

SUCROSE CRYSTAL HABIT IN A REFINERY

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Abstract

Increasing concentrations of molasses caused increasing extents of crystal elongation when pure sucrose solutions were spiked with refinery molasses under laboratory conditions. The molasses was fractionated using a combination of ethanolic precipitation and carbon column chromatography. This fractionation caused no significant loss of c-elongating properties. Addition of the individual fractions to sucrose solutions indicated that the major habit modifiers were in the fraction containing low molecular weight oligomers. This fraction also had the greatest rate-retarding effect. It was also demonstrated that standard dextrans, isomalto-oligosaccharides, malto-oligosaccharides and a "kestose" preparation did not induce significant c-axis elongation under similar conditions and at similar concentrations. Hydrolysis of this fraction with yeast invertase completely removed the habit-modifying properties. This implies that fructose-based oligomers were probably responsible for c-axis elongation in this refinery, with minimal contribution from the polysaccharide components.

Introduction

The shape or appearance of a crystal is called the crystal habit. Although crystals of a given substance may be very different in shape the angles between the faces are characteristic and constant. The general outward appearance of the crystal is governed by conditions during growth which can affect the relative growth rates of the different crystal faces. Several factors can influence these growth rates, including supersaturation, temperature variations and the concentration and nature of impurities. The shape of a crystal grown in the presence of impurities is largely controlled by the faces most retarded by adsorption of the impurities. It is generally conceded that the most profound influence can be attributed to the types of impurities present. Other factors will have considerably less effect on the ultimate crystal shape. There is a distinction between crystallographically elongated crystals and long crystals. If two specified linear dimensions of the crystal are used to measure shape then the natural shape of a pure sucrose crystal grown in water is about twice as long in the b-direction (y) as in the c-direction (z). This can be deduced from the basic rate data published by Vernon³⁴ and by Smythe²⁷ and recently highlighted by Vane.³³ Hence crystals with y/z ratios of about 2 are normal, ratios less than 2 indicate c-axis elongation and ratios greater than 2 imply b-axis elongation.

The classical study by Smythe^{27, 28, 29} showed that the effects of oligosaccharides were the result of highly stereo-specific adsorption. Mantovani¹⁴⁻¹⁷ and his school have also focused on the mechanisms of added impurities, particularly raffinose which is of importance in the beet industry. Observations in the factory environment have tended to link needle grain with polysaccharides, especially when processing deteriorated juices or low quality syrups.

The Australians have been very active in this area. Keniry *et al*¹⁰ postulated dextran as a promising quantitative indicator of the processing quality of cane on the basis of correlations between dextran and molasses purity or crystal elongation. Sutherland,³⁰ Sutherland and Paton³¹ as well as Leonard and Richards¹² separated refractory syrups into polysaccharide and oligosaccharide fractions and concluded that the predominant causative agent in crystal elongation was polymeric and that oligosaccharides were not an important primary cause of elon-

gation. However, these workers all assumed that the almost square crystal shape normally observed in massecuites was ideal. Such crystals are in fact already significantly elongated in the c-direction. Later work by Day⁵ and by Covacevitch *et al*⁶ demonstrated the effect on elongation of temperature, dextran molecular weight, concentration and structure, but also overlooked the fact that the major elongating properties were already present in the base medium. This is presumably why so many authors have commented on the relatively slight elongation obtained with dextrans in pure solutions even at unrealistically high concentrations – by using an elongated (although square) crystal as the reference point the small additional influence caused by dextran is noticed more quickly. That dextran is not usually a major crystal habit modifier can also be inferred from the work of Hidi and Staker.⁷ These authors demonstrated significant enzymic dextran removal under factory trial conditions, but an insignificant improvement in crystal elongation (eg decreasing the dextran in the incoming juice from about 1 700 ppm to less than 100 ppm only improved the y/z ratio from 0,75 to 0,90). In one instance by reducing the level from 2 300 ppm to 150 ppm in B-molasses the crystal shape for C-sugar improved from 0,35 to 0,65 which is still extensively elongated crystal. In a third trial where the average dextran level in C-massequite (4 300 ppm) was decreased by 60% the crystal shape only improved from 0,45 to 0,50. By contrast, Inkerman⁸ reported a marked reduction in the percentage of elongated crystals after "complete" enzymic removal of dextran.

