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Chemistry of Maple Syrup

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Adapted from C.O. Willits and C.H. Hill 1976. Maple Syrup Producers Manual. USDA Agriculture Handbook No. 134 and North American Maple Syrup Producers Manual, 2nd ed, 2006

General Background

Maple syrup is primarily composed of a mixture of sugars, water, and minerals. In addition to these three components maple syrup will contain small amounts of various other organic compounds such as organic acids, amino acids, proteins, phenol compounds and even a few vitamins. Variation in the levels of these various components gives maple syrup the broad spectrum of flavors experienced with syrup from different producers and from different sap runs at the same location. As sap is concentrated into maple syrup some of the minerals may precipitate out of solution forming “sugar sand” in the bottom of the evaporator pan, caught in the syrup filters or precipitated on the bottom of the syrup container. When making any maple confection it is critical that the syrup have a good flavor as most off flavors will only be further concentrated resulting in poor tasting products. Once you have selected syrups with excellent flavor, selecting the syrups based on correct chemistry for the desired confection is second in importance. Third, you must select the cooking, cooling and stirring program that will give you consistently high quality confections.

In maple syrup at 66.0° Brix the sugar is completely in solution and it is a stable solution. When you continue to cook syrup, the concentration of sugar in the syrup continues to increase as temperature increases and as water is lost. The sugar remains in solution at the higher temperature even though much of the water boils away. When the syrup reaches the desired temperature for a particular confection and begins cooling, there is more sugar than can remain in solution at lower temperatures. The solution is said to be super-saturated. Agitation or stirring of any kind can cause the sugar to crystallize and come out of solution until the sugar in solution reaches a stable concentration for its temperature. The fact that sugar solidifies into crystals is extremely important in making confections. The amount of sugar that can be in solution in a given volume of water varies with the temperature of the solution. Hot solutions can contain more sugar and cool solutions less sugar. This is why accurate measurement of the temperature of heated syrup is so important.

It is this ability to increase the sugar concentration above the stable level that enables the production of maple confections. All maple confections depend on producing a syrup solution containing more sugar than can be retained in solution at room temperature (made by additional evaporation) and then either encouraging, controlling, or preventing the subsequent sugar crystallization process that occurs with cooling. When making a sugar glass (non-crystalline hard confection like suckers or hard candy) crystallization is prevented by managing temperature or syrup sugar chemistry. When making a crystallized confection, crystallization is controlled through such actions as regulating the rate and extent of cooling and the degree of agitation or stirring. The slower this crystallization process occurs, the larger the sugar crystals. The chemistry of the supersaturated syrup can be identical, but the products produced can be completely different due to the different ways the syrup is cooled and stirred. At the same time differences in the chemistry of supersaturated syrups cooled and stirred exactly the same can result in very different qualities of the final products.

Crystallization

The crystalline or grainy nature of the precipitated sugar is determined by a number of factors, all of which are influential in making the desired type of confection. These factors include the amount of excess sugar in solution, seeding, the rate of cooling, syrup chemistry and the amount and time of stirring. Large crystals, called rock candy, which represent one extreme, are formed when slightly supersaturated syrup (67° to 70° Brix) is cooled slowly and stored for a long time without agitation. A glass-like non-crystalline syrup represents the other extreme. This is formed when highly supersaturated syrup (the boiling point is elevated 18° F. or more above the boiling point of water) is cooled rapidly to well below room temperature without stirring, as when making sugar on snow. The syrup becomes so viscous that it solidifies before crystals can form and grow. In contrast, if the hot supersaturated sugar solution is stirred while it is cooling, the tendency to form crystals increases. The mechanical shock produced by the stirring causes microscopic crystal nuclei to form. Continued stirring mixes the crystals throughout the thickened syrup, and they grow in numbers and in size. Different sizes of crystals are preferred in different kinds of confections. Granulated sugar for instance is best with a fairly large crystal that can easily been seen and felt with the tongue. To make granulated sugar the syrup is evaporated to the desired temperature and is not cooled at all before stirring is started. For maple cream the desire is to have a smooth creamy texture where no crystals can be felt with the tongue. Here the supersaturated syrup is allowed to cool without stirring until it is somewhere between 50 and 90º F. Both the temperature at stirring and the method of stirring have an effect on the size of the crystals formed in the cream and the stability of those crystals over time. The cooler the temperature when stirring begins the longer, in weeks and months, the crystals will stay the same size and resist growing.

