STARCH IN UBA JUICES

By L. FEUILHERADE

The following paper on the above subject was read by Mr. L. Feuilherade:—

It is a known fact that juices from Uba cane are rather difficult to clarify and that the after products, i.e., syrup, massecuites, runnings, molasses, etc., are all very viscous.

At previous meetings these difficulties have been thoroughly discussed, and it was concluded that the difficulties encountered in the treatment of Uba juices were to be explained by the quality of impurities present and the form under which they exist rather than by the amount present, which coincides with the results we obtained.

The following facts are known:—

1. **Colouring matter** in the Uba is of minor importance, as there is only very little of these troublesome substances present, and is not worth mentioning when we compare the Uba to dark coloured varieties as Black Cheribon, Black Manila, Seedling 55, etc.

2. **Anthocyan** is absent.

3. **Tannins** which are present only in the actively vegetative portions of the cane are not to be found in abundance when the tops are removed with some care.

4. **Chlorophyll** is of little importance as it is insoluble in water and in sugar solution; it is thus easily removed during clarification and is eliminated with the scums.

5. When lime is added to pH 8.0., **Pectin** is precipitated in the form of calcium pectate.

6. **Pentosan,** one of the cane gums, is scarcely affected by lime alone, but is absorbed by the precipitates of calcium sulphite and carbonate.

7. There is a very high proportion of **wax** and **gums** in the Uba juice, and the cloudiness of certain clarified juices may be partly attributed to low phosphoric acid content. To obtain a clear clarified juice it seems that at least 0.030% P_2O_5 must be present in the juice. When phosphoric acid is added in sufficient quantity the wax is partly absorbed by the calcium phosphate together with many other colloids.

Yet, there is a colloid which escapes that treatment, and is to be found, partly in its elementary form and partly hydrolized, in the clarified juice, in all the stages of manufacture, and is finally shared between sugar and molasses. It cannot be removed by any ordinary clarification process, except partly by carbonatation and completely by filtration through a layer of kieselguhr (a patented process) or bone charcoal, but in the latter treatment the pores of the carbon are clogged very rapidly, and revivification of the charcoal is very difficult if not impossible on a practical scale. That colloid is **starch.**

PRESENCE IN THE CANE.

Starch is stored in all young canes and in the actively growing parts of the matured plant, i.e., tops, but is absent in the matured joints. In the Uba cane there is nearly always starch present. It is found not only in the upper part but throughout the cane, and sometimes it is more abundant in the lower matured joints and the nodes. The amount present is independent of the age of the cane, as in many cases we found more starch in old ratoons than in young plant cane. It has also no relation to purity or glucose quotient. To detect its presence in the cane, the cane is gently squeezed to remove the excess of juice, opened, and a dilute solution of iodine—about 1 gm. per litre dissolved with potassium iodide in water—spread on the fibre, which turns blue after a few seconds in the presence of starch. To classify the starch some pieces of a cane containing it were ground in a mortar with water, the liquid was separated and examined under a microscope. The shape of the granules of this starch being spherical and the size variable; the average diameter is about 5 microns, and the hilum is marked as a darker spot in the middle of the globule. It has

no resemblance to other species of starch and seems to form a separate class. As it lies in granules between the fibre it easily passes with the juice when crushing the cane, and when hot water is used for maceration the transference of the carbohydrate to the juice, which was only mechanical, is now a chemical action, as it is dissolved by the hot water and passes completely into the juice, while in the bagasse no traces are to be found. Thus when crushing a cane containing a high proportion of starch hot water must not be used for maceration, as the little gain in extraction and economy in fuel is surpassed several times by the amount lost in the subsequent steps of manufacture.

BEHAVIOUR DURING MANUFACTURE.

Mr. E. Haddon was the first to detect its presence in the juice and to observe its detrimental effects on manufacture. Since then we have had several opportunities to confirm the fact; on some occasions the massecuites in the pans would not grain, and when forced to grain by over concentrating, the grains would not absorb the syrup. In every case it was found that the amount of starch in the clarified juice had increased considerably during the preceding few hours due to canes coming from a different locality being crushed. The appearance of the cane was normal, the wax content did not appear to have varied, the clarification was the same as usual and the same amounts of chemicals were used.

Very often the clarified juice was tested for starch. The approximate method used is only comparative, and the colour test is carried out as follows:—From 10 to 15 c.cs. of clarified juice are placed in a 20 mm. test tube and very little acetic or sulphuric acid added to decolorize the juice and a few drops of iodine solution (4 grams. iodine in a solution of 12 grams. of potassium iodide per litre) run in so that the liquid just turns blue. If the iodine solution is added in excess the change of colour is difficult to observe as it is concealed by the colour of the iodine. The amount found varied from a slight blue coloration to a dark blue colour on applying the test. Every time we detected a large amount of that impurity we were sure to experience trouble during manufacture, difficult crystallization and filtration, viscous massecuites and high purity molasses being the result. When better canes were crushed everything became normal again.

