SYRUPS

1. Introduction

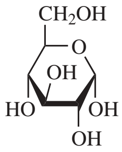
Corn sweeteners, maple syrup, and molasses, all commercially available syrups, are concentrated solutions of carbohydrate. These products, produced for a variety of food and nonfood applications, are in some cases also available in a dry form. Corn sweeteners are prepared from hydrolyzed starch (qv) and include dextrose [50-99-7] (D-glucose), high fructose corn syrup (HFS), regular corn syrup, and maltodextrin (see SWEETENERS), which all have in common the raw material source, general methods of preparation, and many properties and applications. Dextrose, the common or commercial name for D-glucose, is available as a syrup or as a pure crystalline solid. HFS is produced by the partial enzymatic isomerization of dextrose. Corn syrups and maltodextrins are clear, colorless, viscous liquids prepared by hydrolysis of starch to solutions of dextrose, maltose, and higher molecular weight saccharides. Maple syrup, like corn syrup, is a nutritive sweetener produced as a concentrated carbohydrate (sucrose) solution. Molasses is a syrup produced as a by-product of sugar (qv) manufacture.

2. Dextrose

Dextrose (D-glucose) is by far the most abundant sugar in nature. It occurs either in the monosaccharide form (free state) or in a polymeric form of anhydrodextrose units. As a monosaccharide, dextrose is present in substantial quantities in honey, fruits, and berries. As a polymer, dextrose occurs in starch, cellulose (qv), and glycogen. Sucrose is a disaccharide of dextrose and fructose.

Dextrose was first prepared in pure form from grapes in the seventeenth century (1). The finding remained a laboratory curiosity until an attempt was made to prepare dextrose commercially from grapes in 1801 (2). In 1815 it was reported that acid conversion of starch to sugar was the result of hydrolysis of the starch rather than dehydration, and that the starch sugar was identical to grape sugar (3). It is generally conceded, however, that Kirchoff's work in 1811 was the forerunner of the starch hydrolyzate industry (4). A sweet substance was produced by cooking a mixture of potato starch and sulfuric acid. The process was improved to crystallize dextrose from a syrup, although attempts to commercialize the process were later abandoned. By 1842, however, a starch industry had been developed in the United States and crystalline dextrose became an important commercial product once crystallization methods were discovered in the 1920s (5).

Commercial dextrose products are produced in both dry and syrup forms. Dry products are prepared by crystallization (qv) to either an anhydrous, $C_6H_{12}O_6$, or hydrated, $C_6H_{12}O_6{\cdot}H_2O$, form. These include dextrose hydrate [16824-90-1], anhydrous α-D-glucose [26655-34-5] (**1**), and anhydrous β-D-glucose [28905-12-6] (**2**). Syrup products are produced that contain from 95 to over 99% dextrose.



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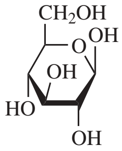


(**2**)

2.1. Properties. Physical properties of the three crystalline forms of dextrose are listed in Table 1. In solution, dextrose exists in both the α- and β-forms. When α-dextrose dissolves in water, its optical rotation, $[\alpha]_D$, diminishes gradually as a result of mutarotation until, after a prolonged time, an equilibrium value is reached (see Table 1). At this point, about 62% of the dextrose is present in the β-form. This equilibrium value is not significantly changed over a wide range of temperatures and concentrations. The same equilibrium value exists in anhydrous melts as well as in glassy materials. Pure crystalline β-dextrose is quite sensitive to moisture, changing to the more stable α-form if exposed to high humidity. At 25°C, α-dextrose monohydrate dissolves fairly rapidly, yielding a solution containing ca 30 wt% dextrose. Very slowly thereafter, further quantities of dextrose dissolve until a saturated solution containing ca 50 wt% dextrose is obtained. The first phase of the dissolving process results from the limited solubility of α-dextrose. The slow, subsequent dissolution is caused by the transformation of part of the dissolved α-dextrose to the more soluble β-form. When saturation is finally reached, a mixture of α- and β-dextrose in solution is in equilibrium with solid α-dextrose hydrate. At 25°C, anhydrous α-dextrose dissolves rapidly and beyond the limit of solubility of α-dextrose hydrate. Because the hydrate is the stable form at this temperature, crystallization of the hydrate occurs to its limit of solubility and the pattern then follows that of the hydrate. The rate of attainment of equilibrium is increased by heating or in the presence of acids or bases. The solubility of the equilibrium mixtures is given in Table 2. Additional data on the solubility of the crystalline forms are available (7).

