RESEARCHES ON UTILISATION OF CANE MOLASSES.

PART III. A dry solid product from cane molasses and its possible technical applications.

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One of the most serious difficulties that stand in the way of more extensive utilisation of cane molasses is its physical condition. The product that is turned out from most sugar factories is a thick, viscous mass, readily absorbing moisture and consequently very inconvenient to handle. Several attempts have been made, therefore, to convert molasses into a solid product that will keep dry and can be easily transported. Among these, mention may be made of direct evaporation under reduced pressure which yields a dark, glass-hard product. This keeps well in air-tight containers, but readily absorbs moisture and reverts to the liquid condition on exposure to even moderately humid air. Except for some slight advantage arising from its compactness, solidified molasses has practically all the defects of the ordinary liquid product. Other methods involve either some form of chemical treatment or admixture with certain plant materials with or without subsequent drying. Most of these are either expensive or otherwise unsatisfactory. Thus, treatment with sulphuric acid for manufacture of fertiliser is effective but fairly expensive (Dubinbaun and Christie, *Int. Sug. Jour.*, 1936, **38**, 440). The product is acid and requires to be neutralised or otherwise suitably admixed with buffering materials prior to application to land. Treating liquid molasses with limestone (Reiner, *Int. Sug. Jour.*, 1935, **37**, 239) does not yield a solid product, at any rate, one that will keep well. Admixture with plant materials (Wemer and Gould, *Int. Sug. Jour.*, 1925, **27**, 676; Wilkins, Reiner and others, *Ibid.*, 1925, **27**, 116; Maclachlan, *Ibid.*, 1933, **35**, 452) yields thicker products, but they are generally sticky and hygroscopic.

More recently, (Sen and Dutt, *Proc. Sugar Convention*, *Cawnpore*, October 1937) some biological methods have been devised for converting molasses into solid materials, but the final products are very different from the original molasses and can be used only for certain specific purposes.

It is largely owing to these difficulties that molasses cannot be transported over long distances (except at considerable cost) or utilised so widely as it otherwise deserves to be. The present enquiry was undertaken therefore with the object of preparing a stable, solid product which can be used for similar purposes and in nearly the same manner as the original molasses.

Principle.—It is well known that slaking of lime in water or aqueous solutions is accompanied by abstraction of water and much evolution of heat. It is also recognised that sugars (especially sucrose) can combine with lime to form sparingly soluble compounds which are also fairly stable. Both of these reactions are utilised in the present method.

That molasses can react with lime to yield plastic materials is well known. Methods have also been devised to utilise this reaction for recovery of cane sugar after precipitating it as a sparingly soluble calcium salt. There is no record, however, of any attempt to combine both slaking and reaction with sugar in one single operation.

Preliminary experiments.—These were carried out in small dishes or glazed earthenware pots. Liquid molasses (obtained through the courtesy of The Mysore Sugar Company) was treated with aqueous suspensions of slaked lime in varying proportions and the resulting suspensions allowed to stand for some time.

It was found that when the proportion of lime (as $Ca(OH)_2$) was at least of the order 1 to 5 of molasses, the product set to a thick mass which could be easily dried by gentle heating. In the absence of heating, the products (especially when the proportion of lime was low) remained wet and sticky for long periods.

With a view to obviating the need for evaporating the water in the lime suspension, some experiments were carried out adding burnt lime directly to liquid molasses and stirring up the mixture to work into a homogeneous paste. This resulted in more vigorous reaction accompanied by considerable evolution of heat. The product set readily to a solid which could be easily powdered on cooling.

Experiments in shallow enclosures.—Portions of Cuddappah slab flooring were partitioned into small squares ($2\frac{1}{2}$ ft. × $2\frac{1}{2}$ ft.) with brick and cement embankments rising up to a height of about 9″. Different batches of liquid molasses about (30 lbs. in each case) were first weighed and transferred to the enclosures. They were then treated with freshly burnt lime in varying proportions. The lime was added in small instalments at a time, the mixing being done with a wooden ladle or a metallic trowel. The mixing was done as thoroughly as possible and the resulting thick, viscous paste then left undisturbed for about 15 minutes.

It was noted that there was rather slow rise in temperature up to about 60°C. After that stage, there was very rapid rise, the boiling temperature being attained in a few minutes.

The boiling was preceded by considerable swelling, the entire mass rising to more than double its original volume. The thick paste became more or less liquid, thus facilitating easy stirring.

The boiling lasted only for about 15 minutes. After that period, the entire mass set to a brittle, solid product. Though generally brownish in colour, it was dotted all over with white crystals of calcium sucrate.

The cooled product could be immediately powdered. Quite satisfactory results were obtained when the ratio of burnt lime (locally available product) to molasses was as 1 : 3. At lower proportions of lime, the product did not set readily to the solid condition, while, at higher proportions, the product contained excessive amount of unattacked lime. In the latter case, the initial mixing was also found to be very difficult.

