

# SOME NOTES ON STARCH IN THE SUGAR INDUSTRY

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This paper is intended merely to give a survey of some of the preliminary work done on cane starch at the Sugar Milling Research Institute. It is hoped in the near future to obtain data that will give a more complete picture of the role played by starch in the S.A. Sugar Industry.

Starch was recognised as a separate entity many centuries ago, but it was not until recent decades, with the development of more refined methods of analysis, that much of the confusion in early literature has been satisfactorily elucidated. It is now generally accepted that all naturally occurring starches are a mixture of two main components, namely, amylose and amylopectin, both of which are polymers of glucose. Amylopectin has a higher molecular weight and viscosity than amylose, and is generally considered to have a branched chain linkage, while amylose has a straight chain structure. Amylopectin forms a paste with water and gives a red-violet colour with iodine, while amylose forms a true solution and gives an intense blue colour with iodine. Since the ratio of amylose to amylopectin varies in starches from different sources, the intensity of colour with iodine varies for starches from different plants. As a result, when a colorimetric method is used for the estimation of starch, it should be standardized against a pure starch from the same plant source.

Attempts were made at the S.M.R.I. to isolate pure cane starch from mixed juice. By centrifuging the juice, starch in the form of insoluble granules was removed, together with bagacillo and other insoluble matter. The mixture was washed with water, alcohol and acetone, and the starch granules were then separated by fractional settling in water. The starch was then extracted by boiling with a strong calcium chloride solution. The solubilised starch was precipitated by an excess of alcohol. By repeated precipitations a practically ash-free starch was obtained. However, during the course of purification, part of the starch could not be redissolved and the final product appeared not to give the same intensity of colour with iodine. This was thought to be due to retrogradation of some of the original starch. However, a later hydrolysis showed this "purified starch" to have a purity of only 85 per cent.

Owing to the difficulty of isolating pure cane starch, it was thought preferable to determine starch in cane products both colorimetrically and by another independent method on the same samples. The colorimetric method could thus be standardised in terms of cane starch. For convenience, "Baker's

Analyzed" soluble starch was used for the colorimetric method as a standard reference. The value obtained for a sample in terms of Baker's starch is multiplied by a factor to obtain the results in terms of cane starch. The intensities of colour with iodine for Baker's and cane starch were found in practice to be very nearly the same, so no corrections were made for the colorimetric method. However, it is not known whether different batches of Baker's starch will give the same intensity with iodine. Balch<sup>1</sup> used sweet potato starch as a standard and assumed it would give the same intensity of colour as cane starch. He admitted that this was unjustified. The comparatively rapid colorimetric method of Balch was slightly modified and compared with the rather laborious but specific method of Pucher, Leavenworth and Vickery<sup>2</sup>. A brief description of the analytical methods follows:—

*Mixed Juice.* To 100 ml. of well mixed juice is added 0.5 ml. of glacial acetic acid and 2 gm. of kieselguhr. The juice is filtered through a paper, precoated with 1 gm. of kieselguhr, fitted on a 5 cm. diam. Buchner funnel. The cake is washed free of juice with water, followed by 70 per cent. alcohol, hot absolute alcohol and hot benzol. The cake is transferred to a 250 ml. beaker with 40 ml. of CaCl<sub>2</sub> solution (S.G.1.3) and mixed thoroughly. The mixture is covered and kept boiling gently for 18 minutes to extract the starch, (extraction with perchloric acid was tried but found to yield lower results). The contents of the beaker are cooled to room temperature, transferred quantitatively to a 100 ml. volumetric flask and made up to volume. In addition 1.7 ml. of water is added to the flask to compensate for the volume occupied by the kieselguhr. The mixed contents from the flask are then centrifuged until a clear supernatant solution is obtained. An aliquot of the clear solution containing 0.5 to 3 mg. of starch is transferred to a 100 ml. volumetric flask and made up to approx. 50 ml. The following reagents are then added in sequence: 5 ml. 2N acetic acid, 1 ml. 10 per cent. KI and 10 ml. 0.01N KIO<sub>3</sub>. The volume is made up to mark and the optical density measured at 600 mμ in a 1 cm. cell. The amount of starch in the aliquot taken is then read off from a graph obtained by analysis of known amounts of starch, conducted in a similar manner.

