

Chemical Changes in Carbohydrates Produced by Thermal Processing

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Carbohydrates are the predominant chemical species in our diet. They are the major source of both energy and bulk or fiber. Chemically, carbohydrates vary from the low-molecular-weight sugars, such as glucose, fructose, and sucrose, to some of the largest natural polymers known, amylopectin and cellulose. Some of these high molecular-weight entities are made up of a single simple sugar; for example, the amylopectin fraction of starch is made up essentially of glucose. With a molecular weight of 400×10^6 , it thus contains about 3×10^6 glucose residues. Other complex carbohydrates consist of numerous sugars and may contain noncarbohydrates, such as proteins, lipids, and phenolics.

Most of our foods are thermally treated in bakeries or canneries before we consume them. In many instances, the thermal treatment is carried out by processing establishments and by the purchaser; for example, bread is baked in bakeries and may be reheated or toasted just before consumption. Almost invariably the thermal treatment changes the food (bread is different from dough, baked potato is different from raw potato). Such changes often involve reactions of the carbohydrates and can be quite complex. It is those changes that we will deal with in this discussion.

Browning Reactions

Given a choice between a raw piece of dough and a baked loaf of bread most of us would choose the loaf of bread. We "know" it has a better aroma and taste than does the dough. How does the thermal processing (baking) change the aroma and flavor? If we take a sample from the center of a freshly baked loaf of bread, we find it to be doughy in taste and aroma. The texture has changed from that of the raw dough, but we shall discuss that phenomenon later. This simple demonstration should convince us that the flavor and aroma of fresh-baked bread comes from changes that occur at the crust and not in the interior of the loaf. Another way of reaching the same conclusion is to try Chinese steamed bread. Steamed bread does not have the brown crust and does not have the flavor and aroma that we associate with freshly baked bread.

Granting that the flavor and aroma comes from the crust, what happens during the formation of crust? When bread or other baked foods are placed in a hot oven the moisture at the outer surface of the piece evaporates rapidly. Although water from the moist interior of the piece will diffuse to the surface and replace the water that has evaporated, the rate of evap-

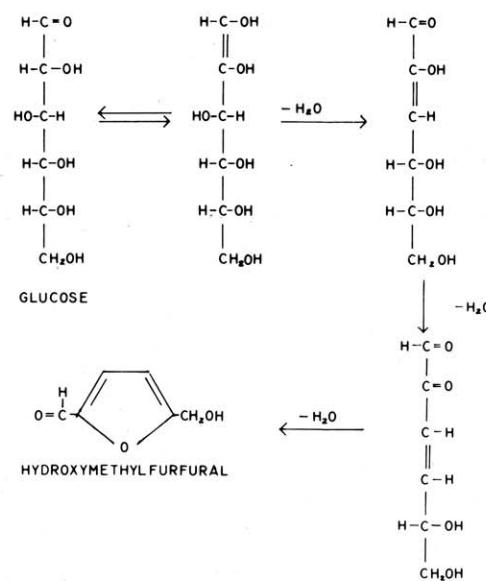


Figure 1. The conversion of glucose to hydroxymethyl furfural.

oration is relatively fast compared to the rate of diffusion. Therefore, as baking proceeds there is a gradient of decreasing moisture from the center to the outside of the piece and the crust becomes very dry. It is the dry and hot surface that induces browning to occur late in the baking cycle.

The chemistry of the flavor and aroma compounds formed during browning is quite complex (1) and clearly outside the scope of this paper. The browning of most baked products is by Maillard-type reactions. The first step of these reactions is the condensation of the free amino group, usually from an amino acid, with the carbonyl of a reducing sugar. Because water is eliminated in the reaction, the reaction is favored by dehydration conditions. After the condensation there are a number of rearrangements that lead to the brown pigments. Free amino groups are found in most, if not all, baked foods. Since sucrose is a nonreducing sugar and is the one most often used in baked food, we may not always get browning. In yeast-leavened products browning does occur because the active invertase in yeast rapidly converts sucrose to glucose