The success of the reaction depends to a very large extent on the quality of lime used for the purpose. Not only should it be as pure as possible but it should also be freshly burnt. Old lime, though carefully preserved, slakes only slowly so that there is very little rise in temperature. The protective layers of calcium-sucrate are soon formed around unattacked lime (especially when it is in the form of small lumps), thus preventing further action. In such cases, the product does not set to a solid condition even after standing for several days.

If the lime is pure and freshly burnt, less than one-sixth of the weight of the molasses would be sufficient for the complete reaction. Even partial mixing in the earlier stages will then be sufficient to start the initial boiling, after which further stirring can be easily carried out. The hot and swollen mass offers very little resistance and can be easily mixed up to attain the desired homogeneity.

Shell lime is generally much superior to burnt limestone, but cannot be easily obtained in most inland towns. If quarried lime has to be used, it may be desirable to first ascertain its composition and even conduct a few preliminary trials before using it on a large scale.

After standing for some time (say, one or two days) the dried product offers some resistance to grinding, so it would be advantageous to powder it as soon as possible after it sets to a solid. The coarse lumps which are first formed, break up quite readily and can be easily powdered by the commoner equipment (disintegrator, ball mill, edgerunner, "KEK" mill or any other grinding machine) available for the purpose.

Properties of the dried product.—In the powdered condition, the solid product can be stored indefinitely (some of our original samples have already stood for over 18 months in open containers and have not so far undergone any change). They can be easily packed in bags or other containers and can be transported over long distances. The only precaution to be observed is that direct contact with water should be avoided, as in that case, the powder tends to form hard and sticky lumps which cannot be easily broken.

On being properly mixed with water, the powder works into a homogeneous paste which sets hard on standing. The hardened mass then dries slowly without cracking. The resulting product is somewhat brittle, but can be strengthened by suitable fillers.

On shaking with excess of water, the product yields a uniform suspension which is initially alkaline in reaction. On standing for some time, however, the product undergoes the same type of fermentation as the original molasses, yielding acid products. The reaction then turns first neutral and finally acid. Similar changes are observed on adding the powdered product to moist soil.

The product has a high nitrogen fixing capacity. 200 mg. of powder added to 10g. of local soil fixed 1.8 mg. of nitrogen in the course of 12 days, which was about 2½ times as much as that obtained with molasses alone.*

Yield and composition of the dried product.—Starting with liquid molasses (100 parts) and the locally available burnt lime (33 parts; it contained only about 50 per cent. calcium oxide) a yield of 120 to 125 parts of the dry solid product was obtained. At other proportions (1 : 6 to 1 : 1) the corresponding yields ranged from about 110 to 190 parts depending on the quantity of lime used. This would show that about 10 per cent. of the weight of the molasses (accounted mostly by evaporation of water) was lost during the preparation. The proximate composition of the product (when the ratio of molasses to lime was 1 : 3) was as follows :—

Chemical composition of the product.

Item		Percentage
Moisture	....	4.5
Carbonate carbon	....	0.7
Organic carbon	....	23.5
Nitrogen	....	0.3
Calcium (as CaO)	....	26.2
Potassium (as K_2O)	....	3.5
Phosphorus (as P_2O_5)	....	0.8

* Study of the subsequent changes has shown that a considerable part of the fixed nitrogen is lost after sometime. The significance of this will be considered in a later communication.

Technical Applications of the Dry Product.

Use as Fertiliser.—Molasses contains a considerable part of the soluble minerals removed by the cane or beet (as the case may be) from the soil. It also contains a high percentage of sugar which can readily ferment increasing the availability of plant nutrients already present in the soil. The sugars also facilitate fixation of atmospheric nitrogen as has been shown by a number of workers both in India and abroad. It has thus all the potential qualities of a good fertiliser.

Application of liquid molasses to land offers, however, a number of practical difficulties. In the first place, its physical condition is such that it will have to be carried in special types of carts and applied to land by regulating the flow through taps. By this method molasses accumulates in high concentrations in restricted areas from which it cannot be easily spread to other portions. A further difficulty arises through the copious formation of free organic acids and allied products in the earlier stages of fermentation. The immediate products of fermentation are highly toxic to plant growth. Owing to uneven distribution of molasses, there is the danger of the toxic products accumulating in high concentrations in certain patches so that the land has to be rested for considerable lengths of time before it can become ready for sowing or transplanting as the case may be.

The dry product obviates the above mentioned defects. It requires no special conveyance and can be easily applied to land in the same manner as any other fertiliser. Being finely divided it gets easily distributed. Its decomposition in the soil proceeds smoothly and rapidly and is completed in a shorter time than would be the case with the original molasses. The association of lime adds to the fertilising value of the new product. In addition to improving the physical condition of soil, lime also assists in neutralising the acid products of the fermentation of molasses in the soil. As has been pointed out before, it also facilitates nitrogen fixation. It would thus be seen that the new product is very much superior to the original molasses.

The product is however somewhat defective in phosphoric acid, but this can be made up by combining the product with a small percentage of crushed bone or powdered rock phosphate. A still cheaper way of making up the deficiency would be to mix the product with press-mud (from sugar factory) which is quite rich in phosphoric acid.