For the determination by hydrolysis, an aliquot of the clear centrifuged solution, containing 5 to 40 mg. of starch, is pipetted into a centrifuge tube. To this is added 5 ml. of 0.3 per cent. iodine solution. After about 30 minutes, the precipitated starch iodine complex is centrifuged and washed in the centrifuge

tube with 20 ml. of an alcoholic sodium chloride solution, consisting of 350 ml. ethanol and 50 ml. of 20 per cent. aqueous sodium chloride diluted to 500 ml. with water. The starch-iodine complex is decomposed by the addition of 20 ml. of alcoholic sodium hydroxide solution, consisting of 350 ml. ethanol and 25 ml. of 5N NaOH diluted to 500 ml. Ample time is allowed for decomposition before the liberated starch is centrifuged and washed with 20 ml. of alcoholic sodium chloride as before. The starch is dissolved in about 15 ml. of 0.7N HCl and heated in a covered water bath in covered tubes for 2.5 hours. This hydrolysis converts the starch to glucose, which after neutralization of the solution with NaOH, is determined by the Luff-Schoorl method. The theoretical factor for converting glucose percentage to starch percentage is 0.90. However, since in practice hydrolysis may not be 100 per cent. complete, it is necessary to determine the factor under the conditions of hydrolysis, using a known amount of starch. Using Baker's starch, corrected for moisture and ash, an average value of 0.914 was obtained.

*Sugars:* 100 gm. of sugar are dissolved in 100 ml. of water and to the solution is added 20 ml. N HCl and 300 ml. of alcohol. After standing for at least an hour, the precipitated gums are filtered off, using a total of 3 gm. kieselguhr for filter aid, as in the case of mixed juice. The cake is washed thoroughly with alcohol and boiled with calcium chloride as in the preceding determination on mixed juice.

*Syrups and Molasses:* 5-10 gm. molasses (or 20-30 gm. syrup) are weighed accurately and diluted to about 50° brix. 2 ml. 1:1 HCl are added, after which an amount of absolute alcohol, amounting to 3 times the volume of the diluted molasses, is added. After standing for 1 hour, the precipitated gums are treated as in the preceding determination.

### Experimental Results

The samples of mixed-juice analysed, were obtained from canes grown at the research institute and milled by the experimental mill. All samples were milled 5 times and a quantity of cold imbibition water was used. Canes were approximately 3 years of age and were well topped before milling.

Syrup samples were composited over a period of 3 days and were sent by mills producing raw or government grade sugars. Starch on all syrup samples was determined by hydrolysis only and the results expressed as a percentage of solids by refractometer.

Sugar samples were weekly composite samples sent by mills to the S.M.R.I. in 1953.

Molasses samples, (except for the last two in table IV which were catch samples), were 3-monthly

composite samples. Starch in most samples of molasses appears to be in a retrograded form for it gives no colour directly with iodine solution.

TABLE I.  
Starch Content of Juice

Sample	Variety	Brix	Colorimetric, mg./litre	Hydrolysis, mg./litre
1	—	—	460	—
2	—	—	365	—
3	Co 301	17.5	221	243
4	N: Co 310	15.1	315	309
5	Co 331	13.5	157	157

TABLE II.  
Starch Content of Syrups

Sample	Starch per cent. Solids
AK	0.147
DL <sub>1</sub>	0.116
DL <sub>2</sub>	0.150
EN <sub>1</sub>	0.174
EN <sub>2</sub>	0.138
IL	0.158
UF	0.135
ZSM	0.163
SZ	0.188
UK	0.088
RN	0.072
DK	0.116
Average	0.137

TABLE III.  
Starch Content of Sugars

(a) Government and Raw Sugars

Sample No.	POL.	per cent. Colorimetrically	per cent. By Hydrolysis
EN <sub>39</sub>	98.0	0.106	0.095
DL <sub>X</sub>	—	0.040	0.044
UK <sub>4</sub>	99.0	0.027	0.031
ZM <sub>8</sub>	98.8	0.025	0.025
SZ <sub>13</sub>	—	0.036	0.035
CK <sub>8</sub>	98.6	0.063	0.060
DK <sub>13</sub>	—	0.054	0.047
RN <sub>1</sub>	97.8	0.060	0.061
MV <sub>8</sub>	98.2	0.033	0.033
TS <sub>8</sub>	98.4	0.069	0.066
AK <sub>R</sub>	98.6	0.026	0.027
Average		0.049	0.048

(b) *Mill White Sugars*

Sample No.	Colorimetrically per cent.	By Hydrolysis per cent.
TS <sub>18</sub>	0.070	0.063
MV <sub>22</sub>	0.024	0.021
EN <sub>14</sub>	0.012	0.012
AK <sub>9</sub>	0.030	0.029
DL <sub>C</sub>	0.022	0.024
RN <sub>C</sub>	0.024	0.029
SZ <sub>C</sub>	0.026	0.020
DK <sub>C</sub>	0.032	0.025
FX <sub>8</sub>	0.020	0.028
CK <sub>4</sub>	0.046	0.033
GL <sub>11</sub>	0.045	0.027
Average	0.031	0.028

(c) *Refined Sugars*

Sample No.	Colorimetrically per cent.	By Hydrolysis per cent.
H <sub>11</sub>	0.019	0.023
NE <sub>C</sub>	0.029	0.016
IL <sub>L</sub>	0.00	0.00

TABLE IV.

