Chapter 2 Literature review

2.1 Confectionery

Types of confectionery

It is common to classify confectionery into three main categories depending on the method of manufacture.

1. Hard Confectioneries (Hard boiled Candy)

These are essentially based on sugar. A water solution of sugar is boiled in an open pan or under vacuum until the desired consistency is reached. During the cooling stage, additives such as colorants, flavorings and other optional ingredients or additives are added, and the mass is poured into moulds. Those that are directly moulded give clear hard candies with a minimum of moisture. In some instances the concentrate syrup after pouring on a tray are pulled or kneaded before the desired shape is given; in this process the product absorbs moisture to a very high level.

2. Medium Hard Confectioneries (Chewy Candy)

These contain sugar, glucose and other ingredients that are usually boiled to a high temperature and a low moisture content. They contain colorants, flavorings, fat, emulsifying agents and modifying agents, and could also contain farinaceous substances. These can be pulled, cast or cut to the desired shape. Some special varieties can include fruits or nuts.

3. Soft Confectioneries (Toffee)

In composition soft candies resemble hard candies, except for a high level of moisture content that imparts flexibility and softness to the product. In some compositions milk is substituted for water, while butter is added as a modifier in certain special varieties. Colorants, flavorings, fruits, nuts or vegetable products are also added for variety in formulation. Softer varieties may also contain corn syrup, gelatin, egg white, etc. Different textures of the product can be obtained by suitable combinations.

2.2 Soft candy (Toffee)

2.2.1 Ingredients of toffee (Jackson, 1990)

The basic ingredients of toffees and fudge are sugar, glucose syrup, milk protein, fat, salt and water.

2.2.1.1 Sugar

Sugar, apart from providing sweetness, creates a structure in toffee which helps to prevent cold flow. Being a disaccharide it does not introduce as much chewiness or toughness as glucose syrup due to the absence of high molecular weight sugars, and it is less liable to create stickiness than the monosaccharide sugars such as invert sugar and dextrose. However the most common defect of toffees is crystallization of sugar or graining during storage, and therefore it cannot be used in excess.

Most authorities seem to agree that the optimum ratio of sugar to non-crystallising sugars in a toffee is 1.1 to 1, and it should be noted that this is the total of sugar and non-crystallising sugars from all sources of raw materials, including sugar from condensed milk or non-crystallising sugar arising from inversion during processing. Dextrose, of course, does crystallise, but in this context the concentration

is too low for crystallisation to occur and non-crystallising sugars may be regarded as all the carbohydrates other than sugar.

At one time various brown sugars were used extensively in toffees for the characteristic flavor they introduced, and although they are still used they are frequently sticky and not suitable for bulk handling. Larger manufacturers these days frequently use granulated sugar with the addition of small quantities of golden syrup, molasses or blended refinery syrups to stimulate the flavor of brown sugars.

Most brown sugars and all the syrups contain a proportion of invert sugar, but, unless some specific requirement such as a need for low viscosity makes it desirable, invert sugar is rarely added to toffee formulations.

2.2.1.2 Glucose syrup

A wide variety of glucose syrups are available for use in toffees, and although their properties vary considerably all have the same effect on sugar solubility. The main effects however are to modify texture and sweetness.

The usual glucose syrup for toffee production is 42-DE (Dextrose equivalent) acid-converted glucose. Apart from retarding sugar crystallization, the reducing sugars, dextrose and maltose, take part in the Maillard reaction with milk protein to develop the color and flavor of toffee. The higher molecular weight sugars in glucose syrups help to give some body and chewiness to the sweet, which many be desirable, but they also introduce some increase of viscosity and toughness. If this should be a problem, very high-maltose syrups with much lower content of high molecular weight sugars can be used and are desirable if high glucose levels are required. This is likely to arise where high temperature conditions during storage give rise to graining problems in the distribution chain.

High-DE glucose syrup can be used to increase sweetness and degree of caramelisation or to reduce viscosity or equilibrium relative humidity (ERH). Although they may be used in toffee for depositing into chocolate shells or layering on biscuits, they are more likely to be used in fudge than conventional wrapped toffees.

Low-DE glucose will reduce sweetness and caramelisation, but increase viscosity, chewiness and toughness. They are useful when increase in chewiness is required. For some purposes the maltodextrins can be used in a similar manner, and since the effect is more pronounced much smaller quantities are required.

Very rarely however will a factory have many varieties of glucose syrup available, and in any case, with premix systems supplying several production line, premix recipe modification for each product may not be acceptable. In these cases the addition of dextrose or a maltodextrin on a single production line to modify carbohydrate composition may be a more acceptable approach.

2.2.1.3 Milk protein

The normal source of milk protein in toffees is sweetened condensed milk. Fresh milk, apart from creating storage problems, contains far too much water, and the excessive boiling required to evaporate off this water leads to coagulation of the protein and roughening of the texture. This may not be wholly due to the boiling, as under some conditions evaporated milk can give the same effect, and it is possible that the protein is affected by the water activity of the solution.

It is possible to reconstitute milk powder into sweetened condensed milk but it is very difficult to eliminate traces of grittiness from undispersed milk particles. Unless suitable homogenizing equipment is available, it is doubtful if this operation is worthwhile.

The functional of milk protein in toffee is complex. Apart from the reaction with reducing sugars to provide the characteristic flavor and color, which is apparently specific to milk protein, it also stabilizes the emulsion of fat in the sugar phase and possibly binds some of the water.

Whey protein and hydrolysed whey protein are frequently offered as alternatives to whole milk for toffee processing. The whey protein in whole milk has very little effect on caramelization because of the relatively small quantity present, and this is largely due to casein. Whey proteins however do caramelize and produce a very similar flavor to casein. The main difference lies in the viscosity of the toffee, which is much more fluid. This also results in poor resistance to cold flow, and the toffees can be distort badly after wrapping.

Hydrolysed whey is whey containing hydrolysed lactose or dextrose and galactose. These sugars, being monosaccharides and reducing sugars, give more caramelisation than glucose syrup, lower viscosity and a different flavor from traditional ingredients.

These factors tend to restrict the use of whey, particularly for replacement of milk in established products, but for products which are not established and are, for example, covered in chocolate, where flow is less of a problem, whey proteins represent an alternative option to condensed milk.

2.2.1.4 Fat

Apart from butter, the fats used in toffees are invariably vegetable fats. Years ago hardened palm kernel oil (HPKO) was almost universal, but due to wide price fluctuation it has in many cases been replaced by other fat blends which may contain partially hydrogenated palm, soya, groundnut, rapeseed and other oils.

HPKO is a lauric fat which is characterised by a narrow melting range and brittle texture. The other oils are non-lauric, and although hydrogenated to the same slip point they have a wider melting range and are not as brittle as the lauric fats.

Fats for toffees and fudge are desirably almost solid at ambient temperature, and this includes storage of sweets in shops during the summer months. The fat however must melt virtually completely at blood heart, since high melting components tend to form a greasy coating in the mouth which is quite unpleasant. This defines the slip point, which must be about 40° C.

The other requirement is resistance to oxidation, which is normally provided by the degree of hydrogenation required to provide a satisfactory melting point. Oxidative rancidity produces off-flavors of a tallowy nature, and it is catalysed by metals, particularly copper and iron. Toffees have been produced in copper pans for many years and oxidative rancidity is not normally a problem. The reason is probably that the emulsification of the fat into the syrup occurs rapidly and contact of the fat globules with the copper is minimal.

Fats can also suffer from lypolytic rancidity, caused by fat-splitting enzymes, frequently derived from other ingredients which have been subjected at some stage to mould growth, although the presence of mould may no longer be apparent. With

lauric fats, lipolytic rancidity is associated with soapy flavors, and although non-lauric fats give less objectionable taints the same care is required. Whilst some ingredients have from time to time been responsible for lipase infection of products, mould growth in any part of the factory, particularly in obscure corners or inaccessible places, must be guarded against. One very prevalent source used to be the unhygienic practice of using damp cloths to moisten the surface of product or clean working surfaces during processing.

Larger manufacturers will be receiving fats as liquid in tankers and storing in heated tanks. Since hot fats are more readily oxidized, the temperature of storage should be maintained at the minimum required to permit handling.

Solid fats have a longer shelf life, but where stocks are held they should be used in rotation and kept as cool as possible.

Butter is frequently used in toffees, mainly for its flavor. It is sometimes said to be an integral part of toffee flavor, and rancid butter is stated to produce better flavor. Whilst butter may modify the flavor it is not an essential part of Maillard reaction and many toffee contain butter. The use of rancid butter is not a desirable practice since it is an uncontrolled ingredient, but enzyme-modified butter fat that is available commercially is a standardized product and fulfils the same purpose. If butter is added to a toffee recipe before emulsification it mixes with the vegetable fat and reduces the overall melting point. If butter is added at the end of the cook, as it frequently is, it is an interesting question as whether it actually mixes with the emulsified vegetable fat. If it does not this could be a factor that this method of processing gives a better butter flavor.

2.2.1.5 Salt

Whilst salt is not essential in a toffee, it undoubtedly has a very beneficial effect as a flavor modifier, and toffees tend to be rather insipid without it. Normal levels of usage are about 0.5%.

