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The use of cassava starch in the artisanal production of maltose

L'utilisation de l'amidon de manioc pour la production artisanale de maltose

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- Abstract -

This paper describes the sweeteners available to the food industry and compares their availability in developed and developing countries. A simple artisanal technology currently being used in cottage industries in Vietnam for producing maltose from cassava starch, using very simple processing equipment and whole rice or maize seedlings as the only source of enzymes, is described. While the potential of this process in developing countries is recognised, possibilities for development of the process to make it even more widely useful, are discussed.

- Résumé -

Cet article décrit les édulcorants utilisables en industrie alimentaire et compare leur disponibilité dans les pays développés et les pays en développement.

Une technologie simple et couramment utilisée à l'échelle artisanale ou semi-industrielle au Vietnam, est décrite : elle permet de produire du maltose à partir de l'amidon de manioc en utilisant des équipements simples et des plantules de riz ou de maïs comme seules sources d'enzymes.

Partant du fait que les potentialités de cette transformation dans les pays en développement sont reconnues, les possibilités de son développement pour qu'elle soit de plus en plus utilisée sont discutées.

Introduction

In most developed countries, a large and diverse range of sweeteners is available to food manufacturers. These sweeteners can be broadly divided into two groups, sweeteners that are carbohydrates and those that are not. The latter group is rather less important than the former and includes:

- naturally occurring high sweetness proteins, which are generally extracted from plants (stevioside, glycyrrhizin, thaumatin);
- hydrogenised carbohydrates such as sorbitol ;
- synthetics (e.g. saccharin, cyclamates, aspartame).

The main use of these sweeteners is in dietetic formulations. Most of them provide a great deal of sweetness (some of them are several thousand times as sweet as sugar) with very few calories and their major market is in developed countries.

1. Sweeteners that are carbohydrates

The more important of the two groups of sweeteners contains substances which have the general formula $C_m(H_2O)_n$. As this is carbon, hydrogen and oxygen in the same proportions as in hydrated (wetted) carbon, these substances are collectively called "carbohydrates". Many carbohydrates occur naturally. Carbohydrates that taste sweet are generically known as sugars. Many carbohydrates do not taste sweet and are not sugars: formaldehyde, a poisonous, pungent smelling liquid with the formula CH_2O, acetic acid $(CH_2O)_2$, starches and cellulose are some of the many exceptions.

Sugars are often classified in terms of the number of monosaccharide molecules, of the general formula $(CH_2O)_5$ or $(CH_2O)_6$ from which they are made up. The smaller molecules have all the characteristics of sugars - particularly a sweet taste. As the molecule gets larger, it becomes less and less like a typical "sugar", in terms of its solubility, its ability to crystallise and most important of all, of its sweetness. Oligo-saccharides (containing a small number of mono-saccharide molecules) only have a little sweetness. The higher poly-saccharides, which contain a large number of monosaccharide molecules hardly taste sweet at all.

Among the wide range of carbohydrate sweeteners are:

- sucrose, also known as cane or beet sugar.
- sucrose-based sugars such as inverted or partially inverted syrup,
- speciality natural sugars - such as maple syrup
- lactose, fructose and other naturally occurring mono-saccharides
- a range of sweeteners derived from starch, including:
- glucose - often in a crystallised form,

- glucose syrup - a viscous solution containing a mixture of several polymers of glucose
- maltose (made from two glucose molecules)
- high fructose syrup, analogous to inverted sucrose
- low dextrose equivalent[1] syrups, used, for example in making ice-cream.

A carbohydrate made up of more than one monosaccharide molecule can often be split quite easily into its constituent monosaccharides. As a molecule of water is taken up at every position where the polysaccharide is split, the process of splitting is known as hydrolysis. Hydrolysis can be achieved either by the use of acids or by the use of naturally occurring substances called enzymes.

Glucose (also called dextrose) is the building-block of nature. It is a monosaccharide with 6 carbon atoms, with the formula $C_6H_{12}O_6$ - or $(CH_2O)_6$. Starch is made from thousands of glucose molecules mostly joined end to end. Cellulose is made up of similarly large numbers of glucose molecules but they are joined together in a rather different way and the bonds between them are not easily hydrolysed. Sucrose (which is also known as cane or beet sugar) is commercially the most common sugar. It is a di-saccharide consisting of a glucose molecule joined to fructose, another monosaccharide.

The relative sweetness of a substance is measured using a widely recognised "sweetness" scale, based on the ill-defined sensation of sweetness that it gives. Sucrose is used as the standard of sweetness and is given a value of 100. Glucose is between 60 and 70 on this scale. Maltose, a di-saccharide consisting of two glucose molecules joined together, rates about 40 on the scale. Maltotriose (three glucose molecules) is rather less sweet than maltose.