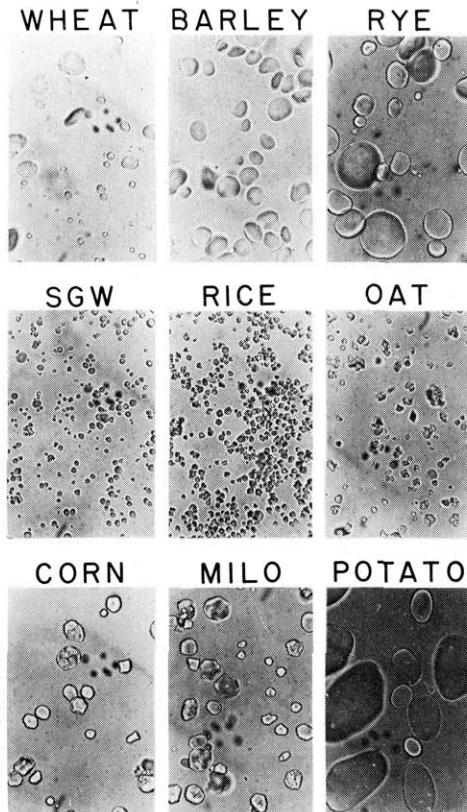


Figure 2. Light photomicrographs of an isolated small-granule wheat starch (SGW) and prime starches isolated from wheat, barley, rye, rice, oat, corn, grain sorghum (milo), and potato (18).

and fructose, both reducing sugars. However, in cake the sucrose is quite stable and our cakes do not brown unless we add another source of reducing sugar. The most common other source is milk, which contains the reducing sugar lactose, or eggs which contain small amounts of glucose.

Sugars also can brown in the absence of free amino groups. This process is also a dehydration followed by various rearrangements and is called caramelization (2). The reactions occur at moderate pH values. The steps thought to lead to hydroxymethyl furfural are given in Figure 1. Hydroxymethyl furfural polymerizes into brown pigments. Caramelization is commonly used in candy and icing preparation, where sugar and small amounts of water are heated to relatively high temperature to give caramel flavor. If butter is used in place of water, a butterscotch flavor is produced.

Starch in Food Systems

Starch is the predominant chemical entity in our foods. It makes up 70% or so of the cereals and tubers (dry weight) that are such a large part of our diets. In addition, starch is found in much lower quantities in many fruits and in beans and other legumes.

Starch in our uncooked food occurs as small packets or granules. The size and shape of the granules vary with the source (Fig. 2). In many cases they vary even within a single source. For example, wheat starch varies both in size and shape (Fig. 3). The large starch granules in wheat are about 35 μm across and are lenticular. The small granules are only 2 to 5 μm in diameter and are spherical.

The molecules in starch granules are ordered. Because of this order the granule defracts plane-polarized light in the characteristic maltese cross pattern (Fig. 4). This property is called birefringence. The birefringence is often confused with crystallinity. However, material can be birefringent (ordered) but not crystalline. Starch, it turns out, is both birefringent

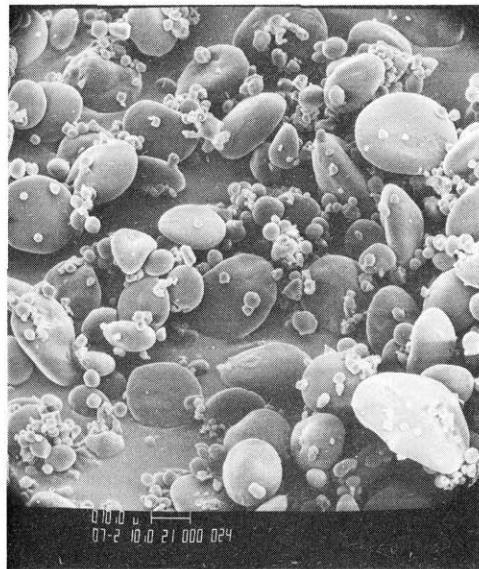


Figure 3. Scanning electron photomicrograph of starch isolated from a flour-water slurry (19).

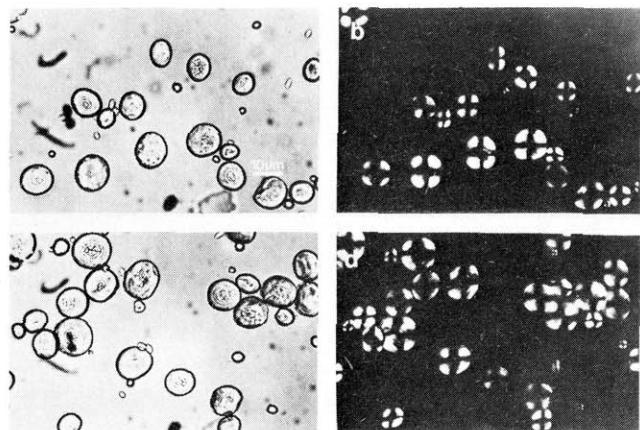


Figure 4. Bright field and polarizing micrographs of wheat starch heated in the DSC to 57°C (a,b) and 64°C (c,d) at a water-to-starch ratio of 0.5 (5).

and partially crystalline. The crystallinity can be seen by X-ray diffraction (Fig. 5).