2.2.1.6 Water

Water is frequently ignored as an ingredient in confectionery, and consequently its use is sometimes not controlled as accurately as it should be. Although it has no effect on color and flavor, it undoubtedly has a major influence on processing and is certainly a factor in texture. In toffees high water levels are not required, and many manufacturers do not add additional water, relying on that contained in the ingredients.

2.2.1.7 Other ingredients

It is possible to produce toffees with no additional emulsifier other than the milk protein, but many manufacturers do use emulsifiers. These are usually soya lecithin or glyceryl monostearate. The purpose of emulsifiers is to stabilise the fat distribution within the sugar mass, because with high-fat-content toffees the manipulation of plastic masses, can squeeze out fat, leading to risk of surface oxidation and unsightly appearance. For this reason, and also to maintain a good fat distribution, which lubricates the cutting knifes, emulsifiers are more frequently used in comparing processing step toffees.

Other additives which may be used to reduce the tendency of toffee to cold flow are modified starches and gelatin. The modified starches are usually high in amylopectin and are derived from waxy maize varieties. Whilst these additives will reduce cold flow, they will almost certainly increase viscosity.

2.2.2 Chemical reactions during confectionery production (Jackson, 1990)

There are three primary chemical reactions taking place during the manufacture of sugar confections and a number of secondary reactions depending on composition.

2.2.2.1 Caramelization

Cane or beet sugar (sucrose) deteriorates in heat conditions to form colored breakdown products in the process known as caramelization. This also takes place when minor traces of acidic impurities are present together with traces of fructose (laevulose). The resultant product is 5-hydroxyl methyl furfural which develops browning in a sugar syrup.

2.2.2.2 Inversion

The reaction can be induced deliberately as a mean of developing desirable characteristics in sweetmeat. An example is when significant quantities of invert sugar are required in a syrup phase to produce a flowing eating texture. Invert sugar is also produced by a process design where it is added to a recipe or developed during cooking as a whole or part replacement for glucose syrup. Finally the reaction can occur accidentally by the presence of trace acidic materials inducing breakdown during processing.

Invert sugar is a mixture of two simpler sugars dextrose and fructose. One hundred grams of sucrose will yield 105 g of invert sugar when treated in the presence of water, and the resultant mixture will contain 52.5 g of glucose and 52.5 g of fructose. It is believed that the early products from the action of invertase, an enzyme commonly used to convert sucrose into invert sugar, are not a 50:50 mixture. An intermediate stage takes place in which a form of fructose predominates in a two-thirds to one-third ratio. This stage is quickly overcome and the expected equal-part mixture of the two sugars is formed.

Invertase is used in sugar confectionery products such as the centre of coated creams to soften these types of sweets whilst they are held on store and before their sell to consumers.

The presence of high levels of invert sugar can result in problems due to the hygroscopic nature of the comparatively high levels of fructose produced by inversion, which will attract water from the atmosphere under adverse environmental conditions. An indicator of the hygroscopic character is given by the level of reducing sugars in a confection. Typically the reducing sugar content reported for a confection is a combination of those parts of the components of glucose syrup which have reducing properties, lactose, any added dextrose, invert sugar solids and any other sugar component with similar properties. Reducing sugar contents for a range of a confectionery products are given in Table 2.1.

The rate of hydrolysis by acid on sucrose during inversion is more than one thousand times the rate experienced with other disaccharide materials such as lactose or maltose, although these substances contain similar chemical linkages. Although only one form of fructose is produced during the breakdown process, two crystalline forms of glucose with different optical properties are produced.

Table 2.1 Typical reducing sugar contents found in sugar confectionery product

Typical range for reducing sugar content	Type of products
(%)	9
3.0-4.9	Paste work
5.0-9.9	Cream paste fudge
10.0-14.9	Butter confections
	Chewing gum
	Gelatin jellies
	Pectin jellies
15.0-19.9	Caramel and toffees
	Hard creams
	High-boiled sweets
	Turkish delight
20.0-25.0	Butterscoth (traditional)
	Marshmallow
	Soft creams

Source: Jackson (1990)

2.2.2.3 Maillard reaction

The third chemical reaction encountered during the manufacture of sweetmeats is the Maillard reaction. This takes place between the amino group present in amino acids, proteins and peptides and the so-called 'glycosidic' hydroxyl groups (reducing groups) in sugars. The reaction products are brown condensation pigments known as melanoidins, which contribute flavor, color and texture. The process is not fully understood, although it is suspected that there are a number of step in the reaction before the final products are formed.

The Maillard reaction occurs during the roasting of cacoa and when milk protein is held under heat in the presence of reducing sugars. The latter conditions apply in the manufacture of caramels, toffee and fudge. The reaction stimulates the development of flavor, the creation of the desirable texture and produces an improvement in handling properties.

Hydrolyzed whey syrups have a greater ability to undergo the Maillard reaction, improving color and flavor. However, lactitol does not take part in this reaction due to the structural changes which take place on hydrogenating lactose.

It was suggested that in manufacture of products where the Maillard reaction is not a desirable feature, enzymic treatment can be used to reduce the degree of browning, but only at the expense of the removal of glucose. At the same time, enzymic methods are used for the removal of oxygen to prevent rancidity of products on prolonged storage.

2.2.2.4 Secondary reactions

Other chemical reactions occurring during sweet manufacture involve the breakdown of protein in gelling agents such as egg albumin. These usually occur under the presence of heat and are accelerated under acid conditions.

2.2.3 Structure of toffee (Jackson, 1990)

Toffee is an emulsion of fat in an aqueous system, but the nature of the aqueous system is complex and not completely understood. It is a mixture of sugars, water and protein which is very resistant to crystallization. This can be interpreted as implying a moisture-binding capacity of glucose solids. If this binding capacity is exceeded, graining once initiated will progress to completion. Many toffee moisture levels are just above this threshold value, but it is possible that the milk protein binds water as well, and this has the action of converting the aqueous phase in a toffee into a glass. This would explain why, although many toffees contain odd sugar crystals at ambient temperature, they never grain internally, and graining invariably starts from the surface, presumably due to moisture absorption.

Toffees have a number of textural characteristics. Hardness is a function of moisture content only. Chewiness and toughness on eating are related to molecular weight of the carbohydrates. "Body" is a function of milk protein quantity and the state of the protein, which appears to be modified not only by seasonal variation in milk but also by the condensing process. It is also affected by quantity, degree of emulsification and hardness of the fat. Body is a factor in resistance to cold flow. High levels of protein also introduce a degree of elasticity into toffees, which can be a problem in cut and wrap processing.

Protein quantity and state also affect yield stress in a liquid toffee, which alters the flow in depositing processes. Newtonian viscosity however is not so much of a problem.

All these factors interact to affect eating texture. For example, toughness due to sugars can to an extent be offset by high fat contents, and varying ratios of milk protein and high molecular weight carbohydrates can modify the chewiness and toughness. They also allow some degree of tolerance on moisture content, presumably in relation to moisture-binding properties.

2.3 Processing of toffee (Jackson, 1990)

2.3.1 Equipment

Whilst originally toffees were made from solid fuel or gas-fired pans, the steam boiling pan has been used for so long that it can be regarded as the origin of modern toffee processing. These pans are fitted with a fairly complex arrangement consisting a bow-shaped stirrer closely contoured to the pan and fitted with hinged scrapers which are thrown outward by centrifugal force to remove the cooking toffee from every part of the heating surface every revolution (Figure 2.1). Within this bow there is a second set of stirring arms which revolve in the opposite direction to the bow.

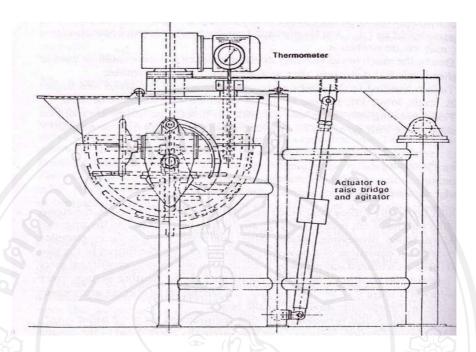


Figure 2.1 Low-type mixer on a tubular frame Source: Jackson (1990)

The reason for this arrangement is twofold. The first requirement for good toffee is very efficient emulsification, and since this was originally carried out in the boiling pan a good mixing action was essential. In addition, toffee masses do not conduct heat very well and the toffee would burn on the pan. The scrapers prevent this and efficient mixing distributes the heat uniformly through the bulk. In spite of this it is probably true to say that no two toffee pans give identical results in terms of finished toffee. The toffee pans are usually fitted with three-speed gear boxes, and the main drive shaft and stirrer assembly can be raised by an arm screw at the end of the cook, to allow the pan to tilt to discharge the toffee.

More modern versions differ mainly in the manner in which the stirrers are removed from the pan.

The emulsification of ingredients is carried out with the stirrers on the high speed. Ideally the fats, milk and glucose should be emulsified before the sugar is added. The reason for this is to disperse the fat into an aqueous syrup to prevent it coating the sugar and retarding solution.

When all the ingredients are thoroughly emulsified the stirrers are slowed down and the steam turned on the low pressure, about 60 psi, to bring the mix to boil. This is done with the pan closed to trap the water vapor and wash any sugar crystal from the pan sides. At this point the pan is opened and the steam raised to full pressure to cook the batch as quickly as possible.