Saska and Polack²³ investigated the effects of dextrans and partially hydrolysed dextrans on sucrose crystal habit and found decreasing elongation effects as the molecular weight decreased – implying that these oligosaccharides were less significant than polysaccharides. Cremata *et al*⁴ contend that low molecular weight polysaccharides accumulated between cutting and milling and caused c-axis elongation.

In the West Indies Tilbury³² could find no statistically significant correlation between dextran content and crystal elongation in C-massequite during a period when high dextran levels were entering the factory. However all samples showed marked crystal elongation. Mantovani *et al*¹⁸ and Shah and Delavier²⁶ observed "cubic" crystals in the presence of added dextran. This cubic tendency implies that growth has been retarded in both the b- and c- directions. Kamoda *et al*⁹ have separated a polysaccharide and an oligosaccharide fraction from refinery final molasses and added this to sugar solutions in a laboratory vacuum pan. Kamoda found that oligosaccharides were the major causative factor. More recently Montenegro²⁰ has confirmed these findings by concluding that the compounds exerting more influence on the elongation of sucrose crystals were the oligosaccharides rather than the polysaccharides and that micro-organisms present in juices produce oligosaccharides capable of causing c-axis elongation.

Many refiners have become categorical that elongated crystals are due to the presence of dextran. As a result there has been a general resurgence of interest, particularly in connection with raw sugar penalty schemes, although much of the evidence linking dextran and needle grain is circumstantial and uncorroborated.

Despite the questionable evidence that sucrose crystal elongation is directly attributable to dextran, the other processing problems associated with polysaccharides or dextrans should not be underestimated. These processing problems will directly affect throughput and exhaustion and are probably of more importance than crystal shape implications.

South African raw sugars usually show negligible dextran levels using the haze technique but are generally c-axis elongated, with the problem occasionally becoming more severe. The associated decrease in throughput is probably the most troublesome aspect. It is interesting to note that Vane³³ classified South African raws as behaving well in the refinery despite y/z ratios of 0,8. Although the Sugar Milling Research Institute has investigated the problem on several occasions no formalised findings have been published. This paper summarises the results of our recent re-investigation of the problem with particular emphasis on refining. Clearly the findings are not conclusive but represent the current status of what is an ongoing project.

Experimental Procedure

Crystallisation apparatus

The laboratory crystalliser consisted of glass tubes (130 × 30 mm with B 29 stoppers and holding about 50 ml solution) attached to a motor-driven wheel (diameter 280 mm). The speed of rotation could be varied electronically and could be monitored electromechanically. In most experiments this speed was about 20 rpm. The entire apparatus was placed in an electronically thermostatted oven operated at 60–61°C.

Preparation, curing and equilibration of solutions

Sugar solutions were prepared by weighing first refinery boilings, impure factory products and water to give a sucrose/water ratio (S/W) of 3,075 (ie a degree of supersaturation of 1,06 for pure sucrose at 60,5°C based on the data of Charles²) and the desired non-sucrose/water level (NS/W). For most experiments the NS/W ratio was equivalent to 0,1 on molasses. The components were dissolved at 70°C in a rotating flask and the clear solutions were cured for several hours in an oven held at 70°C. The cured solutions were transferred to the crystallisation tubes and equilibrated overnight at the working temperature (60–61°C).

Crystallisation procedure

A single crystal technique was used to measure crystal growth rates whilst a multi-crystal approach was used for shape applications. In the former case single crystals (grown from selected coffee crystals to about 75 to 100 mg at 1,04 degree of supersaturation) were tied to stainless wire formers using single filament nylon (diameter 0,15 mm). The tied crystals were pre-warmed in the oven for 10 to 15 minutes before being placed in the hot sugar solution. In the latter case one drop of factory-prepared ball-mill slurry (between 0,5 and 1,5 mg sucrose) was placed on the surface of the solution. The stoppered glass tubes were placed on the wheel with minimum delay.