**Starch Content of Molasses**

Sample	Colorimetrically per cent.	By Hydrolysis per cent.
TS <sub>A</sub>	0.61	0.59
SZ <sub>A</sub>	0.37	0.32
DL <sub>A</sub>	0.55	0.62
UF <sub>A</sub>	0.35	0.37
DL <sub>B</sub>	0.41	0.41
TS <sub>B</sub>	0.70	0.68

The agreement between values obtained colorimetrically and by hydrolysis was fairly good in most cases. The 3 samples NE<sub>C</sub>, CK<sub>4</sub> and GL<sub>11</sub> are obvious exceptions. The figures obtained for these samples were confirmed by repeating analysis in duplicate. The discrepancies in these samples cannot be explained by the presence of dextrans, as no colouration was obtained in the iodine layer when the starch-iodine complex had been removed by centrifuging. It is suggested that possibly the proportion of amylose in these samples is higher than the others. This has yet to be investigated.

It is realized that the data obtained at this stage are too limited to draw definite conclusions, but it would appear that the starch content of S.A. sugar products must rank among the highest in the world.

Starch contents of juices analysed by Balch<sup>1</sup> in Louisiana show an average of 34 mg./litre for 26 samples. The highest figure recorded for any sample was 133 mg./litre which is less than the lowest figure in Table I. L. F. Martin<sup>3</sup> states, "The limit which might be tolerated and the extreme difficulties caused by amounts in excess of about 0.05 per cent. on cane are well known from practical experience with Uba cane in South Africa, and also attempts to produce sugar from sorgo". How the limit of 0.05 per cent. was obtained is not known as the literature gives very few quantitative data. However, it appears likely that some Natal canes may contain starch in excess of 0.05 per cent.

Starch in some mill-white and refined sugars must be regarded as a major impurity. All white sugars from other countries, examined for starch, showed no traces. Balch<sup>1</sup> in Louisiana gives analysis for 58 raw sugar samples. The average for these is only 0.0079 per cent.—well below our mill-white and even refined sugars. An interesting fact is that the per centage of starch from raw to refined sugar in S.A. shows very little drop as compared with ash or reducing sugar contents. Starch found in sugars cannot be accounted for by the starch in the film of adhering molasses and it is apparent that growing sugar crystals have an affinity for starch present in the mother liquor.

Although it is not known what objections, if any, can be raised against the presence of starch in consumption sugars, it is generally accepted that the presence of gums such as starch in raw sugars has an adverse effect on their refining qualities. It is evident that since starch is not concentrated only on the crystal surface, it cannot be removed by washing. Some correlation was found between starch contents of sugars and their filtration rates. Results using the small filtration apparatus available were, however, not reproducible.

Only one sample of the Natal sugars tested contained no starch. This can be attributed to the use by that factory of vegetable carbon, as the following experiment illustrates. Solutions of sugar of 55° brix containing starch were treated with various amounts of vegetable carbon at 80°C. for 30 minutes and were analysed with the following results:

Starch originally present in sugar	Vegetable carbon added to syrup per cent.	Starch finally present in sugar
475	0.1	400
436	0.2	255
436	0.3	116
436	0.4	53
475	0.5	0

The bone-char process and the carbonatation process of the other two refineries are evidently not effective in removing starch. It is interesting to note that in 1926 when E. Haddon focussed attention on the presence of starch in Natal canes (especially Uba), he apparently found the sugar from these latter two refineries to be free from starch.

The evils of starch in sugar manufacture have been mentioned by Haddon<sup>4</sup>, Feuillherade<sup>5</sup>, Balch<sup>1</sup>, Martin<sup>3</sup> and others, and since this has yet to be investigated, mention will only be made of the following effects of starch on sugar manufacture, which it is hoped will be investigated in the coming season:

- (a) Settling rate of clarified juices.
- (b) Increase in viscosity of liquors.
- (c) Crystallization rate of sucrose.
- (d) Filtration rate of sugars.
- (e) Polarizations.

#### Conclusion

The amounts of starch found in Natal sugar products is quite considerable.

It is anticipated that an investigation into the effects of starch on sugar-manufacture in Natal will be carried out in the coming season.