The completion of the cook is usually determined by temperature, but due to the design of many toffee pans it is not possible to insert a thermometer into the boiling toffee. In the past a water crack was used. A small sample of toffee was taken on a spatula or rod, immersed in cold water and the confectioner judged the degree of cook by its texture. With constant temperature water and an experienced operator the method was quickly and reliable and since at the time thermometers were usually

mercury in steel types with slow response, the method was universal. With electronic thermocouple instruments freely available the problem no longer exists, and very few people still use crack testing. It is quite simple to stop the stirrers long enough to take a temperature reading. Hardness differences in toffee are noticeable if temperature varies by $\pm 0.5^{\circ}$ C. However, it should be noted that although boiling temperatures are related to moisture content this is only under specified standard conditions. Different pans can give different moisture content largely due to small differences in manufacturing tolerances and rates of cooking. It is wise to establish the correct boiling temperature for any pan by a trial boiling from time to time. Alternatively, toffee texture can be assessed by some form of penetrometer after the toffee has stabilized. This normally takes some hours and of course must be carried out at constant temperature. By this means continuous checking on performance can be achieved as a routine, and it is faster than moisture determination using an oven.

Once the toffee has boiled the steam is turned off and the pan vented. Any additions of flavor are made if required, and when thoroughly mixed the toffee is removed from the pan as quickly as possible to prevent further caramelisation. Subsequent processing will be considered later, but these days many alternative toffee-boiling processes are available and should be mentioned first.

With the trend towards continuous processing in the industry various means of continuous toffee cooking were investigated. These followed two lines of development, use of existing high-efficiency cookers and a continuous version of the traditional process. Both systems required a continuous supply of product so premix plants were necessary. Many were developed by confectionery manufacturers for their own use, but the machinery manufacturers also entered the field. All premix plants utilized either weighing or metering of ingredients into some form of emulsifying unit. Modern plants use the same principles but are usually microprocessor-controlled. The use of weighing in preference to metering is now almost universal, as it is less affected by product variation such as bulk density or viscosity.

Emulsification of the fat is very important as the globules tend to coalescence during cooking. Not only can this result in fat separation, but changes in the fat globule size affect texture and flow characteristics. It would also appear that changes in the degree of emulsification can occur during storage of premix, but information in this area is lacking.

The caramelisation reaction is time and temperature-dependent but does not progress at a significant rate below about 112°C. Under batch processing conditions the degree of caramelisation is then affected by the quantity of protein, the quantity and type reducing sugar and time taken to reach the final boiling temperature.

With a thin-film or scraped-surface cooker the heat transfer rates are high, and evaporation occurs so rapidly that caramelisation has no time to develop. These cookers are fitted with either pressurized preheaters or steam-jacketed holding vessels after the cookers, with variable residence times, so that the degree of color and flavor development can be controlled.

Coil cookers are also used for lower viscosity products, but all high-efficiently evaporators tend to suffer from the milk protein burning on in some places, and decarbonisation using caustic soda solution is necessary at intervals.

The second approach was a cooker developed specifically for toffee to stimulate the pan operation (Figure 2.2). This employed a preheater unit and two U-

shaped through arrangement in cascade. The first unit or cooker was built up of a number of standard sections to give different capacities, and in theory different steam pressures could be used on each if required. The residence time was controlled by a weir and the cooker contained a complex variable-speed rotor assembly which was machined to closed tolerances but not fitted with scrapers. This rotor was designed to give thorough mixing with a degree of back-mixing, and the flow through the cooker was controlled by a metering pump. The rotor has no central shaft. The stirrer blades are mounted on three equally spaced shafts about halfway between the center and circumference of the assembly, which in operation prevents build-up of toffee on the stirrer. As this rotor is made in one piece, once the cooker length has been decided it cannot be changed without replacing the rotor.

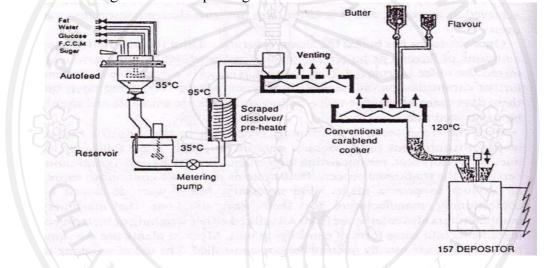


Figure 2.2 Toffee plant Source: Jackson (1990)

The second unit was a blender which was identical in construction but smaller than the cooker. This was for flavor and butter addition. This too had a weir to control residence time. All continuous cookers are difficult to control during start-up and close-down periods due to non-standard conditions. When the feed is stopped the cooker is drained by lowering the weir, but care is needed to maintain the correct temperature.

Recently the plate heat exchanger has been used for confectionery processing, and this can be used for toffee manufacture. The advantages of the plate heat exchanger are compactness and absence of moving parts, apart from the feed pump. In addition to this it is easy to install extra plates and thus vary the capacity. Whilst it can be dismantled for cleaning this is not recommended instead caustic cleaning at intervals will be required.

Another advantage of the plate heat exchanger is that the dissolving and cooking sections can be parts of the same plate assembly. In the event of lack of caramelisation a holding tube can be inserted between two plated towards the end of the cooking stage, effectively introducing a holding stage for caramelisation to develop.

Many confectionery machinery manufacturers offer toffee-cooking equipment, frequently developed from existing machines developed for other processes.

Premix units vary in degree of complexity and numbers of recipes they can handle but are similar in principle, being based on load cell weighing of ingredient addition and microprocessor control. A frequently problem with these units is inaccessibility and difficulty in checking actual operation. A microprocessor-controlled sequence of weighing, mixing and emulsification is usually available.

Dissolvers can be simple stirred vessels, coil circulation systems or may be pressurized dissolvers to facilitate solution of sugar in low-moisture mixes. High-turbulence scraped-surface heat exchangers are also used.

For the final cooking operation, batch units are still manufactured, but continuous plants are either high-efficiency evaporators with caramelisers or longer residence time cookers. Both types are in common use and various claims are made for the relative benefits available. Neither has really gained the ascendancy, and in many cases selection is based on engineering convenience rather than process characteristics.

Having produced a toffee boil it should not be subjected to excessive mixing as this tends to toughen the texture apart from the risk of introducing grain as the temperature falls. With high-fat toffees an additional risk is fat separation, which can give the toffee an almost fibrous texture.

The next stage in processing is sweet-forming. For many years toffee has been run into trays, cut into slabs, or used as a layer in other confections formed into bars, but now a large quantity is wrapped as individual pieces. Three distinct types of process are used, the slab process, the cut and wrap process, and depositing.

2.3.2 Slab process

For many years slabs were lubricated with mineral oil or high-stability vegetable oils, which frequently contain antioxidants to improve keeping properties. It is likely, however, that mineral oil will be banned from inclusion in foods, and only the vegetable oils are permitted.

From the pan cooker the toffee is transferred to bowls which are either manually poured onto the slab, or may be fitted with a carriage which is lifted on a hoist and runs on the side bars of the slab. Whilst boiled sweet can be pumped, due to the increase risk of graining toffee is rarely pumped.

One of the earlier sweet-forming operations was to level the liquid toffee on the slabs and when cool enough to be handled it was cut into sheets, reversed on the slab to even out the cooling and then cut into individual pieces, either in presses or with two-way cutters using circular knives. In many cases slabs have now been replaced by cooling bands or drums. The sweets then go to individual piece-wrapping machines.

2.3.3 Cut and wrap process

With the cut and wrap process the operation is slightly different. The cooling process must be uniform but the handling must not be too vigorous. When the toffee has cooled sufficiently in contact with the slab to be lifted, it is folded in toward the center. This may be repeated and eventually the mass becomes firm enough to lift. It should be lifted across the center so that the surface in contact with the slab folds inwards. It is then laid on the slab again and allowed to spread when the folding is

repeated. The purpose of this is to even out the cooling and bring the batch to a uniform temperature of about 110°F (43°C).

It is then placed in a batch roller which rolls the mass into a cone and draws it out into a rope, which goes through a presizer. This is a series of wheel with semicircular grooves machined in the circumference. The wheels are in pairs, and each succeeding pair has a smaller groove and revolves faster. By this means the rope is drawn down to the required size for the wrapping machine. The machine has a final set of wheels which form the rope into the toffee section required, which is usually rectangular. This shaped rope now passes through a rapidly rotating knife which chops the rope into pieces. The pieces are then pushed against wrapping paper which has been cut from a reel by a machine, into the jaws of the transfer wheel where the various stages of folding and twisting the wrap are carries out and wrapped toffee is ejected down a chute. Other versions fold the paper instead of twisting the ends.

These machines have become progressively faster over the years, and speeds in excess of 1000 sweets per minute are now possible.

Due to the nature of this process the toffee is squeezed and stretched. The squeezing action can express fat from a high-fat toffee, but fat contents of 24% appear to be quite feasible.

The stretching effect is more serious. Although elastic toffee has a degree of elasticity, the colder it becomes the more the elasticity increases. The effect of this is that it can shrink after the pieces have been wrapped and produces distorted ends to the toffees. To alleviate this the toffee should be handled as warm as possible, but in fact it depends on formulation, and operators tend to work by the texture of the rope. In any case it is customary to let the rope slacken and snake before entering the wrapping machine. This allows some shrinkage to occur and reduces the shrinkage after cutting.

