup supersaturation must be held high enough to produce a good rate of crystal growth but below the value that causes new nuclei to form. This upper limit appears to lie close to 1.65 supersaturation, at least on the higher purity syrups and at about the same value on those of lower grade. So even more useful charts can be constructed giving the maximum BPE allowable for the different syrups or the mother liquor purities encountered in pans. **Figures 8 and 9** cover beet and cane syrups respectively. They are simply constructed by multiplying the readings of **Figures 6 and 7** by the factor 1.65. For example. 80 purity cane syrup at saturation has a BPE of 8.10^{0}C when boiling at 75^{0}C and with 65% more solids in solution, the BPE would be (8.10) (1.65) = 13.37^{0}C

BPE Measurement Problems

In actual vacuum pans the determination of liquor supersaturation by the boiling point elevation method requires more careful attention to details of temperature measurement than it is often accorded. Some of the pitfalls are detailed here.

Figure 6. Saturated Beet Syrups

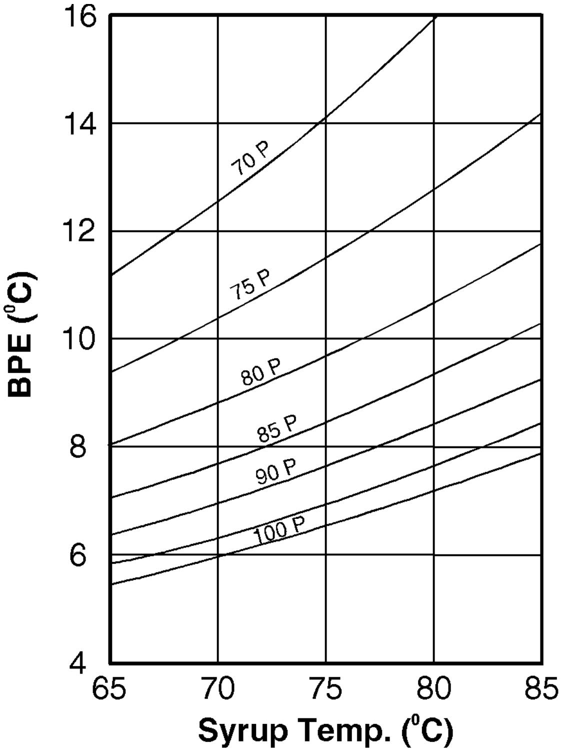


Figure 7. Saturated Cane Syrups

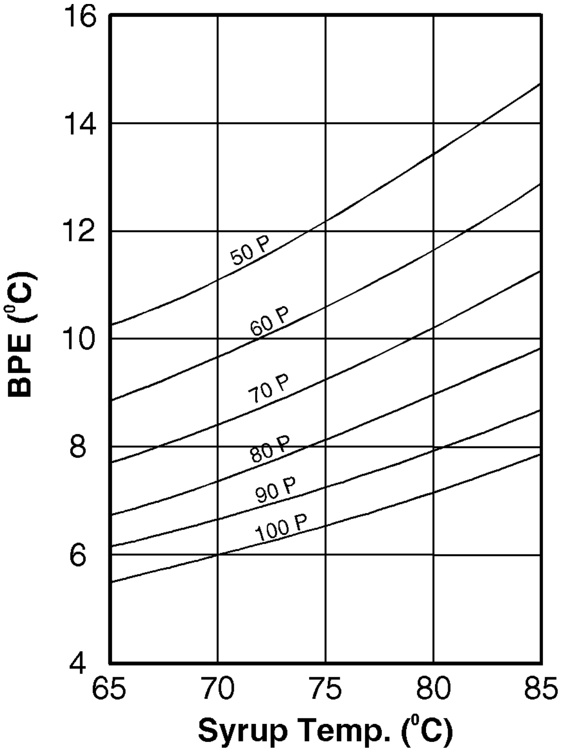


Figure 8. BPE Beet Syrups, 1.65 Supersaturation

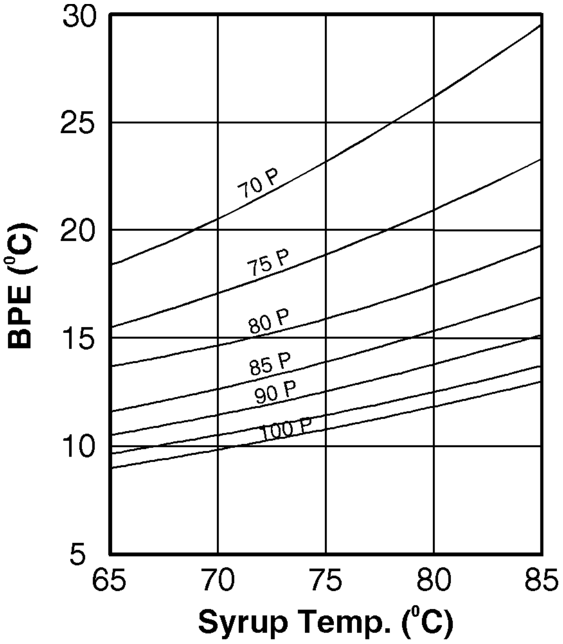


Figure 9. BPE Beet Syrups, 1.65 Supersaturation

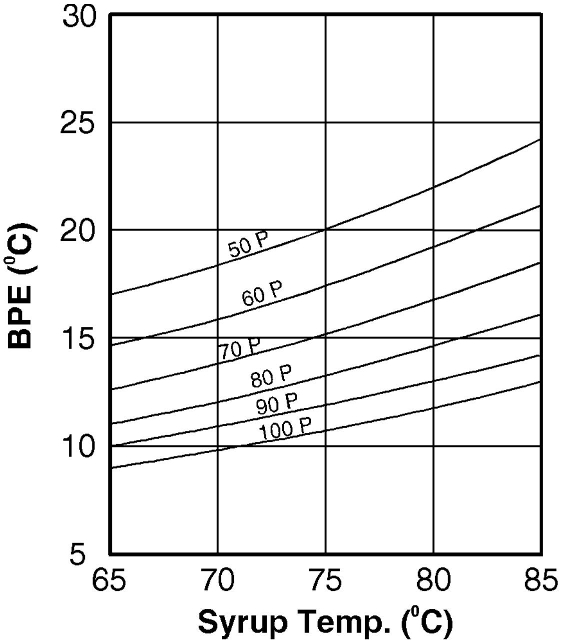


Table 6. BPE Saturated Cane Syrups.
Values are BPE in ^{0}C.

	Syrup Temperature (^{0}C)		
Purity	**65**	**75**	**85**
100	5.48	6.57	7.92
90	6.07	7.26	8.71
80	6.71	8.10	9.81
70	7.64	9.24	11.24