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#### LITERATURE CITED

- <sup>1</sup>Balch, R. T., *The Sugar Journal* 15, No. 8, 11-15 (1953).
- <sup>2</sup>Pucher, G. W., Leavenworth, C. S. and Vickery, H. B., *Anal. Chem.* 20, 850 (1948).
- <sup>3</sup>Martin, L. F., *The Principles of Sugar Technology*, Edit. P. Honig, 188-191.
- <sup>4</sup>Haddon, E., *S.A.S.J.* 10, No. 10 629-631 (1936).
- <sup>5</sup>Feuillherade, L., *S.A.S.J.* 13, No. 5, 305-309 (1929).

**The President** said he was very pleased that the Sugar Milling Research Institute and Mr. Alexander had taken up this very important question of starch in our juices. He himself had offered a paper ("Sucrose Irregularities") to a past Congress on this subject, which was not accepted for publication in our Proceedings. He was glad that the importance of starch was now being recognised, as he firmly believed that starch played a very important factor in the recovery of sugar from juices.

**Mr. Du Toit** congratulated Mr. Alexander on the splendid manner in which he had presented his paper. It was of great interest in this country.

He said that Mr. Alexander had more information on starch than he had given us in the paper and he wondered where starch was chiefly concentrated. Did it appear in the crusher juice or the juice from the last rollers. The amount of starch present in molasses was really very high and that might lead to wrong figures, where a direct polarisation only was used.

**Mr. Alexander** said that working back from figures on syrup showed 200 milligrams in clarified juice, which led him to believe that a lot of starch must be extracted by the mills. He was not, however, able to detail by which milling rollers this might be mostly extracted.

**Mr. Du Toit** said that at the Experiment Station he had carried out some tests but they were rather out of season. The Experiment Station would gladly let Mr. Alexander have samples of all the different cane varieties if he would like to study them.

**Dr. McMartin** pointed out that it was only sugarcane and a few other crops such as sugar-beet that stored excess food stuff in the form of sucrose, mostly it was stored as starch. He thought that a big field of investigation lay ahead, and much work would be required to be done. He asked if Uba had showed such high figures before.

**Mr. Alexander** replied that he hadn't any figures on Natal Uba which he could quote from the past.

**Dr. McMartin** said there might be a seasonal variation in the starch content of different varieties, there might even be differences during different times of the day.

**Mr. Rault** said that Mr. Alexander's findings indicated that vegetable carbon was the best remover of starch. He asked what was the state of dispersion of the starch in various juices and liquors, as he would have expected the thorough filtration given to thick juice and also remelted sugars, by the help of Kieselguhr in his factory would have removed the suspensoids in a fine state of dispersion. The use of filtercel was one of the means of eliminating thermophilic bacteria. His experience with filtrability of various raw sugars had also indicated that for an equal polarisation, the raws from carbonatation were far superior to others.

**Mr. Alexander** said that he did not think that starch could be removed by a filter aid if it was already in solution. It was made soluble by lime and heat.

**The President** asked Mr. Alexander if he had figures on a cold process, such as the A.P.C. process.

**Mr. Van der Pol** said that although he had done few tests he could not see that the A.P.C. process

was much more advantageous in the removal of starch.

**Mr. Carter** asked Mr. Alexander if he thought that there was any direct correlation between the amount of starch present in sugar and its turbidity.

**Mr. Alexander** reported that from the few tests he had done he thought that this was likely.

**Mr. Carter** said that many years ago when Mr. Haddon was carrying out experiments on starch in Uba juice he found much larger quantities of starch than what was found in canes to-day. Mr. Haddon had used an enzyme, "Ubase," in pans to hydrolyse starch.

**Mr. Alexander** thought that his tests indicated rather the other way round when compared with past records.

**Mr. Rault** thought that with a more thorough disintegration by shredders and the increasing percentage of extraneous fibrous matters sent to the factories, there was more chance of starchy products entering the factory and accordingly "cush-cush" straining should be very efficiently carried out. When pre-liming raw juice he had found that the pH had to be raised over 11.0 before clarity could be

reached. Under this high pH, juices looked murky with fine matters in suspension. He thought that the Oliver filter system and its introduction of bagacillo in contact with limed juice, would also be a cause of starch introduction in juice.

**The President** said that although starch in juice might lead to erroneous direct poliarisation, the Jackson and Gillis method No. 4 took care of any interference by starch. Quite a lot of molasses determination was still done by direct poliarisation method, in which case large errors must result.

**Mr. Du Toit** asked Dr. Douwes Dekker if starch did not persist in spite of the use of lead acetate, when working on raw juice.

**Mr. Walsh** said that relative to the effect of starches in sugar on filtrability he was told by someone from overseas that South African sugars were amongst the worst that they received. They had come to the conclusion that it must be due to the growing conditions under which our cane was produced.

**Dr. McMartin** said that in the past it had been proved difficult to produce seed from our canes because the pollen did not contain starch, due, apparently, to unsuitable climatic conditions.