With high-fat-content toffees, presizer rolls can be a minor problem. If fat is expressed from the toffee it comes into direct contact with the rolls, which can result in more rapid oxidation. Ideally the rolls should be stainless steel but in the past there were frequently plates steel or brass or bronze. In use the plating eventually wears away and the base metal comes into contact with the fat.

Cut and wrap processing is considerably more efficient than separate cutting and wrapping operations.

2.3.4 Depositing

The other major means of toffee forming is depositing into silicone rubber moulds. This was largely brought by the development of the CD depositor, which had no sliding valve mechanism. The combination of using the depositor piston and a ball valve removed many of the potential graining sites for high-boiled products, and no lubrication, which has frequently done with water, was required. However, shearing still occurs and high-sugar formulations are at risk in depositors of this type.

One of the problems associated with depositing toffee lies in the flow characteristics. Since the milk protein can introduce a yield stress factor, the toffee will not flow out in the moulds and achieve a uniform shape. This can result in wrapping difficulties, particularly on high-speed machines.

Toffees will typically have an equilibrium relative humidity of about 45-50%, and twist wrapping is no protection against moisture. This implies that an air-

conditioned environment is necessary both during cooling and before final packing, and care must be taken to ensure that the product is not cooled below the dew point.

Deterioration at this stage is not readily apparent, but absorption of traces of moisture will seriously reduce shelf life as crystallization will rapidly develop on the surface and penetrate the whole sweet.

This in effect produces a grained caramel, but controlled graining is achieved by the introduction of seed crystal during manufacture. The usual seeding medium is fondant, which introduces a large number of sugar crystals of about $10~\mu m$. The quantity required is quite small, less than 1% of the batch, and for cut and wrap toffees or any other form of plastic processing the fondant will be folded in during the cooling operation once the temperature is below $100^{\circ} C$. With deposited toffees the process is more difficult as the temperature is higher than that at which the crystal in fondant will be destroyed. This means that the toffee must be cooled before the fondant is added, and even so larger quantities of fondant will be required. In both cases the toffee will grain after wrapping and slightly warm storage temperatures are required. High temperatures are undesirable because the toffee can easily distort before it grains, and also because the grained toffee will have a much higher vapor pressure than the ungrained toffee. On removal to a colder environment condensation can easily occur within the pack.

2.4 Toffee texture (Jackson, 1990)

Toffee textures are sometimes modified by the incorporation of air, which is normally introduced by mixing in a whipped frappe. Beside that, toffees are frequently combined with other confectionery products. In these circumstances attention must be paid to the equilibrium relative humidity of the separate components as, if they are different, moisture transfer will occur within the sweet, leading to changes in texture. This also applies to inclusions such as dried fruit or nuts, which should be stoved to prevent moisture being introduced into the toffee and initiating grain.

Reworking toffee products depends to an extent on the type of process involved. Solid rework can be added back either on the slab or into the boiled batch, but it is imperative that no grain has developed on the surface of the rework. It is safer to redissolve the rework to premix solids and feed it back at the premix stage. It has been said that a proportion of rework improves toffee texture, and whilst this may be subjective it certainly improves flow characteristics in depositing processes (Jackson, 1990).

2.5 Sweeteners

A sweetener is a food additive which adds the basic taste of sweetness to a food product, whereas artificial sweeteners are sugar substitutes (Anonymous, 2009).

2.5.1 Sugar alcohol

2.5.1.1 Maltitol (Grenby, 1996)

Physical and chemical properties

Pure maltitol is a white crystalline powder. It shows an excellent heat stability up to 200°C and dews not take part in Maillard-type browning reactions. Chemically, it is a hydrogenated maltose with the disaccharide structure illustrated in Figure 2.3.

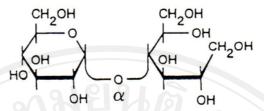


Figure 2.3 Chemical structure of maltitol

Source: Grenby (1996)

Table 2.2 gives a comparison of the physical properties of maltitol and sorbitol. This shows that the melting point of maltitol is significantly higher than that of sorbitol and is relatively closed to that of sugar (186°C). The solubility of maltitol is highly satisfactory, and it does not give crystallisation problems in applications when crystallisation is not desired. The solubility of maltitol exceeds even that of sucrose at a temperature above 62°C.

On account of its good solubility, maltitol exists also in the form of stable non-crystallising syrups. It has only a slight negative heat of solution and gives consequently no cooling effect, unlike sorbitol and xylitol. As maltitol has the highest solubility of all the disaccharide polyols, it has the highest viscosity in solution, significantly higher than sorbitol at the same concentration. Maltitol syrups provide appropriate viscosity profiles for many applications, e.g. delivering the same functions as glucose syrups in traditional confectionery products.

Table 2.2 Physical properties of maltitol in comparison with sorbitol

Property	Sorbitol	Maltitol
Melting point (°C)	93-97	148-152
Solubility	235	160
(g in 100 g water at 20°C)		2
Heat of solution (kJ/kg)	1111	-69
Viscosity of a 70%	180	2500
solution		
(mPa.s at 20°C)		

Source: Grenby (1996)

The hygroscopicity of crystalline maltitol is low and comparable to that of sucrose, as the two have similar water sorption isotherms. Maltitol is a non-volatile humectant with a lowering effect on water activity. It is less hygroscopic than sorbitol, and its equilibrium relative humidity (ERH) is attained more slowly.

When subjected to change in ambient humidity, products stabilized with maltitol syrups are less susceptible to a change in water content than those stabilized with glycerol or sorbitol (Figure 2.4).

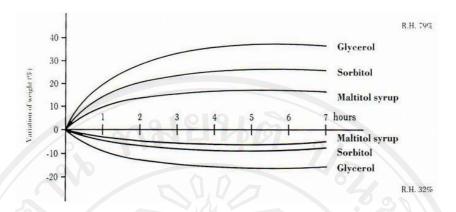


Figure 2.4 Composition of hygroscopicity of glycerol, sorbitol and maltitol syrup R.H.=relative humidity

Source: Grenby (1996)

Sensorial properties

Maltitol has a clean and pleasant natural sweetness. The relative sweetness of the pure form varies from 80 to 90 (sucrose = 100). Only xylitol among the polyols is sweeter than maltitol (Table 2.3) (Grenby, 1996).

Table 2.3 Relative sweetness of polyols and sucrose in solution at 20°C

Sugar	Relative sweetness
Xylitol	80-100
Sorbitol	50-60
Mannitol	50-60
Maltitol	80-90
Lactitol	30-40
Isomalt	50-60
Sucrose	100

Source: Grenby (1996)

Depending on their maltitol content, the sweetness of maltitol syrups maybe lower than this, but in general it is not lower than 65% of the sweetness of sucrose. This sweetness is almost equivalent to that of sucrose/glucose blends used in manufacturing traditional confectionery products. As with most sweetners, the sweetness is influenced by factors such as concentration, temperature, acidity and the nature of other nutrients.

Due to its high sweetening power, maltitol can be used as a sole sweetener in most sugar-free product applications, without the need to add intense sweeteners. When maltitol is present in food in crystalline form it does not give any cooling effect in the mouth. For this reason it is more compatible with fruit flavors than sorbitol or xylitol. In general it has excellent flavoring properties with good flavor release in foods.

Physiological properties

Like the other polyols, maltitol is non-cariogenic, calorie-reduced, non-toxic, and could cause lazation if high doses are ingested.

Caries is initiated with fermentable sugars as substrates, from which dental plaque is formed via dextran and levan production on the surface of the teeth. This is the ideal environment for the growth of microflora containing acidogenic organisms like *Streptococcus mutans* which attack carbohydrates to form acids. The resulting pH-drop can lead to demineralization of the dental enamel and tooth decay.

Several methods have been developed to measure the cariogenicity of food products, for example by following the pH-drop in dental plaque after ingestion of the test substance, e.g. the so-called Muhlemann test. All the commercially available maltitol syrup and powder grades pass this test, since they do not cause a pH-drop below 5.7.

Another way to judge the cariogenic potential of a product is the determination of acid production rates. Measurements have been done on sorbitol and maltitol in comparison with glucose. The results clearly demonstrate that maltitol is even less acidogenic than sorbitol.

Turning to the metabolic utilization of maltitol, due to the fact that no active transport mechanism for penetration of the intestine membranes exists, direct absorption from the gut is only possible by diffusion. This takes place very slowly since the size of the maltitol molecules greatly exceeds the pore size of the gut wall. On the other hand, maltitol can be hydrolyzed enzymetically to sorbitol and glucose or fermented by the microflora of the large intestine to volatile fatty acids, carbon dioxide, hydrogen and methane.

It is very difficult to determine the relative proportions of maltitol metabolized by these two pathways, although the estimation of the caloric value of the maltitol is based on it. A study based on available scientific information calculates a figure of 3.2 kcal/g for maltitol. On the other hand, a recent study administering ¹⁴C-labelled maltitol to rats and following the distribution in the body by measuring the radioactivity, supports a figure of 2.0 kcal/g.