When starch is heated with excess water it undergoes a transition from ordered to disordered that we call gelatinization. As shown in Figure 6, the transition can be followed conveniently with a differential scanning calorimeter. The thermogram is a plot of heat flow versus temperature and the area under the curve gives an estimate of the energy used in the transition. As shown in the figure, the area under the curve decreases as the water content is decreased. Also as water is decreased the thermogram becomes biphasic and the temperature range over which the transition occurs is much broader.

The term gelatinization is often used to describe all changes that occur when we heat starch and water, however, it should be restricted to the loss of birefringence. Once the starch has lost its birefringence, continued heating to higher temperature with water brings about a continuum of changes. These changes can be described best as solubilization. With wheat starch, complete solubilization occurs at about 120°C. As most food systems are heated to less than 100°C and with limited water, our cooked foods are a mixture of solubilized and insoluble starch.

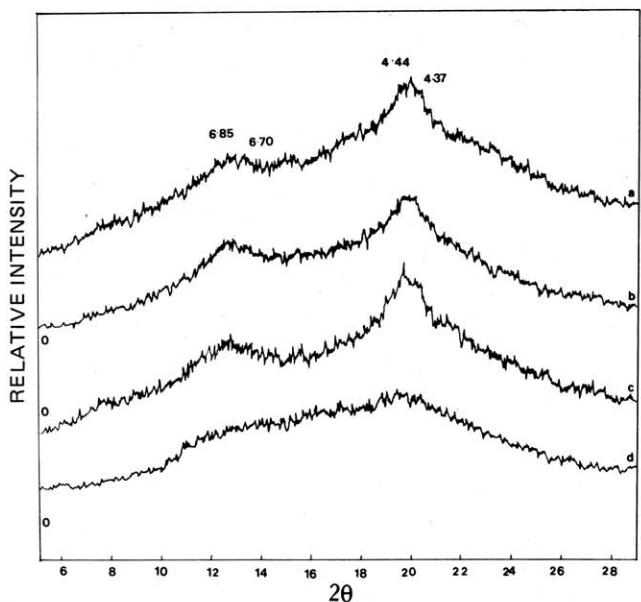


Figure 5. X-ray diffraction patterns of the insoluble residue of wheat starch heated with sodium stearoyl lactylate to: a, 60°C; b, 70°C; c, 80°C; and d, 95°C (20).

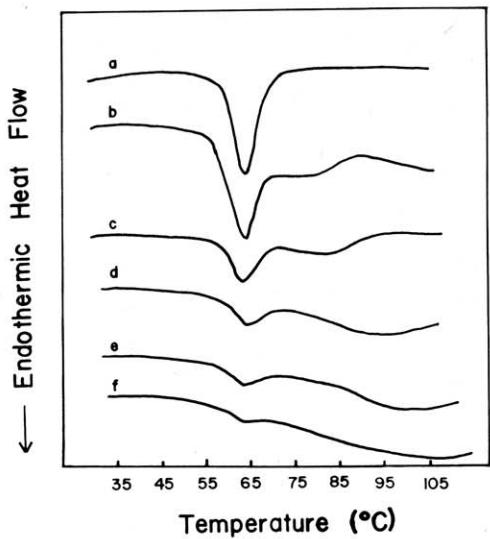


Figure 6. Differential scanning thermograms of wheat starch heated with water-to-starch ratios of: a, 2.0; b, 1.0; c, 0.75; d, 0.5; e, 0.44; f, 0.35 (5).

Raw (uncooked) starch does not absorb much water (about 30% of its dry weight). Evidently, the crystallinity of the starch limits its swelling and thus limits the amount of water it can absorb. With gelatinization, the crystallinity is lost and the granules are free to swell. With swelling the granule is free to take up much more water. Also with gelatinization the starch loses its raw starch taste and becomes smooth or cooked.