After 5 hours the single crystals were removed from the solutions, excess syrup was wiped off with soft tissue and the crystals were weighed. Shape runs lasted 48 hours. The crystal-syrup mixture was poured into small perspex baskets (30 mm ID × 55 mm) fitted with wire mesh (0,35 mm aperture), centrifuged at about 3 000 rpm for about 5 minutes, washed with methanol and re-centrifuged. The washing step was repeated once more and the crystals were air-dried.

Crystal measurement

The large crystals were weighed for rate determination before and after the run and the following formula was used to calculate the growth rate ($\text{kg m}^{-2} \text{sec}^{-1}$):

$$R = \frac{202,266 \times (M_F - M_I) \times 10^{-5}}{t \times (M_I^{2/3} + M_I^{1/3} \times M_F^{1/3} + M_F^{2/3})}$$

where M_I = initial mass (g), M_F = final mass (g), t = time (hrs).

The ratio of the crystal length in the b-axis direction (y) to that in the c-axis direction (z) was used as the shape parameter.

Between 200 and 250 crystals were crystallographically identified and the crystal lengths measured using a manual image analyser (Kontron MOP-Videoplan). The average y/z ratio indicates the crystal elongation. Commercial boilings were usually dispersed in glycerol (saturated with sucrose) before measuring and the shape expressed as \bar{y}/\bar{z} .

Isolation of fractions

Refinery exhaust molasses (200 g) was diluted to 20°Bx and centrifuged at 10 000 rpm for 20 minutes at 15°C. The sediment (0,4 g) was discarded. High molecular weight material was precipitated by adding 3,5 volumes of absolute ethanol to 1 volume of supernatant. After standing overnight the sediment was removed by centrifuging. The sediment was dissolved in warm water (400 ml) and reprecipitated by adding ethanol (1 400 ml) and standing overnight. The suspension was centrifuged. The sediment was dissolved in warm water (300 ml) and ultrafiltered (Amicon CH-4A concentrator with 5 000 molecular weight cut-off) using a washout technique with 1 000 ml water, to remove completely any low molecular weight material. The retentate was freeze-dried (fraction A – yield 3,4 g).

The combined supernatants from the alcohol precipitations were concentrated under vacuum at 40°C (fraction B – yield 188 g).

A carbon-Celite column was prepared by packing a glass column (5 × 100 cm) with a 1:1 slurry of Darco G-60 and Celite 545 in 50% ethanol. The column was washed with water (2–3 l) before use. Water (50 ml) was added to a portion of fraction B (110 g) and the solution loaded onto the carbon-Celite column at about 1 ml min^{-1} .

After collecting 150 ml the solvent was changed to 5% ethanol (2 100 ml) and then to 50% ethanol. Fractions were monitored using thin layer chromatography (tlc) (Schäffler & Morel du Boil²⁴). The monosaccharides, sucrose and traces of trisaccharides eluted between 1 650 and 4 000 ml. This eluant was concentrated under vacuum at 40°C (fraction B1 – yield 90 g). The oligomers eluted between 4 000 and 6 500 ml. This eluant was concentrated under vacuum at 40°C (fraction B2 – yield 6,9 g).

The isolation procedure is summarised schematically in Figure 1.

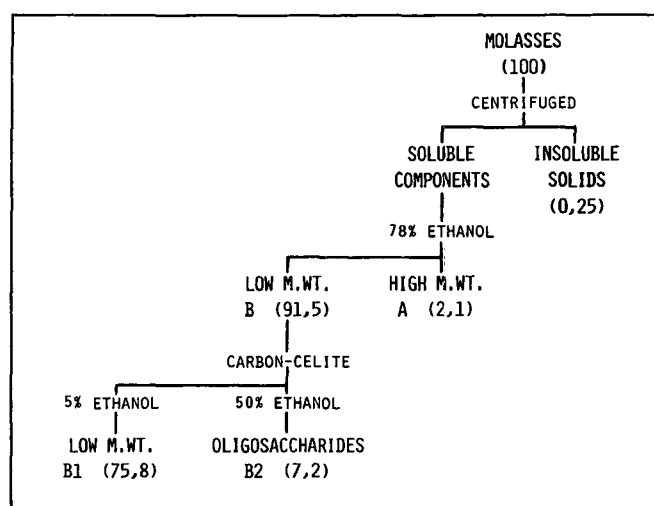


FIGURE 1 Schematic representation of molasses fractionation (yields based on solids recovery).