Nevertheless, it is uncontested that maltitol provides fewer calories than glucose or sucrose due to its different metabolic utilization pattern. Giving an exact figure is impossible, as the caloric value depends on the dose ingested and other factors, but the Commission of the European Community has assayed an energy value of 2.4 kcal/g for all sugar alcohols (EU Direct 90/496/EEC). Several toxicity studies confirm that maltitol products show neither acute toxicity nor genetic or subchronic toxicity. This forced the Scientific Committee for Food of the European Union to consider "hydrogenation products of high maltose-containing glucose syrups as acceptable provided the limitations due to their laxative action were kept in mind".

A recent completed chronic toxicity/carcinogenicity study concluded that no adverse effects are expected from ingestion of maltitol. As a result of these maltitol evaluations, the European Union recently permitted maltitol and maltitol syrups to be widely used in preparation of food stuffs (EU Directives 94/35/EC and 95/2/EC). This will now be followed by local implementation of the Directives in the European countries, and current legislation will be harmonized. Outside Europe, maltitol is already permitted in most countries.

The laxative effect of polyols originates from their slow transport across the intestine membranes and low water retention. It is extremely difficult to determine the exact tolerance level of individual polyols, since the performance of the digestive tract varies with age and type of food ingested, etc. Absolutely no laxative effect was observed for maltitol up to a 30 g dosage and no significant discomfort was experienced below an ingestion level of 50 g/day. These figures do not take into account the adaptation to maltitol which could raise levels of toleration.

Production of maltitol

Like sorbitol, maltitol is derived from starch, which may be enzymetically converted to dextrose (the raw material for maltitol) (Figure 2.5). If the enzymic conversion of starch is stopped after a certain period, syrups with a high maltose content are obtained. Besides maltose, minor amounts of dextrose and higher oligosaccharides are present. Maltitol-based products are produced by catalytic hydrogenation of these maltose-containing syrups. Hydrogenation is conducted at elevated temperature and hydrogen pressure in the range of 20-150 bar. After refining the reaction mixture by ion exchange and carbon treatment, the product is concentrated to the required dry substance. Crystallization or solidification of a very high-maltitol syrup leads to maltitol powder.

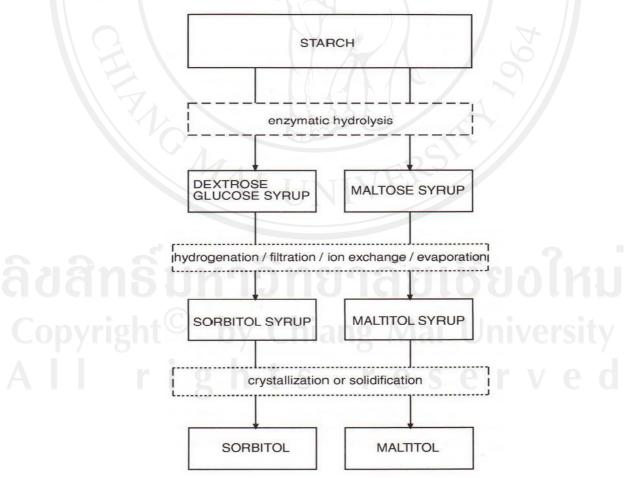


Figure 2.5 Production of sorbitol and maltitol

Source: Grenby (1996)

Compositions of maltitol

On the market there are several grades of maltitol syrup, with different maltitol contents. Three categories can be distinguished (Table 2.4), including those with 50-55% maltitol, the second with 72-77% maltitol and the last with 80-90% maltitol.

An increasing maltitol content intensifies the sweetness of the product. Other components of the syrups are minor amounts of sorbitol, maltotriitol and hydrogenated higher oligosaccharides. For the grades below 77% maltitol, the dry substance content is normally adjusted to 75%, but syrups of 83 or 85% dry substance are also available on request. In order to avoid crystallization, syrups with 80-90% maltitol on a dry basis are produced commercially at 70% total dry matter. Maltitol powder is sold in two forms, a solidified grade with 86-90% maltitol (moisture content <1%) and a pure crystalline grade with minimum 99% purity (moisture content <0.5%).

Table 2.4 Composition of maltitol syrups

Maltitol (%)	Sorbitol (%)	Dry substance (%)
50-55	max. 8	75-85
72-77	max. 5	75-83
80-90	max. 5	70

Source: Grenby (1996)

Applications of maltitol in confectionery products 1) Hard-boiled candies

Maltitol is currently used to produce sugar-free hard-boiled candies, its main advantages in comparison with alternative bulk sweeteners being high sweetness level (90% compared to sucrose) and excellent flavor release. These candies are produced from commercially available syrups, with maltitol levels varying between 50 and 88% on dry substance. In some cases the syrups are prepared by dissolving maltitol powder. When high maltitol levels are used there is no need to add intense sweeteners. Maltitol gives a transparent candy with a smooth glossy surface and pleasant sweetness. Due to its excellent heat stability there is no color development during boiling. Candies containing maltitol have good workability for depositing as well as for plastic moulding. Sugar-free candies with low hygroscopicity and showing no cold flow are achieved following these simple rules:

- Cook the candy mass to be below 1.0% residual moisture content, preferably 0.5-0.8. Maltitol-based hard candies can be produced without the need to adapt traditional or high-speed continuous candy lines as long as the equipment allows cooking temperature and vacuum times higher than those generally applied for glucose/sucrose hard candy. When using traditional cooking equipment, the cooking temperature is preferably 168-170°C with 8 min vacuum time.
- Adapt moulding conditions, taking into account the low viscosity and the high cooking temperature of polyols. A longer cooling time than that

generally used for sucrose/glucose candies must be allowed in order to reach similar plasticity (moulding temperature approximately at 65°C).

- Acid should only be added to a cooled candy mass to avoid syrup decomposition.
- Wrap the sweets as soon as possible after moulding to avoid moisture pick-up. If needed, before wrapping, the sweets should be stored at low RH (below 50% RH) and low temperature (max 25°C).
- Ensure good protection by accurate wrapping and/or packaging.

Originally maltitol candies were made from syrups containing 50 or 75% maltitol on a dry basis. In general 5-8% mannitol was added to the syrup before cooking in order to reduce hygroscopicity of the candies. Further studies have been conducted with aim of reducing the cooking temperature and hygroscopicity level of maltitol hard candies. One of the approaches is to add a mixture of gum arabic and mannitol to the syrup before boiling. Lower boiling temperatures can be applied (e.g. 145°C) but vacuum is still needed.

Recent studies show that improved shelf life properties of candies are obtained with 82-84% maltitol content syrup. This results in a significant decrease in hard candy moisture pick-up in comparison with other compositions, including maltitol/mannitol blends. However, for un-wrapped candies exposed to high humidity/temperature conditions during storage, the hygroscopicity levels of candies based on 83% maltitol syrup could still be too high. A further decrease in moisture pick-up is obtained by increasing maltitol content to 87-89%.

This higher maltitol content provokes more rapid stable micro-crystallization, resulting in reduced hygroscopicity but also giving slight cloudiness after 3 weeks wrapped storage. Using this syrup the cooking temperature can be reduced from 168 to 155°C, without significant hygroscopicity increase in the hard candy. The corresponding residual moisture content becomes 1.8% instead of 0.8% using optimum manufacturing conditions. Sugar-free hard candies based on syrups with 83-88% maltitol have similar hygroscopicity levels to conventional candies. Shelf life can be further improved by dusting the candies with high purity (min. 99%) crystalline maltitol. In some cases maltitol syrups are combined with other disaccharide polyols.

2) Toffees and chewy candies

Maltitol-based soft-boiled candies are made from maltitol syrups, using conventional processing equipment. High maltitol syrup (e.g. 75% maltitol) is recommended. In this case there is no need to add intense sweeteners to the formulations.

3) Toffees

Maltitol syrups are used as sole sweeteners. Different types of milk sources can be used. For taste and color reasons non-sweetened concentrated milk is preferred, but whole milk powder and de-lactosed whey powder are also suitable. As with all polyols, maltitol does not react with proteins and will not give the typical toffee taste and color. For this reason it is necessary to add toffee flavor and caramel color to the cooled toffee mass before moulding.

In this way, sweetness, taste and texture characteristics of maltitol-based toffees are made very similar to those of traditional sweetened products, using similar process conditions. In general the cooking is a few degrees centigrade higher than for standard recipes. This results in a lower final humidity and the right texture. The shelf life properties are very similar to glucose/sucrose-based products.

4) Chewy candies

Maltitol-based chewy sweets are produced like conventionally sweetened products. For the sugarless products slightly higher cooking temperatures have to be applied in order to obtain the right texture. Maltitol-based chewy products need in general a longer pulling time. They are based on maltitol syrups, but in some cases a combination of maltitol syrups and maltitol powder is used. Stickiness can be avoided by adding small amounts of lecithin. The grainy type has a shorter and softer texture.

5) Chocolate

Both dark and milk chocolate with outstanding flavor can be produced with crystalling high purity (min. 99%) maltitol, by applying normal manufacturing processes. Higher conching temperatures than generally recommended for other sugar alcohols can be used without recrystallization and problems from any increase in viscosity. Dry conching at high temperature gives additional advantages in terms of production technology and flavor development. Well-tempered moulded maltitol chocolate is non-hygroscopic and has excellent gloss and good breaking characteristics. The smooth melting profile and natural sweetness of chocolate containing crystalline maltitol are very similar to a sucrose-based product and make this product a high-quality sugar-free alternative, allowing c. 12-15% calorie reduction.