A range of sweeteners based on glucose polymers can be produced by hydrolysing starch. The bonds between the glucose molecules in starch can be broken either by acid at high temperature or by the use of amylases. Amylases are enzymes that exist widely in nature, in animals, bacteria, fungi and plants. There are two main groups of amylases, known as alpha amylases and beta amylases. Alpha amylases randomly break the bonds between glucose molecules, producing oligosaccharides (dextrins) and a thin starch paste. Beta amylases cut off pairs of glucose molecules (i.e. producing maltose) until they reach a branch in the chain, at which stage they stop working, leaving limit dextrins. In nature, these amylases usually occur as a mixture, which is called a diastase.

The conventional manufacture of starch based sweeteners is best done as a downstream operation in a conventional starch plant, where starch slurry is taken straight from the starch process and converted to glucose in a separate part of the same plant. In this way common services can be used, particularly laboratory

(1) Dextrose equivalent (DE) is a percentage measure of the extent of hydrolysis of a starch paste. Unhydrolysed starch paste has a DE of zero. If the starch were to be completely hydrolysed it would become pure glucose (dextrose) which has a DE of 100. The higher the DE of a syrup is, the sweeter it is likely to be.

facilities and the use of steam. The cost of drying the starch is also avoided. The manufacture of hydrolysis products of starch involves the use of high pressures, high temperatures, vacuum evaporation, sophisticated control systems and sophisticated enzymes (which are almost exclusively produced in developed countries). The level of technical expertise that is needed is quite high. However, this type of operation can produce very high quality products which can be used in a very wide range of sweetening applications.

2. The choice of sweeteners and mixtures of sweeteners

Different sweeteners provide different types of sweetness or taste, different amounts of "body" or "mouth feel" and different amounts of sweetness. Some of the naturally occurring non-sugar sweeteners are thousands of times sweeter than sugar. Thus, there are sweeteners which have widely different calorific values for a given amount of sweetness, a very important factor in formulating foods used in diets. Most sweeteners enhance the sweetness of other sweeteners with which they are mixed, a effect known as synergism. Sucrose has a tendency to crystallise, which is objectionable in some products (for example in jams and clear boiled sweets) but if other sweeteners are present in significant amounts, the likelihood of sucrose crystallising is very much reduced and may be eliminated altogether. With the range of products available, the food manufacturer in a developed country has great scope to tailor his sweetening additives to suit his particular requirements.

3. Sweeteners currently available in developing countries

In contrast to the availability of many different sweeteners in developed countries, food manufacturers in most developing countries have access to only a very restricted range of sweeteners. They often even find it difficult to get sufficient cane sugar - and what there is is often very expensive. Sugar is only processed at central factories, usually on a large scale. In many developing countries, sugar factories are inefficiently run and frequently produce a poor quality product. Refined sugar often has to be imported. Although it is quite possible to produce crystalline sugar on a relatively small scale, the process is comparatively inefficient. The work in small scale factories is laborious and the wages these factories can pay are low. Research and development is urgently needed to improve the efficiency of this process, making it possible for factory owners to pay better wages to their employees.

In most developing countries, starch based sweeteners are usually even more difficult to obtain than sugar and all non-sucrose sweeteners have to be imported. The problems of making starch based sweeteners using conventional technology are similar to those of making sugar, but the economic justification for carrying out this operation in developing countries is usually even poorer than it is for sugar. Highly specialised technical staff are needed to run the process efficiently. Such people are expensive and are not always easy to find. As good quality starch is needed to get a good quality product, if the glucose plant is not part of a sophisticated starch factory, it may even be necessary to import the starch. It is just not economical to carry out the conventional process on a small scale and few developing countries have the demand to warrant the installation of a factory to make both starch and glucose. This is unfortunate, as any local production of sweeteners will almost certainly allow savings in foreign exchange. It also leaves the food processor in these countries with little choice of which sweetener he should use.

However, an artisanal process for making sweeteners from starch has been developed and has been used for perhaps 30 years in some countries in South East Asia. The existence in Vietnam of this low technology industry for making maltose from cassava starch has only recently been reported by Quach (1990; 1991) in the western press. Li *et al.* (1991) reported variations of the technique used in Vietnam being used in China. The process as carried out in Vietnam makes use of the amylases in rice seedlings to break down starch to produce sugars. During recent trials, it was confirmed that maize seedlings can be used instead of rice - thus whichever of these cereals is cheaper or more easily obtained can be used.

The Vietnamese process for making maltose, using elementary equipment in very small artisanal factories, has now been assessed. In June 1994, the cost in Vietnam of one of these artisanal factories was estimated as US$ 500. It is hoped that by publishing a manual about this potentially valuable process, FAO can give it much wider prominence so that food processors in developing countries will have access to a wider choice of sweeteners.