Crude oligosaccharide preparations

Three broad classes of oligosaccharides were prepared and subjected to the same carbon column clean-up as described above for molasses.

- (a) **Isomalto-oligomers** were prepared by refluxing dextran (Sephadex T-150) (5 g) in 0,3N sulphuric acid (25 ml) for 2 hours. The solution was cooled, neutralised with sodium carbonate and freeze-dried (Saska²³).
- (b) **Malto-oligomers** were obtained from a commercial glucose syrup (DE 42).
- (c) **Sucrose-derived oligomers** were prepared by reacting sucrose with invertase according to the method of Gross.⁶

Hydrolysis of oligosaccharides

Fraction B2 and preparation (c) were hydrolysed using invertase. The sample (0,3–0,4 g) was dissolved in 0,2M sodium acetate-acetic acid buffer, pH 4,6 (3 ml), and invertase (BDH 39020) (0,6 ml) was added. After reacting at ambient temperature for 2 hours, the enzyme was inactivated by boiling the solution for 2 minutes. The cooled solution was neutralised (Amberlite IR 45 (OH)), filtered and freeze-dried. A control was prepared in a similar way, but with the enzyme omitted.

Chemical analysis

All impure products and fractions were analysed for sucrose using a gc technique (Schäffler & Morel du Boil²⁵) and for water by a Karl Fischer method (MacGillivray & Nurok¹³). Low molecular weight fractions, column eluants, oligosaccharide preparations and hydrolysates were monitored or profiled using 11c (Schäffler & Morel du Boil²⁴). The solvent polarity was varied by adjusting the ethanol component (28 to 38%) and the development time varied between 1 hr and 48 hrs depending on the application (ie fast monitoring or detailed resolution).

Results and Discussion

Data presented in Table 1 highlight two points. Firstly there is a wide range in crystal shape from one refinery to the next and secondly that as boiling progresses and the impurity levels increase the crystal shape always gets more elongated. For example first boilings generally lie in the range 1,0 to 1,6; second boilings in the range 0,9 to 1,4; third boilings in the range 0,6 to 1,3 whilst fourth boilings are between 0,5 and 0,9. Recovery house boilings have even lower ratios (approximately 0,3).

TABLE 1
Crystal shape (\bar{y}/z) for different boilings at several refineries

Refinery	\bar{y}/z Ratio			
	Boiling 1	Boiling 2	Boiling 3	Boiling 4
A	1.05	0.90	0.55	0.55
	1.30	1.10	1.00	0.55
B	1.55	1.40	1.25	0.85
	1.35	1.15	0.85	—
C	1.45	1.15	1.20	0.60
D	1.60	1.35	0.90	0.80
	1.40	1.20	0.90	0.65
E	1.35	1.20	1.10	—

In view of this progressive deterioration in crystal shape with increasing impurities it was decided that exhaust molasses from a third recovery boiling would be a suitable source of concentrated elongating constituents. All further experiments were based on this molasses sample.

Under controlled laboratory conditions increasing levels of this molasses were added to pure sucrose solutions so that the S/W ratio remained constant at 3,075 while the NS/W ratio increased from 0,05 to 0,60. When the (\bar{y}/z) ratio is plotted against NS/W the influence of increasing impurity levels can be clearly seen (Figure 2).

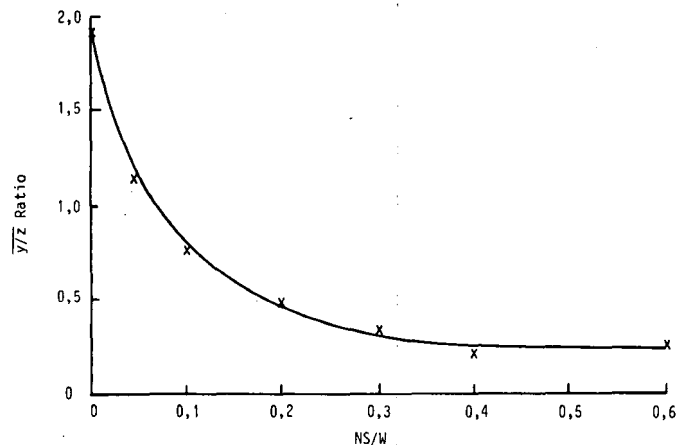


FIGURE 2 Effect of impurity concentration on crystal shape.