Chocolate evaluated studies have shown that 50/50 combinations of crystalline maltitol with low-calorie bulking agents such as polydextrose and/or insulin give further calorie reductions up to 23%. In this case the cocoa butter content is also reduced. When combining crystalline maltitol with the above polysaccharides, the conching conditions have to be adapted to maintain high conching temperatures. This is the so-called 'dry/wet' conching method which also gives a good work ability to normal chocolate mass rheology and yields good sensorial properties. Industrial production has confirmed the good workability and sensorial quality of maltitol chocolate. There are now sugar-free chocolates offering 25-30% reduction in the fat content of the chocolate, reformulating for example by using less cocoa butter and adding defatted cocoa powder. In order to ensure good flow properties of the chocolate mass, addition of a specific emulsifier such as polyglycerol polyricinoleate is advised.

6) Chewing gum

The main components of sugar-free chewing are gum base, polyol powder(s) as solid phase, and sorbitol or maltitol syrup as liquid phase. The gum base level varies in general between 20 and 30% depending upon the type of base and the required chewiness. Maltitol can be used in the liquid as well as in the solid phase. Although machinability, texture and stability of a chewing gum composition depend on the equilibrium between the three main components, the liquid phase plays an

important role in the water exchange with the surrounding air. Maltitol syrup with maltitol contents from 50-75% of dry substance prevents the chewing gum drying out and hardening during storage so that plasticity is maintained. Maltitol syrup is used at levels of 10-40%. Mannitol is added to prevent stickiness during processing. Maltitol powder can be used to texturise and to maintain the composition in a substantially anhydrous form. The incorporation level of maltitol powder is preferably between 45 and 55%.

2.5.1.2 Sorbitol (Grenby, 1996)

Sorbitol and mannitol have existed as commercial products for more than 60 years. Today, sorbitol and mannitol are used in food, confectionery, oral care, pharmaceutical, and industrial applications because of their unique physical and chemical properties. Sorbitol and mannitol are classified as sugar alcohols or polyols.

Sorbitol was first discovered by a French Chemist named Joseph Boussingault in 1972. He isolated it from the fresh juice of the mountain ash berries. Mannitol is found in the extrudates of trees, manna ash, marine algae, and fresh mushroom. Although present in natural sources, sorbitol and mannitol were not commercially available until 1973, when they were first manufactured in full production scale by Atlas Company, Wilmington, Delaware (now SPI Polyols, Inc.).

Production of sorbitol and mannitol

Glucose syrups, invert sugar, and other hydrolyzed starches are important raw materials for the manufacture of sorbitol and mannitol. Sorbitol is produced from the catalytic hydrogenation of glucose. The hydrogenation reaction is driven by a catalyst, such as nickel. After the reaction is complete, the catalyst is filtered out and the solution is purified. It is then evaporated to 70% solids and sold as sobitol solution.

Crystalline sorbitol is made by further evaporating the sorbitol solution into molten syrup containing at least 99% solids. The molten syrup is crystallized into a stable crystalline polymorph that has one single melting point (99-101°C) and heat of fusion (42 cal/g, assuming 44 cal/g represents a fully crystallized crystalline sorbitol). The stable polymorph of sorbitol is known as gamma (γ) sorbitol was determined from the work of Atlas Powder Company and University of Pittsburgh researchers in the early 1960s. Most commercially available crystalline sorbitol is the gamma polymorph.

When hydrogenated invert sugar used as the raw material, both sorbitol and mannitol are produced in the solution because they are isomers. The mannitol and sorbitol are separated on the basis of their different solubilities. Mannitol is crystallized from the solution because of its lower solubility than sorbitol in water. The resulting product is the most stable polymorph, the β -polymorph. Mannitol is then filtered, dried and sold as white powder or free-flowing granules (directly compressible material).

Physical and chemical properties of sorbitol and mannitol

Sorbitol and mannitol are six-carbon, straight-chain polyhydric alcohols, meaning they have more than one hydroxyl group. Both sorbitol and mannitol have six hydroxyl groups and the same molecular formular, $C_6H_{14}O_6$. They are isomers of one another and have different molecular configurations. The difference between

sorbitol and mannitol occurs in the planar orientation of the hydroxyl group on the second carbon atom (Figures 2.6 and 2.7). This dissimilarity has a powerful influence and results in an individual set of properties for each isomer.

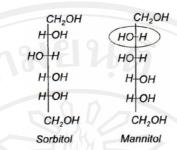


Figure 2.6 The chemical structures of sorbitol and mannitol Source: Nabors (2001)

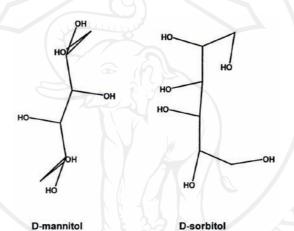


Figure 2.7 The planar configurations of sorbitol and mannitol Source: Nabors (2001)

The major difference between the two isomers is that sorbitol is hygroscopic and mannitol is nonhygroscopic. Therefore, sorbitol is used as humectant because of its affinity for moisture, and mannitol is used as a pharmaceutical and nutritional tablet excipient because of its inertness and stability against moisture.

Sorbitol solution is hygroscopic, attracting and releasing moisture under varying humidity conditions, but it does so very slowly. Polyols of lower molecular weight, such as glycerin, tend to gain and lose water more rapidly. Sorbitol provides improved moisture control and is more likely to maintain equilibrium with the surrounding environment. This slower rate of change in moisture content protects the food products in which sorbitol is used, thus maintaining the same quality of the product and extending the shelf-life.

There are many different polymorphs of both sorbitol and mannitol. The most stable polymorph of sorbitol is (γ) -sorbitol. The most stable polymorph of mannitol is the (β) -polymorph. Working with the most stable polymorph is important because one needs to be certain that the product being used will not change during processing, (i.e., an unstable polymorph converting to the stable polymorph). Use of the most stable polymorph ensures that the properties of the finished product will not change. Most of the commercially available sorbitol and mannitol products are of the most

stable polymorphs. One of characteristics affected by polymorph is solubility. The solubility in water of γ -sorbitol is very high (235 g/100 ml at 25°C). The solubility in water of β -mannitol is lower (22 g/100 ml at 25°C).

Sorbitol and mannitol are sweet, pleasant-tasting polyols. This characteristic makes them popular in confectionery and pharmaceutical taste-masking applications. Sorbitol is approximately 60% as sweet as sucrose, and mannitol is approximately 50% as sweet. They both have a negative heat of solution, which gives them a cooling sensation in the mouth. Sorbitol's heat of solution is -26.5 cal/g (at 25°C), and mannitol's heat of solution is -28.9 cal/g (at 25°C).

Like many polyols, sorbitol and mannitol have a laxation threshold associated with them. The average adult can consume up to 50 g of sorbitol and 20 g of mannitol in a day without a laxation problem.

Absorption and metabolism

Sorbitol and mannitol are widely accepted by the food and pharmaceutical industries as nutritive ingredients because of their ability to improve the taste and shelf-life of regular foods and special dietary products.

Sorbitol and mannitol are slowly absorbed into the body from the gastrointestinal tract and are metabolized by the liver, largely as fructose, a carbohydrate that is highly tolerated by people with diabetes. Sorbitol is absorbed and metabolized in the liver by the way of pathway located entirely in the cytoplasmic compartment. This pathway is illustrated in Figure 2.8.

Ingestion of sorbitol and mannitol does not usually cause an immediate demand for extra insulin. The initial steps in the metabolism of sorbitol and mannitol in the liver, their uptake by the liver cells, and their conversion to glucose are independent of insulin, but the subsequent use of glucose by the muscle and adipose tissues is influenced by insulin. The person's condition at the time of ingestion will determine the amount of insulin required. In the calculation of nutrient intake, sorbitol and mannitol should be considered as carbohydrates; however, they have lower glycemic indices than other carbohydrates so can usually be used safely by people with diabetes.

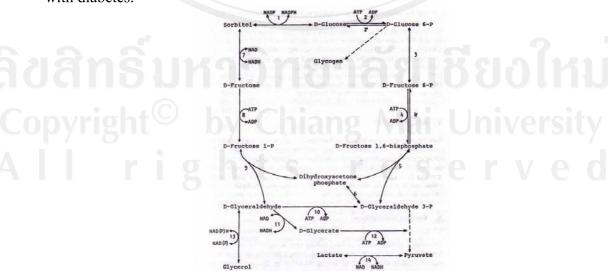


Figure 2.8 Mannitol and sorbitol metabolism

Source: Nabors (2001)

The caloric value of sorbitol is 2.6 cal/g and the caloric value of mannitol is 1.6 cal/g in the United States. These are lower than the caloric value of sucrose, which is 4 cal/g.

Sorbitol and mannitol do not increase the incidence of dental caries, a condition started and promoted by acid conditions that develop in the mouth after eating carbohydrates and proteins. Results from pH telemetry tests show that sorbitol and mannitol do not increase the acidity or lower the pH of the mouth after ingestion. This means that they will not promote tooth decay. For this reason, sorbitol and mannitol are used in oral care and pediatric applications. The usefulness of polyols (e.g., including sorbitol and mannitol) as alternatives to sugars and as part of a comprehensive program including proper dental hygiene has been recognized by a numerous authorities, including the American Dental Association.