Organic colloids are "emulsoids" or "hydrophiles," that is to say, a solution of "drops" of concentrated colloid solution—called disperse phase—in water, which is then termed "disperse medium." "Emulsoids" have a more pronounced influence on surface tension than "suspensoids," and, moreover, exert a protective action on other colloids. The measure of effective colloidal protective action, called "Gold Number," is very difficult to determine in cane products on account of the darker colour of these products. It is a pity that no accurate method is available for the measure of the "Gold Number" in juices as very useful data would have been derived from it, proving very beneficial to manufacture and rendering the chemist's task easier. Emulsoids do not affect yields from a strictly melassigenic standpoint—except when in large proportion—but the increase in viscosity may result in decrease in yield and increase in molasses formed on account of the limited time available. The quality of the sugar is also influenced unfavourably by them.

Starch is present in the juice as an emulsoid. As said above, sulpho-defecation is of no use to remove starch not even when phosphoric acid is added. Experiments were performed using large amounts of lime and phosphoric acid, working at different pH without perceptible elimination of this colloid. No doubt that by escaping precipitation and remaining in the clarified juice, starch conveys with it colloids—which, under ordinary circumstances, would have subsided—by exerting over them its protective influence. Crystallization is hindered by starch on account of adsorption, a property possessed by stable collids by which they prevent the formation of crystals.

During the process some of the starch is hydrolized to **dextrins.** These dextrins increase viscosity which, although scarcely remarked at the early stage, become quite notable when the juice has been concentrated since the amount of colloids per cent. volume of material has thus been increased considerably. It is obvious that boiling and crystallization will become difficult and will require much attention, whilst separation of the crystals will be a tedious task and will require a very large capacity in centrifugals.

SUGAR FROM UBA CANE CONTAINS STARCH.

A certain amount of starch and dextrins is retained in the sugar no matter whether the sugar has been washed and steamed or is merely raw. In certain cases the amount is such that it is not necessary to add any starch, for the determination of sulphurous acid in white sugar by titration against iodine as the blue colour obtained is deep enough to indicate that the final point has been reached. In other cases the amount is small, and in solution there is scarcely any change of colour visible on applying the test. In such cases the sample is poured gently along the sides of the tube. After being in contact with the sugar for several minutes the characteristic starch iodide formed is visible as a bluish ring just above the sugar. There is no doubt that a sugar containing a lagre amount of starch is bound to give trouble in refineries as the pores of the charcoal will be clogged and filtration will be hampered.

PRESENCE IN MOLASSES CAUSES ERROR IN ANALYSIS.

The remainder of dextrins and starch are found in the molasses which are generally viscous enough to denote the presence of an abnormal impurity as the amount of wax present is not large enough to account by itself for such a high viscosity. An error is introduced in the analysis of molasses containing these substances in large proportion as these dextrins which have different dextro- rotatory powers before and after inversion are not removed by ordinary lead clarification, they are only precipitated by adding ammonia to the liquid in which the lead acetate has been added in slight excess. The presence of dextrins is ascertained by decomposing the ammoniacal precipitate with oxalic acid, filtering and treating the filtrate with a few drops of iodine. A reddish brown colour will indicate dextrins. (E. Haddon, Revue Agricole de l'Ile Maurice, November/December, 1928, page 269. The method of analysis to correct the error due to dextrins is also described in that paper, and I suggest using that method in conjunction with the ordinary methods of analysis to see if the same difference is obtained on all the factories.)

ELIMINATION OF STARCH.

Two methods available at present for the elimination of starch: filtration of the clarified juice through a layer of kieselguhr or the reduction of starch and dextrins into glucose. Both methods have been patented by Mr. E. Haddon (Revue Agricole, March/April, 1928, page 80.) In the last method a powerful enzyme, called "Ubase," is used for liquefying starch. Besides the elimination of these impurities, it has the advantage of promoting crystallization by increasing the ratio of reducing sugars in the molasses which contains so little glucose generally in Natal. Experiments were performed at Umfolozi both in the mill and in the laboratory giving good results. The difference in viscosity between ordinary and treated massecuites was obvious and in the sugar from the treated massecuites no starch was found.

This method of transforming starch into glucose gives an opportunity of determining the amount of the polysaccharide in the juice as otherwise it is a very difficult task on account of all the impurities present. The method consists of determining as exactly as possible the amount of reducing sugar in the clarified juice by means of Fehling's solution, then another portion of the juice is heated to 70°C. and treated with the enzyme for about twenty minutes or half-an-hour. Reducing sugars are again determined and the difference between the two figures obtained multiplied by 0.9 (0.512 starch corresponds to 0.569 glucose) gives the amount of starch per litre of juice.

It is to be hoped that a fair trial will be given to these patents at the beginning of the season as I am sure that many benefits for the Sugar Industry of this country growing as it does only Uba cane, can be derived from them. There is still much to be learned about starch, and it is not during the two years since its presence has been known, that the strange behaviour of this impurtiy could be mastered. Many experiments can be performed in the laboratory but, unfortunately, the chemist is always over busy with the working of the factory and has very little time available to devote to these experiments. Anyhow, let us trust that at the next meeting more data will have been gathered by different colleagues and that some definite conclusions will be reached.