Dextrose in solution or in solid form exists in the pyranose structural conformation. In solution, a small amount of the open-chain aldehyde form exists in equilibrium with the cyclic structures and . The open-chain form is responsible for the reducing properties of dextrose.

Dextrose shows the reactions of an aldehyde, a primary alcohol, a secondary alcohol, and a polyhydric alcohol. In acid solution, either after standing for a prolonged time or after heating, dextrose undergoes polycondensation, ie, dehydration, yielding a mixture of di- and oligosaccharides, most of which are the disaccharides gentiobiose [554-91-6] and isomaltose [499-40-1]. In acid solution and at high temperature, dehydration leads to formation of 5-hydroxymethylfurfural [67-47-0], which is a water-soluble, high boiling, and relatively unstable compound. Polymerization of 5-hydroxymethylfurfural yields dark-colored compounds that act as intermediates in the discoloration of sugar solutions. Further degradation of dextrose under these conditions also yields levulinic acid [123-76-2] and formic acid [64-18-6].

In mildly alkaline solution, the principal reaction of dextrose is partial transformation, ie, isomerization, to fructose and other ketoses. D-Mannose, saccharinic acids, and other decomposition products form to a lesser extent. In highly alkaline solution and particularly in the presence of atmospheric oxygen, a complex mixture of products of decomposition and rearrangement results. Mild oxidation in slightly alkaline solution results in a quantitative yield of D-gluconic acid. More vigorous oxidation with nitric acid yields glucaric acid, tartaric acid, oxalic acid, and other compounds resulting from fragmentation of the dextrose molecule. Alkaline Fehling's solution is reduced by dextrose. Roughly five atoms of copper are reduced per molecule of dextrose. Catalytic hydrogenation of dextrose is practiced commercially to manufacture sorbitol [50-70-4].

When dextrose is heated with methanol containing a small amount of anhydrous hydrogen chloride, α-methyl-D-glucoside is obtained in good yield and can be isolated by crystallization. Similar reactions occur with higher alcohols, but the reaction products are more difficult to isolate by crystallization. Dextrose reacts with acid anhydrides in the presence of basic catalysts, yielding esters. Complete reaction gives the pentaacylated derivative.

The reaction of dextrose with a nitrogen-containing compound, eg, amino acids or proteins, yields a series of intermediates which form pigments of varied molecular weight (Maillard reaction). The type of pigments produced is dependent on reaction conditions such as pH, temperature, and concentration of reactants.

Dextrose is the fundamental intermediary metabolite in carbohydrate metabolism. Other utilizable monosaccharides are largely converted to dextrose before being further metabolized. Starch, glycogen, and the common disaccharides are hydrolyzed enzymatically in the alimentary canal. The resulting monosaccharides are absorbed into the portal vein blood, by which they are transported first to the liver and then to all other parts of the body. In the liver, monosaccharides other than dextrose, eg, galactose and fructose, are largely converted to dextrose before they reach other tissues. When dextrose is taken up by body tissues, it is phosphorylated to glucose-6-phosphate, which can enter the glycolytic pathway or be stored as glycogen. Dextrose metabolism is discussed in more detail in Reference 8.

2.2. Manufacture. Dextrose is manufactured almost exclusively from corn (maize) starch in the United States. In other countries, starch from sorghum (milo), wheat, rice, potato, tapioca (yucca, cassava), arrowroot, and sago are used to varying degrees along with corn starch. Prior to the 1960s, commercial dextrose was produced using acid and acid–enzyme hydrolysis processes that yielded only about 86 and 92–94% dextrose, respectively. The development of thermostable bacterial α-amylase enzymes led to total enzyme processes that eliminated acid degradation products and increased dextrose yield to about 95–97%.