Controlling Crystallization

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The formation of sugar crystals in many confections and recipes is controlled by the temperature and stirring procedures. However the syrup chemistry is also an important factor. Controlling the size of crystals or preventing crystals with crystal inhibitors is used in making many sugar confections and candies. Large crystals of sucrose have a harder time forming when molecules of invert sugars are present. Crystals form something like building blocks locking together. If some of the molecules are a different size and shape, they won't fit together, and a crystal doesn't form or grows with much more difficulty. The influence of invert sugars, common in natural maple syrup, on crystallization should be well understood by maple confectioners. Many times maple producers complain of batch failures when making confections because the natural mix of types of sugar in the syrup was out side of the normal range for the confection desired. The use of corn syrup to make maple suckers and hard candy or use of invertase to make shelf stable maple cream all are related to the higher concentration of invert sugars and their role in controlling growth of sucrose crystals. The influence of invert sugar on making maple confections is discussed in depth in the next section.

Inhibitors

Crystallization inhibitors also can include various acids, fats and proteins. The addition of acids, like cream of tartar, fruit juices or vinegar, inhibits crystal size. Fats, like margarine, butter, cream, whole milk, or chocolate, also inhibit crystal size, as does protein in the form of milk, egg white, and gelatin. Fat and protein inhibit crystallization by providing physical barriers, coating the crystal face and preventing one molecule from growing on another, thus keeping the crystals small or stopping crystallization altogether. Corn syrup or honey is often used in candy making since they promote super-saturation by inhibiting the formation of crystals. Many specialty products can be made using maple syrup along with various crystal inhibitors. These candies do not have sugar crystals when they have sufficient crystal inhibitors in them or when they are cooked to such a high temperature that all the water has evaporated and the syrup is too viscous for the crystals to orient themselves into a crystalline structure. Examples include caramels, taffies, brittles, hard candies, marshmallows, fluff, meringues, frostings and gumdrops. The excessive use of a fatty de-foamer in making crystalline confections may result in unexpected soupiness or lack of proper crystal formation

Invert Sugar

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Sucrose is a twelve carbon sugar having the chemical formula C12H22O11. Invert sugars are six carbon sugars, such as glucose (dextrose) and fructose (levulose), which are structurally different but both with the chemical formula C6H12O6. You may also see them referred to as hexoses or reducing sugars. For purposes here I will refer to them independently as glucose and fructose or together as invert sugars. Invert sugars are produced by the splitting of sucrose, commonly by the action of microorganisms, acids or the enzyme invertase. Sucrose is common table sugar and is the only sugar in sap when it comes from the tree. Some of the sucrose in sap is converted to invert sugar as a result of microbial fermentation during handling and processing. This change occurs in all sap and is most common in syrup produced from sap that is collected late in the season when temperatures are warmer.

Advantages

A small amount of invert sugar is desirable in maple syrup that is to be made into maple confections. Invert sugars are more soluble in water than sucrose at room temperature meaning more total sugar can be held in solution before crystallization occurs. This helps keep the product moist, and it also encourages smaller sugar crystals to form. Too little invert sugar in the syrup can cause the product to be grainy; too much may prevent formation of crystals. Other properties of invert sugar include an increase is sweetness compared to sucrose alone, reduced viscosity making it easier to spread creams or frostings, softening of a product's texture, reducing water activity making products more resistant to yeast, mold or bacteria fermentation, and depression of the freezing point so products stored in the freezer are less likely to crystallize or change in crystal structure.

Maillard Reaction

Invert sugar is one of the ingredients of the Maillard browning reaction. This is one of the chemical reactions that happens when heating syrup and can lead to darker color and stronger flavor. When cooking syrups for confections, producers should recognize that high invert levels may increase the darkening particularly where invertase or acids have been used to create a very high level of invert sugar. Converting too much of the sugar in maple syrup to invert sugar can alter the taste so that it becomes more like the characteristic honey flavor.

Invert Sugar in Grades

In general, all grades of maple syrup contain some invert sugar, and the amount varies among different grades. Lighter syrup (Grade A Light Amber), particularly that made early in the production season, generally has the least invert sugar; very dark syrup (Grade B or Extra Dark for Cooking), particularly that made late in the production season, has the most invert sugar. The grade of syrup can be a very general guide in selecting syrup for making a specific confection but testing has shown a wide variation in invert levels in the different grade classifications. A simple test using the common glucose meter used to monitor blood sugar levels can be very helpful in selecting and blending syrups to make the most consistent products. This can be especially valuable if syrup is being purchased for the purpose of making confections. For complete information on testing for invert sugars in maple syrup see the fact sheet titled “Invert Sugar in Maple Syrup”.