Cooking starch or starchy foods in water leads to an increase in the viscosity of the cooked product, gravies and sauces being good examples. The rather large increases in viscosity (Fig. 7) can be followed conveniently with an amylograph. In the amylograph a dilute starch:buffer (4% starch) solution is heated at a constant $1\frac{1}{2}^{\circ}\text{C}/\text{min}$ and the relative viscosity recorded. The rapid increase in viscosity appears to be the result of two factors (3, 4). The uptake of water by the starch granules decreases the amount of water remaining in the system. The starch that is solubilized during the heating then is dissolved in less total water resulting in a more viscous system. In limited water systems, such as cake batters or bread doughs,

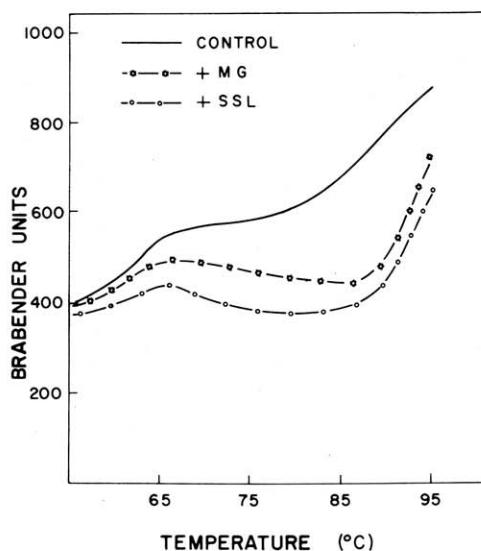


Figure 7. Effect of 2% monoglyceride (MG) or sodium stearoyl lactylate (SSL) on the Brabender viscosity of wheat starch (3).

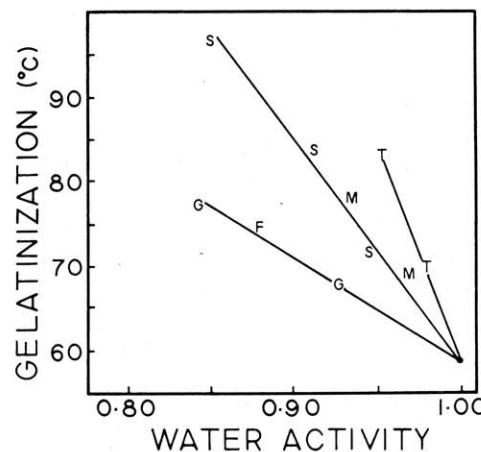


Figure 8. Water activity of sugar solutions versus gelatinization temperature; F = fructose, G = glucose, M = maltose, S = sucrose, T = maltotriose (7).

the viscosity becomes very large, and the cake or bread sets.

The temperature at which starch gelatinization occurs depends first on the source of starch. For example, potato starch gelatinizes at a lower temperature than does corn starch. Generally, we must speak of a gelatinization temperature range rather than a specific temperature. With most starches, the temperature range over which gelatinization occurs in excess water is $7\text{--}10^{\circ}\text{C}$. As water becomes more limiting (Fig. 6) the temperature range becomes much broader (5). The temperature at which starch starts to gelatinize does not change as water is limited (6, 7). The second major factor that affects starch gelatinization temperature is which and how many molecules are dissolved in the available water. Small molecules dissolved in water will decrease the water activity. As water activity is decreased gelatinization temperature is increased. Sugars, of course, will affect water activity. In addition to their effect on water activity, sugars (Fig. 8), will cause starch gelatinization to occur at higher temperatures apparently by an additional mechanism (7, 8). In many of our food systems this is used to control the temperature at which the product sets.

Starch heated beyond its gelatinization temperature forms a paste, which, when cooled, becomes a gel. The gel results from the hydrogen bonding between water and the soluble

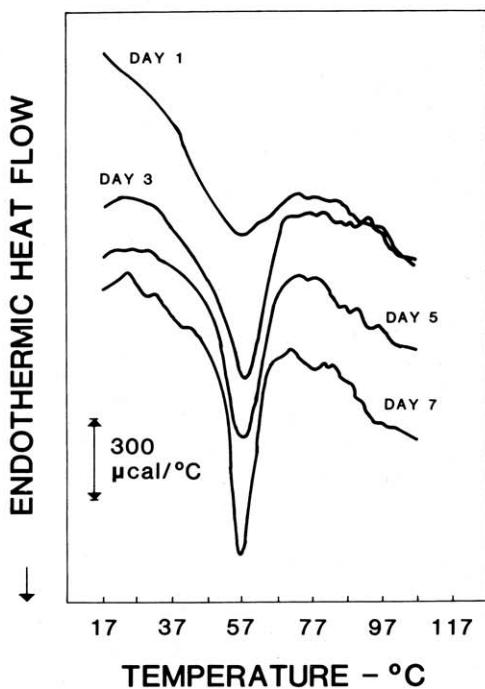


Figure 9. DSC thermograms of bread samples stored for 1, 3, 5, and 7 days (10).

starch molecules. With time, and particularly with freezing and thawing, water is expressed from the gel (syneresis). This is caused by the hydrogen-bonding of starch with starch, which eliminates water. Modified starches (primary cross-linked starches) are fixed in space and thus cannot get close enough together to hydrogen bond. Thus, such starches produce gels that have good freeze-thaw stability.