Hence although physical parameters probably play some part in determining crystal shape the overriding influence is obviously the concentration of crystal habit modifiers.

Nevertheless we chose our arbitrary laboratory crystallisation temperature to be not too dissimilar from factory boiling temperatures. False grain became a problem in pure solutions at S/W ratios greater than 3,075 or when turbine-stirred vessels such as that used by Smythe²⁷ were tried. Although such vessels offer the advantage of being readily water-jacketted so that temperature variations are minimal we had no success with this type of vessel. This was the main reason we chose to use a rotating wheel with attached vessels. The major disadvantage when working at temperatures in the region of 60°C was the poor heat transfer properties of the air bath. Consequently, even with a rigid experimental protocol, solution temperatures initially dropped by about 5 to 6°C, and although they recovered to within 1°C of working temperature in less than 20 minutes, the final temperature recovery was of the order of 1 to 1½ hours. This has two implications for growth rate experiments. In the first place it is impossible to measure true growth rates and only possible to compare rates under similar conditions. In the second place it is impossible to reproduce the temperature profile from one run to the next. Inevitably growth rates measured under these far from ideal conditions will show considerable variation with a tendency to overestimate rates and can only be used to indicate gross trends. The major advantage of this crystalliser is that it allows several different solutions to be compared at the same time under identical conditions.

It is generally conceded that habit modifiers retard growth in specific directions thus leading to a reduction in the overall growth rate. Hence potent habit modifiers are also probably potent growth rate retardants although rate retardants will not necessarily affect crystal habit. Growth rates are only comparable at the same degree of supersaturation. Broadfoot and Steindl¹ have indicated that solubility could affect the supersaturation by about 5% in the NS/W range used, but that with the accuracy associated with growth rate measurements it is reasonable to assume constant supersaturation for a particular molasses in this NS/W range. Rates were compared at constant S/W ratios. This means that measured rates include a solubility influence as well as a habit influence in addition to the previously mentioned temperature effect. Figure 3 illustrates the general pattern observed, ie as impurities increase the rate decreases. Comparison of Figures 2 and 3 indirectly confirms the observation that elongated crystals grow more slowly. For this particular combination of impurities and with equivalent conditions, boiling times would have increased about three fold if the crystals had a \bar{y}/z ratio of 0,6.

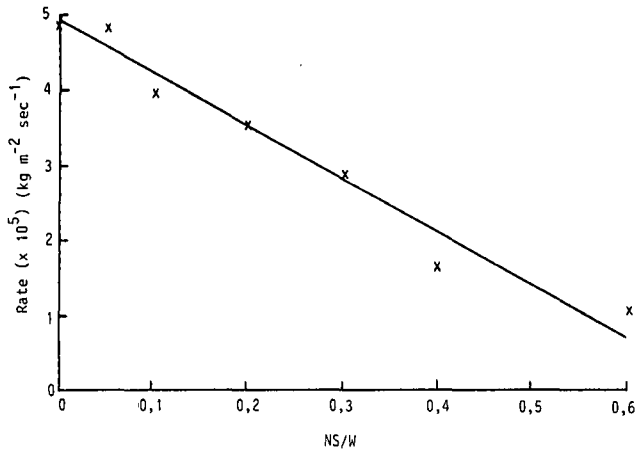


FIGURE 3 Effect of impurity concentration on crystal growth rate at 60°C and S/W = 3,075.

The data displayed in Figure 2 were found to fit a linear regression of the form:

$$\ln(\bar{y}/z) = -1,79 - 0,632 \times \ln(NS/W) \quad (r = 0,976).$$

Clearly the slope of this line will depend on the concentrations and potency of the habit modifiers present. We feel that this aspect may allow the distinction between synergistic and additive effects once responses have been established for the different components. At present, in the absence of the identity of these factors, all non-sucrose concentrations have been made equivalent to those of the original molasses by simple proportion on the basis of the yields of different component classes. Most further runs were carried out at a single NS/W level so that only direct comparisons are possible at this stage.