Application in Fermentation Industries.—The association with lime would render the product eminently suitable for acetic, lactic, citric and other types of industrial acid fermentations. The mild alkalinity of the medium will prevent the accumulation of free acid which would otherwise retard the fermentation. The formation of other side products will also be prevented by the presence of lime. It would thus appear that the product has immense possibilities in the fermentation industry—in technical acid fermentation such as those for the manufacture of acetic, lactic, citric, and other acids.

Utilisation in the Plastic Industry.—Another direction in which the dry product may find considerable practical application is the plastic industry. In this line there is a great deal of work still awaiting to be carried out. It may be mentioned, however, that, on treatment with water, the product turns into a pasty mass, which steadily increases in viscosity, eventually thickening to a strong, stony hard product. This property can be utilised in making a number of articles of utility and value. In fact, there is very considerable demand in this direction and it is expected that the product will form a very useful addition (in many cases even a substitute) for the more expensive natural as well as synthetic resins in a number of industries. As an instance of this may be mentioned the possibility of making dolls and toys for which there is a very large market. A number of other uses can also be suggested, and in this direction, systematic work will be needed to standardise the conditions for pressing and curing the finished product, the type of fillers to be used and the inclusion of materials to improve the heat resistance and electrical insulating properties.

Road Surfacing.—On being applied as a paste, the product works well with road-surfacing materials and will thus prove quite useful in that direction. The procedure for applying it would consist in distributing it either as the powder or as a watery paste made together with rubble and other binding materials. On being rolled in the usual way, the entire mass sets hard and presents a smooth, strong surface which can stand all kinds of heavy vehicular traffic. While being superior to the original molasses, it is not entirely water-proof, so it would be desirable to combine it with some other non-washable materials. In this connection, the possible combination of the product with concrete or asphalt would be worth careful consideration. Attention may also be drawn to the recent work of Sen and Dutt who have shown that by suitable combination of lime, molasses and asphalt, a cheap and durable road surfacing material can be obtained.

Use as Adhesives :—Preliminary experiments have already shown that the product will be very useful as spreader-adhesive for insecticidal and fungicidal sprays. The resulting spray is not completely water resistant but holds better than the untreated one.

Possible utilisation in the recovery of cane sugar :—The mode of separation of the lime compound during the preparation and the comparatively low water solubility of one of the compounds formed with cane sugar would suggest that, if the conditions of preparation and subsequent treatment can be suitably regulated, it should be possible to recover the cane sugar from the new product. The first step in the process would be the conversion of cane sugar into the least soluble lime compound followed by its separation from the associated materials. Glucose, fructose, caramel, soluble salts and other undesirable components can be separated by taking advantage of their greater solubility in water. The cane sugar compound together with some carbonate of lime would be left behind. On suspending the residual solid in water and bubbling in carbon dioxide, it may be expected that free cane sugar will pass into solution accompanied by the separation of the carbonate of lime as the precipitate. The sugar solution which may be separated by filtration can be subsequently concentrated in the usual way. The possibilities of this process have already been demonstrated by workers in America and elsewhere through direct addition of milk of lime to molasses. The new product may also be expected to behave in the same manner, and as this aspect of the application would perhaps be the best way of utilising molasses, it will be extremely important to pursue this line of enquiry. It may be pointed out that recovery of cane sugar is probably the most desirable form of utilising molasses and even a partial success in this direction would go a long way towards strengthening the sugar industry.

Cost of production.—The cost of making the product will depend largely on the price that is placed on the molasses (now remaining largely unused) and the rate at which burnt lime is available in any particular locality. It is expected, however, that in most places it will work out to less than Rs. 10/- per ton. Judging from its chemical composition and its possible technical applications, the value of the dry product (as compared with other materials used for similar purposes) may be rated at about Rs. 20/- per ton.

SUMMARY.

A simple method of preparing a solid product by direct combination of burnt lime with cane molasses has been described. The procedure consists in adding freshly burnt lime in suitable proportion (1 : 6 to 1 : 3 depending on the quality of lime and nature of the product required) to liquid molasses as turned out from the centrifugal. The lime is added in small quantities at a time and thoroughly incorporated. After some time, there is rapid rise in temperature and the entire mass boils with copious evolution of heat. On cooling, the product sets to a solid mass which can be easily ground to fine powder.

Starting with 100 parts of liquid molasses and 33 parts of burnt lime, between 120 to 125 parts of dry product are obtained. There is only about 10 per cent. loss and that is mostly due to evaporation of water. The final product keeps well in all weathers, even in open containers. It can be stored in bags or transported over long distances. Its physical properties and chemical behaviour have been described.

The possible applications of the product (1) as a fertiliser, preferably after admixture with press-mud, (2) in plastic industries either by

itself or in association with other binders, (3) as a spreader-adhesive for insecticidal and fungicidal sprays, (4) for road-surfacing, preferably in combination with some water resisting materials, (5) in different industrial acid fermentations and (6) for the recovery of cane sugar, have been discussed.

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