Starch gels when stored, particularly at low temperature, often become cloudy. This is caused by a recrystallization of the starch, a process called retrogradation. The recrystallization does not give the same crystal structure (X-ray diffraction pattern) as found in ungelatinized starch granules. Von Eberstein et al. (9) have shown differential scanning calorimetry (DSC) data for both amylose and amylopectin retrogradation. In dilute systems the amylose fraction of the starch will retrograde very rapidly. However, in food systems where water is quite limiting, the amylopectin appears to be the fraction that slowly retrogrades. Bread crumb that had retrograded for different periods of time gave, in general, a larger DSC peak with longer storage time (Fig. 9).

This retrogradation phenomenon generally is considered to be a major factor in bread staling and, indeed, the firming that is found in many starchy foods. It appears that staling probably involves more than just retrogradation, but retrogradation undoubtedly is one of the factors. It is interesting that bread can be refreshed simply by heating (toasting). This is clearly shown in Figure 10, in which bread staled for 5 days was heated in "browning bags" to various temperatures and the firmness determined. The use of the browning bags allows the bread to be heated without a significant moisture loss. With this reheating, the crystal structure of the retrograded starch disappears. The relationship between crystal structure and firmness, however, does not appear to be strictly causative (10).

Hydrolysis of Carbohydrates

Carbohydrates by their very nature as hydrates of carbon are not stable under extremes of thermal processing. High heat will bring about dehydration, as discussed previously. With large molecules, such as starch, large increases in thermal

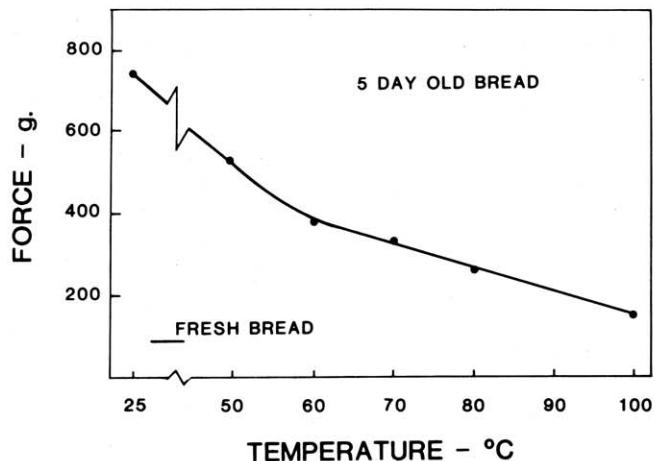


Figure 10. Effect of reheating temperature on freshness of a five-day-old bread sample (10).

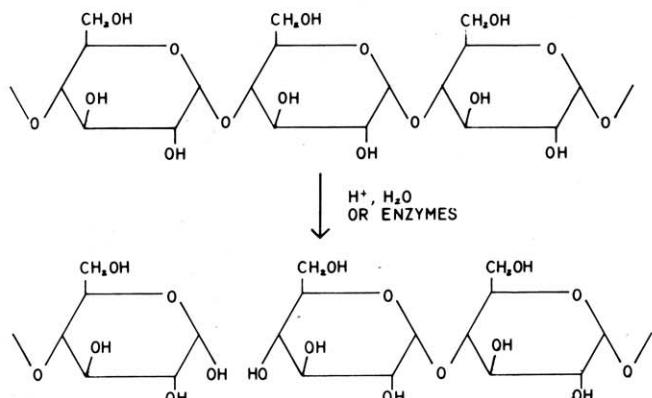


Figure 11. Hydrolysis of an α -1,4-glycosidic bond in a segment of a starch chain.

energy will result in the formation of dextrans. One type of starch modification still used is a dry roasting process that produces dextrans (11).