Chairman: We are very glad to have Mr. Feuilherade with us at this meeting. This matter was mentioned at the Congress last year and reference was made to the recently published articles on the subject in the local Sugar Press. But, unfortunately, neither Mr. Haddon nor Mr. Feuilherade could be present with us on that occasion, and the matter was postponed. I am glad that Mr. Feuilherade is with us to-day and has read to us this very interesting paper. The sugar juice is a very complex substance. The non-sugars are very numerous and varied in quantity and quality, especially as regards the colloid portion of them. When we are dealing with a substance such as glucose which in spite of its varied chemical activities is at all events a distinct chemical individual, we are dealing with a very different problem to that of the group of substances to which we give the name of starch. I say a group of substances because I think there is no doubt that starch cannot be regarded as a chemical individual; there are a large number of closely allied substances all of very obscure constitution chemically, and an immense field is opened up for research by this paper. Undoubtedly starch, or, at all events, substances which will give a blue coloration with iodine, is present in Uba cane at all stages of its growth, especially in its immature stage, but that is not characteristic of Uba cane because it can be found in other thin canes. In the case of thick canes, such as Badila and a few others we tried at the Experiment Station, the presence of starch shown by the blue coloration was much less marked or even entirely absent. This paper opens up a big field, and we should be very glad to have further discussion.

Mr. McRae: We are all very pleased to have this paper from Mr. Feuilherade, but I was rather surprised the other day to see in the "International Sugar Journal" that someone in Java had actually

patented a process for clarification by adding starch to the cane juices. (Laughter.) This was published in the January issue of the "Sugar Journal." (Reads.) It is rather interesting that we should get two such opposite views on the action of starch in this matter. There is another thing I should like Mr. Feuilherade to explain. You will remember when the papers first appeared on Ubase it was stated that Ubase would liquefy 400 times its weight of starch in 13 minutes, and the other day Mr. Haddon published a paper in the "Agricultural Review" of Mauritius, and he stated there that he required 0.09 grammes of Ubase per litre, which worked out to only 30 times the weight in starch it is going to convert, and that it is going to take five to six hours.

Mr. Feuilherade: The experiments were carried out on the sludge instead of on the clarified juice. He thought it would be more suitable to do that.

Chairman: What evidence is there that the Ubase which you mention hydrolizes starch to the exclusion of other carbo-hydrates? Are you quite satisfied that the Ubase would not hydrolize anything but starch?

Mr. Feuilherade: Before using it for the determination of starch we first experimented on glucose, sucrose and all the substances present generally in the cane juice. We did not find any influence at all on those. Of course there are many substances in the cane juice on which we did not experiment.

Mr. de Froberville: There is certainly a substance which occurs in the sugars in general, because when I have tested on a good many occasions raw sugar for $S.O_2$ by the iodine method and correcting by thiosulphate, I never used to put any starch at all in the solution; there was enough blue coloration after being treated with iodine and the hypo. Generally you put a few drops of starch to obtain the blue colour, but it was quite unnecessary in these instances; the solution was blue enough just at the end point of titration to give you the right end point. This proves there must be something, if not starch, then something which gives a blue colour with iodine.

Mr. Dymond: Is there anything secret in the production of this Ubase? Enzymes are a very complicated sort of thing, and to pick on an enzyme which will attack solely starch is quite an event, and we would like to know how Mr. Haddon evolved this enzyme which attacks one thing only in cane juice.

Mr. Feuilherade: I am sorry I cannot answer that as Mr. Haddon is the only one who can deal with that.

Dr. Hedley: Has this been tried on a large scale? The only secret I know is the price? It is a tremendous price.

Mr. Feuilherade: Yes, it is very dear.

Dr. Hedley: I spoke to the agents in this country and they told me they only get about 6d. a pound reduction even if they took a large quantity. They said they did not feel inclined to go in for it unless they could sell a very large quantity of it. The keiselguhr method appears to be much more hopeful.

Mr. Feuilherade: Apart from the price, Mr. Haddon has to pay a very high duty on the Ubase. It is considered as a drug, but I think if more work was done with it in the country it would be considered as a raw material for the sugar industry.

Chairman: It would be very interesting if we could have the composition of Ubase to know where it differs from ordinary diastase of starch, for example.

Mr. Jacobs: I went into this question of Ubase to see if we could carry out some experiments. I found on Mr. Haddon's recommendations that we would need something like over a ton of this a week. As the price was something like £2,000 a ton it was rather prohibitive. I think the keiselguhr method is a more hopeful one.

Mr. Feuilherade: The amount of Ubase used is only a very small quantity indeed. (Refers to figures.)

Mr. Jacobs: But that would work out to quite a considerable quantity when treating all your juices.

Chairman: It is very desirable that more work should be done in this matter of determination of starch in sugar-house products, and to get some collective information on the subject to supplement the valuable work that has been carried out at Umfolozi which we very much appreciate.

At 5.25 p.m. the Conference was adjourned to 10 a.m. the folliwing day.