Overall recoveries after the various fractionations gave 90% for sucrose and 80% for non-sucrose, indicating the possibility of both physical and selective losses. However when the various fractions were recombined in proportion to actual yields it was obvious that there had been no significant loss of elongating properties (Table 2). It should be pointed out that these rsd's represent the variation of shape within a batch of crystals. The average batch to batch mean with molasses impurities at NS/W = 0,1 was $0,76 \pm 0,05$ (rsd = 7%) for ten batches.

TABLE 2

Crystal shape (\bar{y}/z) in reconstituted molasses (NS/W equivalent to 0,1 molasses impurities)

Combined fractions	\bar{y}/z	rsd (%)
Molasses	0,75	30
A + B	0,75	33
A + B1 + B2	0,75	32

The rate and shape measurements obtained with the individual fractions when added at levels equivalent to those in the starting molasses sample are summarised in Tables 3 and 4.

TABLE 3

Comparison of growth rates in various molasses fractions

Fraction	Rate ($\text{kg m}^{-2} \text{sec}^{-1}$) ($\times 10^5$)	
	Mean	sd
Sucrose	5,7	0,8
Molasses	3,1	0,3
A	6,5	0,4
B	4,2	0,3
B1	5,1	0,8
B2	2,2	0,3

TABLE 4

Comparison of crystal shape in various molasses fractions

Fraction	\bar{y}/z		
	Mean	sd	rsd (%)
Sucrose	1,85	0,50	27
Molasses	0,75	0,22	29
A	1,95	0,61	31
B	0,80	0,27	34
B1	1,70	0,47	28
B2	0,90	0,31	34

Clearly both the habit-modifying and rate-retarding properties are mainly in the oligosaccharide fraction with very little effect from the polysaccharides. Furthermore, the polysaccharide fraction (which contains approximately 50% dextran by the Roberts²² method) only slightly increases the elongation to give a (\bar{y}/z) ratio of 1,5 when added at five times the concentration found in molasses, ie the elongating properties are not very powerful. This is in agreement with the relatively small extent of elongation in the presence of standard dextrans (Table 5).

TABLE 5

Comparison of elongation with molasses polysaccharide and with standard dextran

Compound	NS/W*	\bar{y}/z	rsd (%)
Fraction A	0,007	1,60	28
Fraction A	0,035	1,55	23
Dextran (T-40)	0,033	1,70	36

* Fraction A at NS/W = 0,007 is equivalent to using unfractionated molasses at NS/W = 0,100

The main elongating effects have been isolated in the oligosaccharide fraction. The obvious possible components of this fraction include the iso-maltose homologues (as dextran anabolic or breakdown products), the maltose homologues (as amylose anabolic or breakdown products) and the fructosyl-sucrose or glucosyl-sucrose oligomers. Crude extracts of each of these classes were added to sucrose as though fraction B2 consisted entirely of each class. The results are presented in Table 6.

TABLE 6

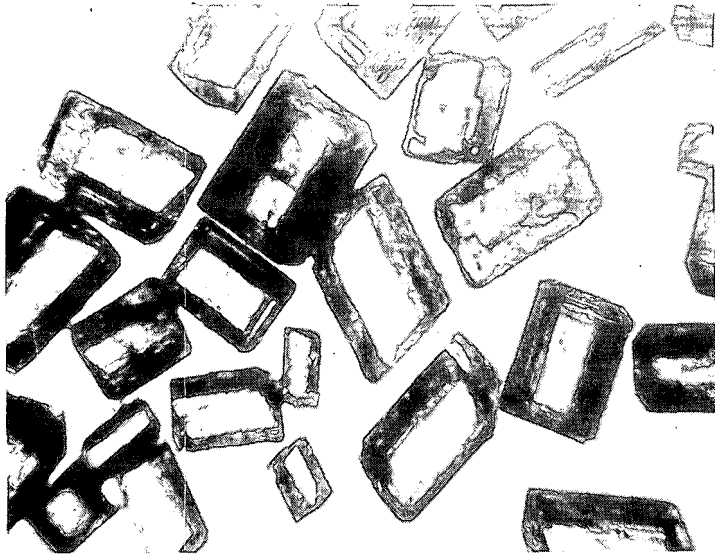
Effect of oligosaccharide classes on crystal elongation