At less extreme temperatures carbohydrates, and particularly starch, can be hydrolyzed in aqueous systems (12). The amount of thermal energy required is greatly dependent on the pH of the media. At low pH, the amorphous regions of starch will hydrolyze at a reasonable rate at room temperature (Fig. 11). Near neutral pH, the hydrolysis is slow even at elevated temperatures (see table).

Extrusion Cooking

The cooker-extruder has become popular for thermal processing of both food and feed products (13). The cooker-extruder is actually an inefficient pump. Most of the heat used for the thermal processing is generated from friction. In a cooker-extruder, both temperature and pressure increase as the feed material progresses down the barrel. Thus, thermal processing is rather severe. The fact that the system is closed and thus excludes oxygen undoubtedly limits the amount of chemical change that we see in the carbohydrates during extrusion.

Much of the effectiveness of the cooker-extruder is because of factors other than the thermal processing, such as the shear imparted by the rotating screw and the effect of the rapid change in pressure as the feed material exits the extruder die. Both of those factors are important in the changes brought about in the extrudates.

Effect of Microwave Heating of Starch in Sealed Tubes ^a

Conc. of Starch (%)	Duration of Heat Treatment (min.)	pH	Reducing Sugar/ Starch (%)
10	16	4.5	3.1
20	16	3.8	7.9
30	16	3.8	19.3
30	18	3.2	41.7
30	20	3.1	53.4

^a Adapted from ref. (12).

Cookies and Candies

Although they may not seem so, many cookies and candies are very similar. Of course, the wide variations in both cookies and candies make generalizations difficult. The most pronounced changes that occur during thermal processing of either cookies or candies is the browning reaction that affects flavor and aroma.

As a result of thermal processing of sugar in these very limited water systems, practically no change in the chemical structure of the carbohydrates is found. In fact, with the limited water and high amounts of sugar found in many cookies, the starch does not gelatinize during baking (14). Instead, the water-to-carbohydrate ratio is changed, and thus, upon cooling, the sugar is found in a much different physical form. An example would be the heating of sugar, water, and minor flavor components to a certain boiling temperature (determined by the sugar/water ratio) and then rapidly cooling the mixture to give a glass that we know as hard candy. Improper temperature control will yield a system in which the sugar will recrystallize and thus change the texture of the candy.

In cookies the system is much more complicated because, in addition to sugar and water, the formula contains flour, baking soda, leavening acids, milk, and many other ingredients. During baking, water is driven off, and the sugar/water ratio is changed. Generally, a glass is not formed because of all the impurities. However, after cooling, a crystallization of the sugar may occur that changes the cookie from a soft, pliable type to one that breaks with a snap (15).

Gums

The naturally occurring gums or hydrocolloids are chemically quite diverse (16, 17). Most of the important gums are primarily carbohydrate, but their diversity of composition makes changes due to thermal processing difficult to summarize. Most gums are useful because they alter the viscosity of solutions. Unlike starch, which is heat triggered, most gums are not greatly affected by heat. The gums are usually classified according to their source for the naturally occurring one, for example, agar, alginates, arabic, carrageenan, guar, karaya, locust bean. The synthetic gums are more often classified by the chemical type, carboxymethyl cellulose or xanthan, for example.

Gums are used in foods to increase viscosity, to stabilize,

to emulsify, and to alter the texture of the products. Applications would include stabilization of icings and glazes, increasing the viscosity of salad dressings, and many others. Perhaps the most common effect of gums with thermally processed food is the modification of crystal growth in ice cream manufacture. The physical alteration of crystal growth give rise to smooth ice cream. Without such modification ice crystals will grow large giving a gritty or icy product.

Summary

Carbohydrates are a major part of our diets and vary widely in their chemical make-up. Most of our food is thermally processed before consumption. The changes occurring as a result of that thermal processing are also quite varied. The carbohydrates are involved in the browning that occurs during thermal processing. That browning is responsible for much of the color and aroma of foods.

Starch is our most predominant chemical entity in our foods. The changes that starch undergoes as it is heated with water has a great influence on texture and taste (raw versus cooked) of many of our foods. In foods, starch acts as a heat-triggered water sink. The binding of the water by the starch leads to a rapid increase in the viscosity of the media. Thus, gravies or sauces thicken and bread doughs or cake batters set. The temperature at which those changes occur depends upon primarily the sugar content of the water in the food. It is also thought that starch is responsible for the staleness of foods such as bread, primarily by a recrystallization process called retrogradation.

Thermal processing also can cause other changes in carbohydrates. These can be hydrolysis of starch to form dextrins or sugars or simply a change in physical form as found with candies and cookies.

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