60	8.87	10.60	12.85
50	10.35	12.14	14.68

Consider a high purity refinery grade syrup being boiled at 75^{0}C. The BPE at saturation is 6.57^{0}C and at the probable 1.65 supersaturation limit is only 10.84^{0}C or a difference of 4.27^{0}C and this is the entire range of interest in the pan operation. During the boiling of a strike, low supersaturations below say 1.3 are of only academic interest and the careful operator would not long exceed 1.6 so the change in BPE over this range is only 2^{0}C. True, the spread is greater on syrups of lower purity, but even on them, good thermometric practices must be followed if significant measurements are to be obtained. Measuring devices are capable of more than adequate accuracy but their application to vacuum pans must be done with care.

Obtaining the reference temperature of water boiling at pan vapor space pressure is relatively easy but a common practice of expanding “wet” steam over the measuring element should be avoided because, in the expansion, the vapor phase becomes superheated and may not be adequately desuperheated by the water phase present before reaching the element. The same problem exists if a reference pot of water connected to the pan vapor space is heated by steam injection; the superheated steam bubbles contacting the element can be hotter than the water and increase the measured temperature at a higher steam flow. A far better way is to flash considerably hotter water or condensate over the measuring element at a point near enough to the pan vapor space that there will be no appreciable pressure drop.