Oligosaccharide	NS/W*	\bar{y}/z	
		Mean	rsd (%)
Sucrose	—	2,00	29
Fraction B2	0,013	0,90	41
Isomalto-series	0,014	1,75	33
Malto-series	0,014	1,80	30
F-S and G-S series†	0,014	2,05	32

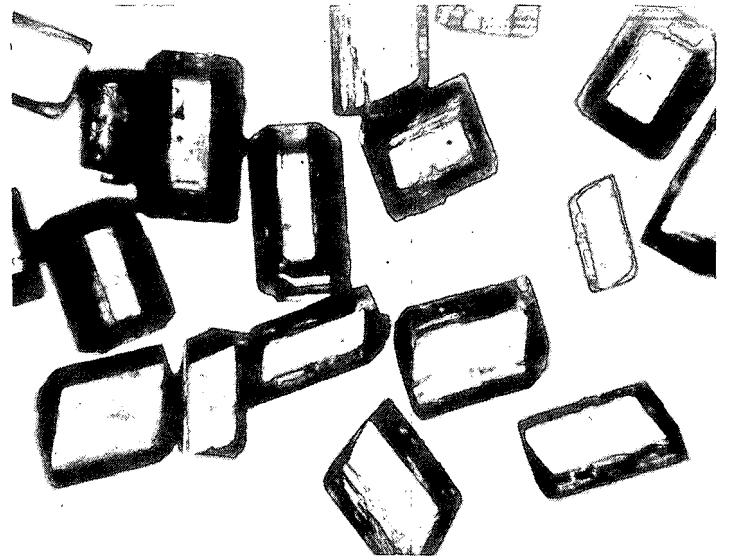
* Fraction B2 at NS/W = 0,013 is equivalent to using unfractionated molasses at NS/W = 0,100.

† F-S = fructosyl-sucroses, G-S = glucosyl-sucroses

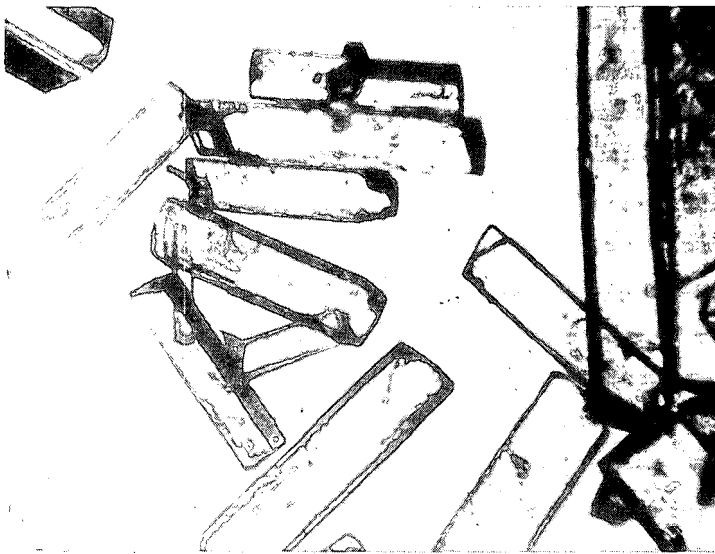
Only fraction B2 has any significant c-elongating effect. The shape of sucrose crystals grown in the presence of either malto- or isomalto-homologues is very little different from that of pure sucrose. The addition of oligosaccharides prepared from sucrose (probably mainly 6- and neo-kestose) causes slight b-axis elongation. Crystals grown in the presence of fraction B2 were not only extensively elongated in the c-direction, but were often small and extensively conglomerated. Moller,¹⁹ Pot²¹ and Kuijnhoven *et al*¹¹ have indicated that there is probably a critical interval of small particle size in which conglomeration takes place. The observed conglomeration may be induced because of the relatively long residence time in this crystal size range as a result of the slow growth rate. Typical shapes of these crystals are illustrated in Figure 4.