4. The artisanal production of maltose from starch

In the process carried out in Vietnam, paddy rice was germinated and allowed to sprout. Most of the main crop varieties grown in Vietnam have been used, although some are better than others. After about 10 days, when the seedlings are about 10 cm long and the main root about 6 cm long, they are ready for use. Alternatively, they can be dried for later use. The whole plant (shoots, seed and roots) is used. If the seedlings are to be used fresh, they are chopped up (or pounded in a pestle and mortar) just before they are needed. At the factories which were studied, only fresh seedlings were being used. If dried seedlings are to be used (some people believe that dried seedlings give a better product) half the quantities indicated below for fresh seedlings are needed.

Two batches of 40 kg of wet starch were each mixed with 10 litres of water heated to 60°C, to produce a slurry. The starch contained about 45% moisture - it was much as it comes out of a settling basin in an artisanal starch factory. If dry starch had been used, 25 kg of it would have been slurried with 25 litres of water. 4 kg of chopped rice seedlings were then added to each batch and mixed in. The starch was badly fermented, and half a litre of water saturated with $Ca(OH)_2$ (lime) was also added, to raise the pH. 120 litres of boiling water was then mixed (with constant stirring) with one of the batches of slurry. The starch became gelatinised, but as the enzymes in the rice thinned the paste very quickly, it never became thick. Within a minute it was fluid - barely thicker than water. This mixture was then heated to boiling and similarly mixed with the second batch of slurry and rice seedlings. As with the first batch, the second batch quickly became thin. The drum containing the liquid was covered, both to exclude bees and other insects and to retain the heat. After 3 hours or so, when the temperature had fallen to 62°C, another 8 kg of chopped rice seedlings were added and stirred. Once again the drum was covered and conversion was allowed to proceed.

The temperatures in the process are quite important - if the liquids are too hot, the enzymes that convert the starch into maltose may be inactivated and if they are allowed to get too cool, the activity of the enzymes will be reduced. It has been found by experience that if the quantities indicated above are used, the temperature will remain high enough for conversion normally to be complete within 7 or 8 hours.

After 7 or 8 hours all the starch had been converted into maltose and the liquid was clear and still quite hot. At this stage a simple test should routinely be made for the presence of starch - a drop of this maltose "juice" in a dilute iodine solution should show no blueness.

The juice was then boiled briefly and filtered to remove the rice seedlings. The juice can be boiled and filtered as soon as conversion is complete, but it is often convenient to leave the liquid overnight: once all the starch has been hydrolysed to maltose, no further hydrolysis will occur. The used seedlings were pressed to squeeze out excess juice, then washed to remove more of the sugars. The residual material was thrown away, but it can be used for animal feed, or can be dried and burned. The sugars in the press water and the wash water were recovered by using these liquors instead of some of the water at the beginning of the process.

To investigate the possibility of saving fuel and thereby reducing costs, tests were run in which quite concentrated juice was used in place of the water at the begining of the process. In one run, the "water" that was used contained over 20% by weight of sugars. Making 1 kg of syrup from juice that contained 40% of solids (as was done in this test run) requires less than half as much fuel as is needed to make 1 kg from juice which contained the more normal 23% of solids. It may be possible to use even more concentrated juice and save even more fuel. If the solids content of the juice were to be 50% just prior to evaporation, only a quarter as much fuel would be needed.

The filtered juice was evaporated in an open pan, in much the same way as sugar juice is evaporated to make panela, shakkar, jaggery or gur. To minimise problems of foaming, a squat basketwork "chimney" was tied down in the pan. This chimney was about 60 cm high and about 2/3 of the diameter of the pan. Foaming juice rises inside the chimney and overflows down the outside, increasing the surface area from which evaporation can occur. In most countries where sugar juice is evaporated, animal or vegetable fats or oils are used to control foaming. In the Vietnamese maltose industry, because of the widespread use of these chimneys, very little anti-foaming oil needs to be used.

At first, the temperature rises very slowly indeed, but it rises increasingly quickly as evaporation proceeds and in the latter stages of boiling, it rises so quickly that it is best to reduce the heat produced by the furnace. Shortly before boiling is complete, a little metabisulphite or hydrosulphite is added to lighten the syrup. It is a matter of experience to know exactly when boiling should be terminated, but the signs are easily learned. Drops of syrup fall off a test stick in a particular way - almost forming threads of sugar. The point at which boiling should be terminated can also be recognised by the boiling temperature -boiling should be terminated when the temperature reaches 111°C. On cooling, the maltose syrup will become very viscous and almost (but not quite) solid.

The chemical analysis of the resulting syrup probably varies somewhat from factory to factory and from batch to batch. The presence of alpha amylase in cereal diastase means that there will always be some glucose present, but the major constituent will usually be maltose, with a significant amount of maltotriose (made up of three glucose molecules) which is the normal by-product obtained when starch is enzymatically converted to maltose using beta amylase. Syrups prepared in Vietnam in June 1994 contained 60% maltose, 16% glucose and 24% of higher polymers.