The boiling point of syrup or massecuite can only be measured accurately at the boiling surface. Below this, the pressure is higher due to the hydrostatic head of syrup and, since heat is being supplied from below, the rising syrup temperature will only fall to equilibrium when it reaches the surface. The usual picture of circulation patterns in vacuum pans is far from realistic. Rising currents of overheated liquid from a calandria surface do not ascend directly to the surface, turn, and flow downward through the center well. Some of the hot material finds its way into the down-flow stream and never reaches the minimum temperature at the surface. Therefore, a temperature as commonly measured in the center well is valueless when massecuite level exceeds that at the point of measurement: temperatures several degrees higher are normally found at the higher massecuite levels during the greater part of the strike. This does not mean that existing crystals are necessarily dissolving at the low levels where higher temperatures exist. Suppose a 100P syrup boiling at 75^{0}C at the surface is at a supersaturation of 1.30 there or contains 4.5 S/W; such a syrup would drop to saturation only if its temperature were increased to 95.5^{0}C and it is doubtful that such a temperature would be reached anywhere in the pan even with quite poor conditions of circulation. But a temperature indication only 2.3 higher than that at the surface would indicate that the supersaturation was not 1.3 but fairly near the 1.65 limit. In truth the syrup at 77.3 is at a lower supersaturation than that at the surface, actually 1.26 instead of 1.3. But the BPE at the massecuite surface is at the lowest temperature that it has in the pan and therefore at the highest supersaturation so that is the place that the measurement must be made.

Some mechanical problems arise in measuring massecuite temperature at a continually changing surface level. One solution is to use a series of matched elements. switching from one to another as the level rises. The more practical method. previously mentioned, is to monitor the temperature of the vapor rising from the boiling surface which is at the same temperature of ebullition and as long as there are no intervening steam or water leaks to add or subtract heat from the fragile superheated vapor, a reliable minimum massecuite temperature can be obtained at any level. Many successful installations have proven this to be a sound method.

Conclusion

This has been an attempt to correlate available information on solubility of sucrose in the pure and impure syrups boiled in vacuum pans. It is realized that there is no such thing as a typical beet or cane sugar syrup due to the diversity of the nonsucrose components that can be present but the tables and charts presented represent reasonable averages from the information at hand.

Boiling point elevation provides a practical means of measuring the supersaturation of boiling Syrups. The values given here are subject to revision as better experimental results become available and should be used with some caution especially on lower purity liquors. In the meantime, it is hoped that this compilation will be of use to those actively engaged in the study of the sugar boiling process.

(1)Brown and Nees Private Communication
(2)Charles D. F. In Honig "Principles of Sugar Technology"
(3)McGinnis (Ed) Beet Sugar Technology, 2nd ed 1971, Beet Sugar Development Foundation, Ft.

Colllns CO
(4)Thieme, J. G. In Honig "Principles of Sugar Technology"
(5)Vavrinecz, G. Z. Zuckerind 87.481.877
(6)Wiklund. O. Socker hand 2 1946 p 65
(7)Vavrinecz, G. Z. Zuckerind V23-(1)(10-16) 1973
(8)Spengler Boettcher Werner Z Zuckerind 88 534 (1938)
(9)Batterham & Norgate Int Sugar J. 1977 359

The Van Hook Definition for Supersaturation

Another ratio, credited to VanHook, is sometimes used to evaluate the supersaturation of impure syrups and finds some use in crystallizer operation. He pictures a syrup as a solution of sucrose in an impure solvent consisting of water and non sucrose materials so compares its sucrose content to that which would be present if sucrose were removed by crystallization until it was just saturated at the same temperature. The N/W ratio is not changed but the syrup purity is lower

The Claassen concept used here considers a syrup as a solution of sucrose and impurities in a pure solvent, water. Both ratios yield the same supersaturation values on pure syrups but the Van Hook numerical values become lower as beet nonsucrose content increases and higher on cane syrups.

In the operation of sugar vacuum pans and cyrstallizers it makes little difference which ratio is used to evaluate the degree of supersaturation since one is only interested in the relative syrup condition within the metastable zone between saturation and the upper stable limit. Once these limits are established for the syrup of interest, either ratio can be used to determine the relative amount of crystallization driving force. The Claassen ratio is recommended since it is more easily understood.