In an enzymatic process, starch is hydrolyzed (thinned or liquefied) with a bacterial α-amylase. The resulting substrate is then hydrolyzed to dextrose (saccharified) using glucoamylase, a fungal enzyme that preferentially cleaves dextrose from the partially degraded starch. The initial extent of liquefaction is generally in the range of 10–20 dextrose equivalent (DE). DE is a measure of the reducing-sugar content calculated as dextrose and expressed as a percentage of the total dry substance. Several industrial enzyme liquefaction processes are used commercially (9) (Fig. 1). These processes are referred to as (*1*) enzyme–heat–enzyme, (*2*) low temperature, (*3*) dual enzyme/dual heating, (*4*) dual enzyme/single heating, and (*5*) thermal liquefaction.

Enzyme–Heat–Enzyme Process. The enzyme–heat–enzyme (EHE) process was the first industrial enzymatic liquefaction procedure developed and utilizes a *B. subtilis*, also referred to as *B. amyloliquefaciens*, α-amylase for hydrolysis. The enzyme can be used at temperatures up to about 90°C before a significant loss in activity occurs. After an initial hydrolysis step a high temperature heat treatment step is needed to solubilize residual starch present as a fatty acid/amylose complex. The heat treatment inactivates the α-amylase, thus a second addition of enzyme is required to complete the reaction.

In the EHE process, a starch slurry is prepared and calcium, as the chloride or hydroxide, is added as a cofactor to provide heat stability to the enzyme. The starch slurry is passed through a stream injection heater and held at temperature for about one hour. The resulting 4–8 DE hydrolyzate is then subjected to a heat treatment in a holding tube, redosed with enzyme, and allowed to react for one hour to a DE level of 10–15.

Low Temperature Process. The low temperature process was developed when *B. licheniformis* and *B. stearothermophilus* α-amylases became commercially available in the 1970s. These enzymes are more thermostable, more aciduric, and require less calcium for stability than the *B. subtilis* enzyme used in the EHE process. Consequently, the high temperature EHE heat treatment step was no longer required to attain efficient liquefaction.

In the low temperature process, the slurry is heated to 105–108°C and held at temperature for 5–10 minutes. The resulting 1–2 DE hydrolyzate is flashed to atmospheric pressure and held at 95–100°C for one to two hours in a batch or continuous reactor. Because the enzyme is not significantly deactivated at the first-stage temperature, a second enzyme addition is not needed. This process is used worldwide throughout the starch-based sweetener industry and has been judged the most efficient process for dextrose production.

Dual-Enzyme Processes. In some cases, especially in syrup production in Europe, a liquefaction process is used that incorporates both a thermostable enzyme and a high temperature heat treatment. This type of process provides better hydrolyzate filterability than that attained in an acid liquefaction process (9). Consequently, dual-enzyme processes were developed that utilized multiple additions of either *B. licheniformis* or *B. stearothermophilus* α-amylase and a heat treatment step (see Fig. 1).

In these processes, the starch slurry is prepared in the same manner as in the low temperature process. In a dual-enzyme/dual-heating process, the steps are the same as the low temperature process until the completion of the second-stage reaction. Then, a 2–5-min heat treatment followed by a second enzyme addition and another reaction step is employed. In a dual-enzyme/single-heating process, the starch slurry is immediately heated to 145–150°C for one minute or less. Although the enzyme is rapidly inactivated, sufficient hydrolysis takes place to provide a partially thinned hydrolyzate that can be pumped to a second stage where additional enzyme is added and the reaction continued at 95–100°C for 20–30 minutes. The temperature is then lowered for the remainder of the reaction.

Thermal Liquefaction Process. In the thermal liquefaction process (see Fig. 1), a starch slurry containing no enzyme or added calcium is heated for several minutes. The slurry is slightly acidic and sufficient acid liquefaction is achieved to reduce viscosity. The hydrolyzate (at essentially zero DE) is flash-cooled to 95–100°C, α-amylase is added, and the pH is adjusted. The reaction then goes to completion.