Sorbitol application in confectionery 1) Chewing gum

Crystalline sorbitol is widely used as a bulking agent in sugar-free chewing gum. Crystalline sorbitol does not promote dental caries. It provides sweetness and a pleasant cooling effect, which are synergistic with other flavoring agents such as spearmint, peppermint, cinnamon, wintergreen, and fruit flavors. The level of crystalline sorbitol used in a sugar-free chewing gum is typically between 50-55% by weight. High-intensity sweeteners such as aspartame and acesulfame potassium can be used with crystalline sorbitol to improve the sweetness and flavor release. The size of the crystalline sorbitol granules is very important in regard to flexibility, chew, cohesion, and smoothness in chewing gum. The particle size distribution of crystalline sorbitol used for sugar-free chewing gum is typically 94.5% through the U.S. Standard Testing Sieve Number 40.

The process of making sugar-free chewing gum is basically a blending operation that uses a horizontal sigma blade mixer. The mixer is equipped in a circulating water-heated jacket. The temperature of the water is heated to between 50-55°C. Crystalline sorbitol is mixed with the preheated gum based (the temperature of the gum base is 50-55°C) and the humectant solution until the mixture homogenous. The mixing time is typically about 8 to 9 min. Gum bases are derived from natural sources and are synthetically produced to provide desired chewing properties. The humectant solution is usually a sorbitol solution, glycerin, and/or a maltitol solution. The humectant is used to prevent the sugar-free chewing gum from becoming too dry or stale during storage. The flavoring is then added to the homogenous mixture and mixed for an additional 3 to 4 min. The gum is removed from the sigma blade mixer and shaped into thin sheets by running it through a set of rollers several times. A dusting agent, mannitol powder, is usually used to dust the surfaces of the gum sheets to reduce the tendency of the gum to stick to the rolling, cutting, and wrapping equipment. The thin sheets of gum are then stored in a constant temperature room (25°C and less than 40% relative humidity) for 24 h. They are then cut and wrapped into individual sticks of chewing gum.

2) Sugar-free hard candy

To make a sugar-free candy, sorbitol solution is used as the primary ingredient. In hard sugar candies, the corn syrup serves this purpose. Sorbitol is used

for its sweet, cool taste and its ability to crystallize and form a hard candy. Sorbitol is noncariogenic, so sugar-free hard candies made with it will not promote tooth decay.

Sorbitol is used to make sugar-free candies by a batch depositing method. In this method, sorbitol solution is cooked at high temperatures until most of the water is driven off. The molten sorbitol is slowly and evenly cooled to a certain temperature, at which time flavor and a small amount of crystalline sorbitol are added. The crystalline sorbitol is used as a seed that nucleates the melt and starts the crystallization of sorbitol. The melt is deposited into molds and allowed to crystallize further. The sorbitol continues to crystallize and sets up into a hard candy.

The type of sorbitol solution used can control the rate of sorbitol crystallization. In the manufacture of sorbitol solution, mannitol is also produced because it is an isomer. Sorbitol solution 70%, contains a small amount of mannitol (approximately 3%). Adjusting the mannitol levels up or down can increase or decrease the candy's set time. If the candy manufacturer has an automated batch depositing process and wants the candy to set up quickly, the mannitol level in sorbitol solution can be adjusted down. Alternatively, if the candy manufacturer has a manual process and does not want the candy to set up too quickly for fear of it setting up in the depositor, the mannitol level in sorbitol solution can be adjusted up. The mannitol inhibits or controls the rate of sorbitol crystallization.

3) Confections

Sorbitol is related to sugars but has a different carbohydrate structure. Despite the chemical relationship, sorbitol modifies the crystallization of sugar by complexing. As a result, it influences the rate of crystallization, crystal size, and crystal-syrup balance in sugar-based confections.

In grained confections and similar candies, sorbitol functions as one of the doctors used to modify crystal structures to extend shelf-life. In the production of any confection, there is a point at which sucrose crystallization should take place to achieve maximum shelf-life. If crystallization takes place on either side of this "optimal point," the crystals will be either too large or too small to achieve the stability required for maximum shelf-life. Including sorbitol in the doctor system of the confection will complex the total sucrose/doctor system. This provides the confectioner a broader area to crystallize the confection and still be at the optimum point as measured by quality and shelf-life. Sorbitol also improves texture and moisture retention because of its humectant properties. It is unique because, unlike other doctors, enough sorbitol can be used to extend shelf-life without adversely affecting texture or taste.

2.5.2 Honey

Production and types (Belitz and Grosch, 1999)

In the production and processing of honey, it is important to preserve the original composition, particularly the content of aroma substances, and to avoid contamination. The following kinds of honey are differentiated according to recovery techniques:

Comb Honey (honey with waxy cells), i.e. honey present in freshly-built, closed combs devoid of blood combs (young virgin combs). Such honey is produced in high amounts, but is not readily found in Germany. In other countries, primarily the

USA, Canada and Mexico, it is widely available. Darker colored honey is obtained to recover virgin combs not more than one year old and from combs which include those used as brood combs.

Extracted honey is obtained with a honey extractor, i.e. by centrifugation at somewhat elevated temperatures of brood-free combs cells. This recovery technique provides the bulk of the honey found on the market. Gentle warming up to 40°C facilitates the release of honey from the combs.

Pressed honey is collected by compressing the brood-free honey combs in a hydraulic press at the room temperature.

Strained honey is collected from brood-free, pulped or unpulped honey combs by gentle heating followed by pressing.

Beetle honey is recovered by pulping honey combs which include brood combs. This type of honey is used only for feeding bees.

Processing (Belitz and Grosch, 1999)

Honey is marketed as a liquid or semisolid product. It is usually over saturated with glucose, which granulates, i.e. crystallizes, within the thick syrup in the form of glucose hydrate. To stabilize liquid honey, it has to be filtered under pressure to remove the sugar crystals and other crystallisation seeds. Heating of honey decreases its viscosity during processing and filling, and provides complete glucose solubilization and pasteurization. Heating has to be gentle since the low pH of honey and its high fructose content make it sensitive to heat treatment. As with other foods, continuous, high temperature-short time processing (e.g. 65°C for 30 s followed by rapid cooling) is advantageous.

Processing of honey into the semisolid product involves seeding of liquid honey with fine crystalline honey to 10% and storing for one week at 14°C to allow full crystallisation. This product is marketed as creamed honey.

Physical properties (Belitz and Grosch, 1999)

Honey density (at 20°C) depends on the water content and may range from 1.4404 (14% water) to 1.3550 (21% water). Honey is hygroscopic and hence is kept in airtight containers. Viscosity data at various temperatures are given in Table 2.5. Most honey behave like newtonian fluids. Some, however, such as alfafa honey, show thixotropico properties which are traceable to the presence of proteins, or dilating properties (as with opuntia cactus honey) due to the presence of trace amounts of dextran.

The specific heat (20°C; 17.4% water) is 2.26 J/g/°C. Because of poor heat conductivity, the possibility of heating honey with microwaves is a viable approach. Heating 1 l honey for 1 h from 30 to 55°C requires 25 kw of energy.

Table 2.5 Viscosity of honey at various temperatures

Type of honey	Temperature (°C)	Viscosity (Poise)
Honey 1 ^a	13.7	600.0
	20.6	189.6
	29.0	68.4
0/	39.4	21.4
	48.1	10.7
90	71.1	2.6
Honey 2 ^b	11.7	729.6
	20.2	184.8
// 29.	30.7	55.2
	40.9	19.2
	50.7	9.5

a Melilot honey (Melilotus officinalis; 16.1% moisture content).

Source: Belitz and Grosch (1999)

Composition (Belitz and Grosch, 1999)

Honey is essentially a concentrated aqueous solution of invert sugar, but it also contains a very complex mixture of other carbohydrates, several enzymes, aroma substances, pigment, waxes, pollen grains, etc. Table 2.6 provides compositional data. The analytical data correspond to honey from the USA, nevertheless, they basically represent the composition of honey from other countries.

Table 2.6 Composition of honey

Constituent	Average value (%)	Variation range (%)
Moisture	17.2	13.4-22.9
Fructose	38.2	27.3-44.3
Glucose	31.3	22.0-40.8
Saccharose	1.3	0.3-7.6
Maltose	7.3	2.7-16.0
Higher sugars	1.5	0.1-8.5
Others	3.1	0-13.2
Nitrogen	0.04	0-0.13
Mineral (ash)	0.17	0.02-1.03
Free acids ^a	22	6.8-47.2
Lactones ^a	1 6 7.1 F A	0-18.8
Total acids ^a	29.1	8.7-59.5
pH value	3.9	3.4-6.1
Diastase	20.8	2.1-61.2

^amequivalents/Kg.

Source: Belitz and Grosch (1999)

b Sage honey (Salvia officinalis; moisture content 18.6%).

2.6 Yogurt

Yogurt is probably the most popular fermented milk. It is made in a variety of compositions (fat and dry matter content), either plain or with added substances: fruits, sugar, and gelling agents. Beverages and edible ices derived from yogurt are also produced.