(a) Molasses at NS/W = 0,1



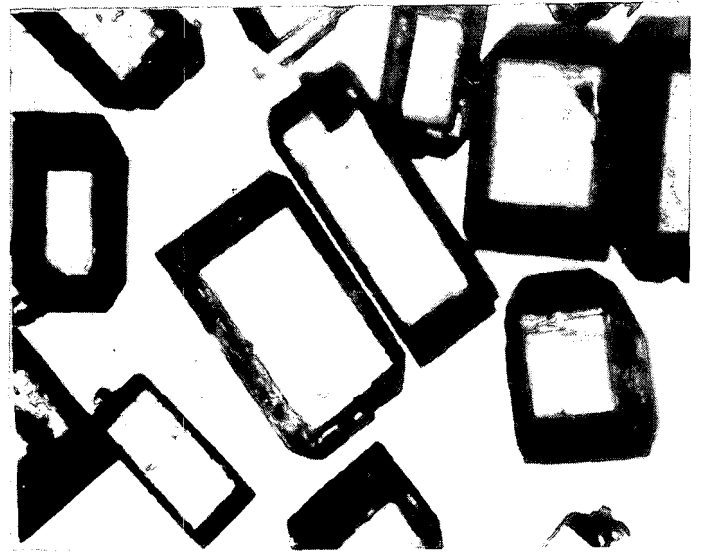
(d) Fraction B equivalent to NS/W = 0,1



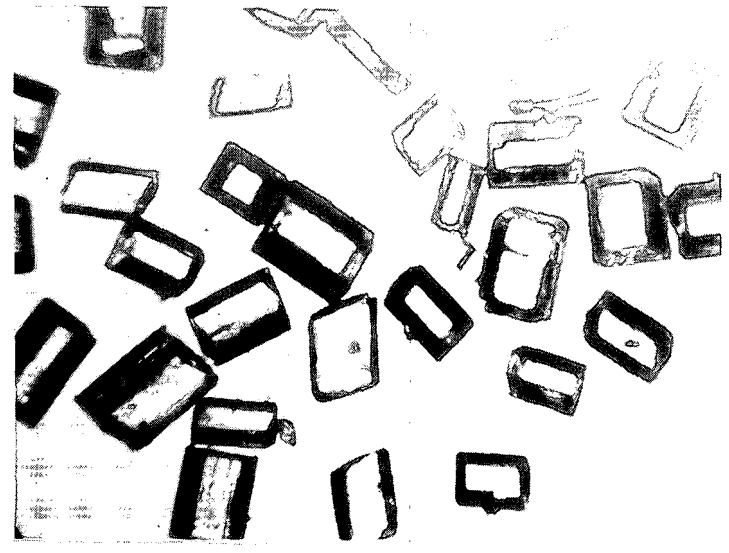
(b) Molasses at NS/W = 0,4



(e) Fraction B1 equivalent to NS/W = 0,1



(c) Fraction A equivalent to NS/W = 0,1



(f) Fraction B2 equivalent to NS/W = 0,1

FIGURE 4 Sucrose crystals grown in the laboratory from solutions with added molasses impurities:

Invertase hydrolysis of fraction B2 and of the kestose-preparation completely removed the elongating properties so that normal shaped crystals were obtained when sucrose solutions were spiked with these hydrolysates. The control showed minimal improvement in elongated morphology (Table 7).

TABLE 7
Influence of invertase hydrolysis on elongating properties

Preparation	$\bar{y/z}$	
	Mean	rsd (%)
F-S and G-S series	2.25	38
(F-S and G-S) after hydrolysis	1.80	30
B2	0.90	34
Control (B2 + buffer)	1.10	34
B2 after hydrolysis	1.95	29

Hence fructosyl-oligosaccharides were probably responsible for the extensive c-axis elongation observed in this refinery.

Conclusion

The extensive sucrose c-axis elongation observed in a refinery has been mainly attributed to the presence of fructose containing oligosaccharides. The polysaccharide components were found to exert little influence at the concentrations encountered.

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