Saccharification. Regardless of the starch liquefaction process, dextrose is produced by the action of glucoamylase during a subsequent saccharification step. Glucoamylase is produced in submerged fermentation from strains of *Aspergillus niger*. A broth is obtained containing two or more glucoamylase isozymes and an α-amylase. Other enzymes, such as transglucosidase and protease, as well as cellulase may be present in small quantities. The presence of α-amylase is beneficial in saccharification. Transglucosidase, however, is not desirable because this enzyme catalyzes the formation of isomaltose and reduces dextrose yield. Generally, *Aspergillus* mutants that do not produce transglucosidase are used.

Saccharification is generally conducted batchwise (although continuous systems are also used) in large agitated tanks containing several hundred thousand or million liters of hydrolyzate. The liquefied hydrolyzate is adjusted to 58–60°C and 4.0–4.5 pH and dosed with an amount of glucoamylase to provide a maximum dextrose level in 24–96 hours. At the normal saccharification solids of 30–35 wt%, ca 95–96% dextrose is produced. If the reaction is allowed to continue beyond the normal end point, dextrose level is lowered because glucoamylase catalyzes a reverse reaction that forms isomaltose and maltose by the condensation of a β-anomer of D-glucopyranose with either an α- or β-D-glucose molecule. Because of the reverse reaction, maltose level reaches an equilibrium early in the saccharification. Isomaltose formation, however, is slow. This sugar continues to accumulate. An equilibrium level of 12–14% disaccharides can eventually be reached. The production of reversion products via the reverse reaction is the principal deterrent to achieving a quantitative yield of dextrose in an industrial process.

Dextrose yield, however, can be increased by conducting saccharification at a lower solids level where the reverse reaction is minimized. For instance, dextrose yields of 98.8, 98.2, 97.5, and 96.9% dry basis can be achieved at solids levels of 10, 15, 20, and 25%, respectively (10). Low solids operation, however, is not used commercially owing to problems associated with microbial contamination and cost of water removal. Dextrose level can be increased by 0.5–1.5% at normal reaction solids by using an enzyme such as pullulanase (11) or a *B. megaterium* amylase (12) in conjunction with glucoamylase. Each enzyme works by a different mechanism (13). Both are effective in lowering levels of not only isomaltose but also higher saccharides and providing an increase in dextrose yield.

Refining. After saccharification, the hydrolyzate is clarified by precoat filtration, or possibly membrane filtration, to remove traces of insoluble fat, protein, and starch. Treatment with powdered carbon, granular carbon, and/or ion-exchange resins is then used to remove residual trace impurities, color, and inorganic constituents. The refined hydrolyzate can be dried to a solid product, evaporated to a high dextrose syrup, or processed to crystalline monohydrate or anhydrous dextrose. A typical process for production of crystalline dextrose is shown in Figure 2 (7).

For production of crystalline dextrose monohydrate, a refined 95–96% dextrose hydrolyzate is evaporated under reduced pressure to a syrup containing 75–78 wt% solids and then cooled and passed to crystallizers. The common form of crystallizer is a horizontal cylindrical tank fitted with a slowly turning agitator, cooling jacket, and cooling coils. A substantial bed of seed crystals comprising 20–25 wt% of the previous batch is left in the crystallizer and the refined syrup, at ca 46°C, is mixed with the seed crystals at an initial temperature of ca 43°C. Alternatively, a continuous precrystallizer may be used to form seed crystals (7). The agitated mass is slowly cooled to ca 20–40°C over a period of 3–5 days. By then, ca 60 wt% of the dextrose has crystallized as the monohydrate in a form suitable for separation and washing. The actual values for concentration, initial and final temperature, and rate of temperature drop vary depending primarily on the dextrose content of the hydrolyzate. The resulting magma in the crystallizers is passed into perforated-screen centrifuge baskets, spun to remove the mother liquor, and sprayed with water while spinning to wash out residual mother liquor. The wet sugar, at 99.5% or higher purity and containing ca 14 wt% total moisture, proceeds to rotary dryers, where it is dried in a stream of warm air to a final moisture of 8.5–8.9 wt%, slightly less than the theoretical 9.1 wt% for one molecule of water of crystallization. The lower final moisture content is a way of minimizing caking tendency by reducing the probability of free water present in the product. Crystals are screened to produce fine and course-grade products.