2.6.1 The yogurt bacteria (Walstra et al., 1999)

2.6.1.1 Growth of the sugar bacteria

The essential flora of yogurt consists of the thermophilic lactic acid bacteria, Streptococcus thermophilus and Lactobacillus delbrueckii ssp. bulgaricus. For a satisfactory flavor to develop, approximately equal numbers of both species should be present. They have a stimulating effect on each other's growth (protocooperation). The proteolytic rods enhance growth of the streptococci by forming small peptides and amino acids, the main amino acid being valine. Milk contains too little of these amino acids and the cocci, which are very weakly proteolytic, form the acids too slowly. The cocci enhance the growth of the rods by forming formic acid out of pyruvic acid under anaerobic conditions, and by rapid production of CO₂. The stimulatory effect of formic acid remains unnoticed in intensely heated milk because in this milk formic acid has been formed by decomposition of lactose. The production of formic acid by the cocci is, however, essential in industrial pratice, where more moderate heat treatments of yogurt milk are applied, e.g., 5-10 min at 85°C. Due to mutual stimulation during combined growth of the yogurt bacteria in milk, lactic acid is produced much faster than would be expected on the basis of the acid production by the individual pure cultures. Some antibiosis also occurs in vogurt in that the cocci cannot grow after a certain acidity has been reached. The rods are less susceptible to acid and continue to grow. Protocooperation and antibiosis are of great importance in the growth of the yogurt bacteria as well as for the quality of yogurt (Figure 2.9).

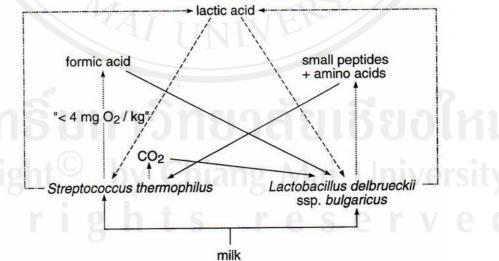


Figure 2.9 Outline of the stimulation and the inhibition of the growth of yogurt bacteria in milk. - · - · -, formation of lactic acid; · · · ·, formation of growth factors; —, stimulation; - - -, inhibition.

Source: Walstra et al. (1999)

The cocci as well as the rods contribute significantly to the properties of yogurt. The properties of the bacterial strains used should be matched to each other because not every combination of strains is suitable. Furthermore, both species should be present in large numbers in the product, and hence in the starter. The optimum ratio of diplococci to rods depends on the properties of the strains and is often approximately 1:1. This ratio between the yogurt bacteria is best maintained if the inoculum percentage is, say, 2.5, the incubation time 2.5 h at 45°C, and the final acidity is approximately 90-100°N. The ratio between the species keeps changing. Initially, the streptococci grow faster due to the formation of growth factors by the rods, and probably also due to the latter compounds being added via the inoculum (especially in the manufacture of set yogurt). Afterwards, the cocci are slowed down by the acid produced. Meanwhile, the rods have started to grow faster because of the growth factor (CO₂ and formic acid) formed by the cocci. As a result, the original ratio is regained. The yogurt should then have attained the desired acidity. Continue incubation or inadequate cooling causes the rods to become preponderant.

Obviously, a correct ratio between the species in the starter can be maintained, or be recovered if need be, by proper selection of the propagation conditions. Currently, concentrated starters are increasingly being used, ensuring a correct bacterial composition of the starter.

2.6.1.2 Metabolites of the yogurt bacteria

S. thermophilus and L. delbrueckii ssp. bulgaricus form products that contribute to the flavor of yogurt as well as to its structure and consistency. L. delbrueckii ssp. Bulgaricus can produced amino acids such as valine, histidine, glycine and S. Thermophilus can produced formic acids.

2.6.2 Manufacture of set and stirred yogurt (Walstra et al., 1999)

Traditionally, set yogurt was made of concentrated milk. The milk was heated on an open fire until one-third of the water had evaporated. Then the milk was allowed to cool, and when a temperature of about 50°C was reached, the milk was inoculated with a little yogurt. After fermentation, a fairly firm gel was obtained. A similar process is still being used, but either the milk is evaporated under vacuum or some milk powder is added. One may use the same process for making set yogurt from nonconcentrated milk. The yogurt obtained is less rich in flavor, is far less firm, and is prone to syneresis (wheying off). Generally some gelling agents are added to prevent syneresis and to enhance firmness, especially if pieces of fruit are added. Another difference between both products is the titratable acidity. Since a satisfactory flavor and texture are only obtained at a pH below 4.5 and the concentrated milk has a greater buffering capacity, the latter is fermented to an acidity of about 130°N, versus 90-100°N for nonconcentrated milk.

Another type is stirred yogurt, virtually always made from nonconcentrated milk. After a gel is formed, it is gently stirred to obtain a smooth and fairly thick, but still pourable, product. There are other differences in the manufacturing process. Set yogurt is fermented after being packed, implying that final cooling has to be achieved in the package. Stirred yogurt is almost fully fermented before it is packed. Another difference is that only certain strains of yogurt bacteria produce the correct consistency or thickness after stirring, and only so when incubating at a fairly low

temperature. However, the bacteria make less of the desired flavor compounds at lower temperatures. In order to ensure that stirred yogurt has a distinct yogurt flavor, it is necessary that the starter be propagated under the same conditions as for set yogurt. This means at about 45°C, and with such an inoculum size and incubation time as to reach about equal numbers of cocci and lactobacilli.

Acidification will go on after the product has been cooled. To minimize or even prevent ongoing acidification, stirred yogurts or yogurt-like products are sometimes pasteurized; this also prevents growth of any yeasts and molds present. To allow pasteurization without the product becoming inhomogeneous, it is necessary to add thickening agents (pectins, modified starch, gelatin).

Processes for continuous, i.e., flow—through, manufacture of stirred yogurt have been developed. This would have considerable advantages, such as better control of fermentation and further manufacture, smaller losses, and more efficient use of water and energy. For the manufacture of set yogurt, continuous preincubation, to a stage where no setting occurs as yet, is also possible; to prevent texture defects, the pH at the stage of packing should not be lower than about 5.2.

2.6.3 Physical properties (Walstra et al., 1999)

The physical structure of yogurt is a network of aggregated casein particles onto which part of the serum proteins have been deposited due to their heat denaturation. The network encloses fat globules and serum. The largest pores of the network are on the order of $10~\mu m$. The existence of a continuous network implies that yogurt is a gel, a viscoelastic material characterized by a fairly small yield stress (say, 100~Pa). If the gel is broken up, as in the making of stirred yogurt, a fairly viscous non-Newtonian liquid can be formed; it is strongly shear rate thinning and thus has an apparent viscosity. Set and stirred yogurt have markedly different textures.

2.6.3.1 Firmness of set vogurt

Firmness of set yogurt is often estimated by lowering a probe of a given weight and dimension into the product during a given time. The reciprocal of the penetration depth then is a measure of firmness. Firmness is not closely related to an elastic modulus but rather to a yield stress.

2.6.3.2 Viscosity of stirred yogurt

Stirred yogurt should be smooth and fairly viscous. A good product also gives the impression of being "long" or "stringy"; when slowly pouring it, a fairly thin thread readily forms that behaves somewhat elastically when it breaks. Viscosity is most easily determined by means of a Ford cup; a given amount of yogurt is allowed to flow from an opening at the conical lower end of a cup, and the time needed for that is a measure for the viscosity.

The product is strongly shear rate thinning. After a high shear rate is applied, the apparent viscosity at lower shear rates is permanently decreased and the viscous behavior becomes closer to Newtonian. This implies a lasting structural breakdown. (For completeness, the viscosity increases a little on prolonged standing). This is all in agreement with the behavior of a liquid containing gel fragments. The viscosity increases with the viscosity of the continuous liquid ("solvent" or "whey") and with

the volume fraction of gel fragments. The latter is larger than the volume fraction of casein particles because the fragments contain a lot of interstitial solvent.

Vigorous agitation of stirred yogurt during further processing must be avoided to prevent the product from becoming too thin. Packing machines can be especially damaging.

2.6.4 Flavor defects and shelf life (Walstra et al., 1999)

A main quality problem with yogurt is that souring tends to go on after delivery to the retailer, and the product may be too acidic when consumed. Moreover, the yogurt may become bitter due to excessive proteolysis; this would also depend on the starter strains used. The development of these defects generally determines the shelf life. Of course, the product is cooled to slow down acidification, but it is difficult to cool it fast enough. Set yogurt is present in a package and cannot be stirred; stirred yogurt should not be stirred too vigorously because it would then become too thin. And even at refrigerator temperatures, acidification and other changes caused by the enzyme systems go on, albeit slowly.

Other defects may be caused by contaminating organisms, mainly yeasts and molds. The off-flavors may be characterized as yeasty, fruity, musty, cheesy, or bitter, and, occasionally, soapy-rancid. A flavor threshold is generally reached at a count of about 10⁴ yeasts and molds per ml. The growth of these microbes is largely determined by the amount of oxygen available, and hence by the head space volume and the air permeability of the container.

Another defect is too little of the characteristic flavor (which is of less importance in yogurts with added fruits). It may be due to a low incubation temperature, an excessive growth of the streptococci, or by the lactobacilli being weak aroma producers. Insufficient acidification, e.g., because the milk is contaminated with penicillin, also leads to a bland product. Finally, off-flavors in the milk used for manufacture may naturally cause flavor defects in the product.

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