5. Future development

There are several areas of research that FAO would like to see being pursued, that might increase the utilisation of sweeteners which can be made from cassava and other sources of starch in artisanal processes.

5.1. The use of different sources of starch.

It is probable that any starch can be used to produce maltose. The purer the starch, the lighter the colour of the product is likely to be. Impurities, particularly protein, can produce coloured substances which will make the product darker. Li *et al.* (1991) report the use in China of whole sweet potatoes as the source of starch for the production of maltose. However, the product has to be filtered several times and activated carbon is usually used to lighten it. Whole cassava flour (made from pulverised dried chips) is sometimes used in Vietnam in place of cassava starch. The maltose produced from cassava flour is rather darker than that produced from cassava starch. Any cyanide that may have remained in the cassava flour does not obviously reduce the activity of the rice amylases. Using commercial enzymes, Van Wyk *et al.* (1978) produced glucose from green bananas. They made no mention of the quality of the glucose they produced.

5.2. Increasing the sweetness of the syrup.

An artisanal process to produce glucose rather than maltose might be a valuable extension of the process. Glucose is sweeter than maltose, but a syrup which contains more glucose would contribute less "body" in the final product. Alpha amylases produce glucose, while beta amylases produce maltose (Shaw and Chuang, 1982) so the glucose level in the product might be increased either by protecting the existing alpha amylase from thermal damage or by using a supplementary source of alpha amylase. An attempt to hydrolyse some maltose by boiling the juice with a little vinegar was unsuccessful.

Most of the published data on the effect of temperature on rice amylases refers to alpha amylases: there is little information on the beta amylases found in rice. Most rice alpha amylases work best below 50°C and are destroyed at 70°C. Above a certain temperature amylases begin to become deactivated. Numokawa and Funaba (1980) found that at 65°C, rice alpha amylase activity was lost within a minute. Shaw and Chuang (1982) found the optimal temperature for one relatively heat stable rice alpha amylase they studied was 60°C. While there is little information in the literature on the thermal destruction of rice beta amylases, the fact that the maltose process works very well, even though the temperature is frequently well over 65°C, suggests that the beta amylases found in rice are much less affected by heat than the alpha amylases found in rice. The success of the factory trial using maize seedlings suggests that the beta amylases found in maize are also fairly stable. At the end of the process, just before the juice is boiled for filtering, the temperature may be within the range in which rice alpha amylases will work efficiently. The addition of a third batch of seedlings at this stage (or delaying adding the second batch until the temperature is lower) might be effective in hydrolysing more of the maltose to glucose.

5.3. Alternative sources of enzymes.

Amylases suitable for carrying out the process occur in a number of plants, but for countries where rice is expensive or not readily available, the most suitable alternative sources are likely to be other germinating cereals. Maize seedlings were successfully used in preparing a batch of maltose in an artisanal factory in Vietnam. Barley malt is a possible source and this is reportedly what is used in China for converting whole sweet potatoes to maltose. Sorghums - particularly red sorghum - are used commercially in Southern Africa as sources of amylases, but sprouting sorghum contains large amounts of cyanide (far higher levels than those that are present in cassava) and before sorghum is used to convert starch to maltose, it must be established that enough of the cyanide is boiled off during the evaporation stage of the process to make a product that is safe to eat. A trial run in Vietnam using sweet potato shoots and cassava starch produced a very dark juice, but sweet potatoes, particularly varieties with a relatively high amylase content might be investigated further as possible sources of amylases.

5.4. Minimising the quantity of cereal required.

Ways should be tried to minimise the quantity of seeds that are used - both because of the cost of the cereal and because the addition of dissolved materials will darken the product. The optimal stage of seedling development should therefore be established. Shaw and Chuang (1982) found rice amylases reached maximum activity after 8 days, but the time needed to reach maximum activity will vary between varieties.

6. The potential uses of maltose in developing countries

While the main use of maltose in the West is as a highly fermentable constituent used in the brewing industry, maltose can also be used in a wide range of foods. It is not as sweet as sugar, but it synergistically augments the sweetness of sugar, reduces its tendency to crystallise and gives an excellent "body" to foods in which it is incorporated. In Vietnam, it is used in partial replacement of sugar in the production of jams, candies, biscuits, biscuit fillings and cakes.

The production of maltose may be profitable in many developing countries, particularly where the price of sugar is significantly higher than that of starch (which is often available as a by-product from making other products from cassava) or where sugar is not readily available. It may be considered as a way of supplementing the use of sugar in the manufacture of a range of products, particularly in factories that use relatively large amounts of sugar. Most important of all, it may prove to be a way of adding value to the product range of even quite small manufacturing operations that make starch from cassava or other crops.

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