Mother liquor at 90% dextrose from the first crop of crystals can be concentrated and crystallized in a similar manner to recover an additional crystal crop. Depending on quality, some mother liquor can be partially recycled to the initial crystallization step to increase crystal-phase yield as a single crystal crop. The overall yield depends on the dextrose content of the original hydrolyzate and the extent to which hydrolyzates are refined. The mother liquor from the second crystallization contains less than 80% dextrose. The material is evaporated to 71% solids and sold as hydrol to the tanning and fermentation (qv) industries and for the manufacture of caramel color.

An exceptionally pure grade of dextrose monohydrate is obtained by dissolving crystalline monohydrate dextrose in water, carbon-treating to remove color and other impurities, ultrafiltering to remove pyrogens, and crystallizing an α-anhydrous fraction containing 99.9% dextrose. This recrystallized dextrose is marketed as a USP-grade product for special therapeutic purposes, eg, intravenous injection.

Anhydrous α-dextrose is manufactured by dissolving dextrose monohydrate in water and crystallizing at 60–65°C in a vacuum pan. Evaporative crystallization is necessary to avoid color formation at high temperatures and hydrate formation at low temperatures. The product is separated by centrifugation, washed, dried to a moisture level of ca 0.1%, and marketed as a very pure grade of sugar for special applications.

Anhydrous β-dextrose can be crystallized from concentrated solutions or melts at 90% solids at a temperature above 100°C. By carefully controlling conditions, a product containing a high percentage of anhydrous β-dextrose can be obtained.

Total sugar products are also produced by dehydrating hydrolyzate to a mixture of crystals and amorphous glass. This product is not produced in significant quantities in the United States or Europe but is popular in Japan and Korea where it represents 40–50% of total crystalline dextrose sold (14).

Syrup products at 95–96% dextrose are prepared by evaporating refined hydrolyzate to 71 wt% solids. Liquid $\geq$99% dextrose products are prepared by dissolving crystalline monohydrate dextrose in water or by chromatographic separation of refined hydrolyzate. In the latter case, a 95% dextrose-refined hydrolyzate at 60% solids is fed to a simulated moving bed column containing a cation exchange resin in the sodium form. The separation process produces a product containing $\geq$99% dextrose and an oligosaccharide by-product containing 60–80% dextrose (7).

Dry dextrose is shipped in 45.4-kg bags or in bulk by trucks and railcars. These products are hygroscopic and need to be protected against high temperatures and humidity during storage. Best preventive storage conditions are 30°C and 55% relative humidity. If the temperature is allowed to reach 40°C, the monohydrate can be transformed to the anhydrous form. Liquid products are shipped in tank trucks, railcars, and barges. Occasionally, dextrose may crystallize from solution at low temperatures. In this case, steam is applied to solubilize the dextrose prior to unloading.

2.3. Economic Aspects. The average yearly U.S. producer price index for corn sweeteners, which includes dextrose is given in Table 3. Factors contributing to dextrose price include corn costs, demand, processing capacity, production costs, and sucrose price. Dextrose production supply, and use are given in Table 4. U.S. corn sweetener exports to all countries are listed in Table 5.

2.4. Analysis and Specifications. Typical product analyses include solids level, ash, color, conductivity, purity, and minor saccharide levels (17). Specifications for anhydrous and monohydrate crystalline dextrose are available (18). High quality anhydrous dextrose produced for the pharmaceutical industry is prepared in accordance with additional specifications (19).

2.5. Health Factors. Dextrose products are substances that are presumed to be GRAS by the FDA (20). A study of the health aspects of dextrose, fructose, and corn syrups has indicated that these sweeteners are not hazardous at levels of normal human consumption with the exception of a small contribution to the formation of dental caries (21).

2.6. Uses. The main use of dextrose is in food processing (qv), where it is of value for its physical, chemical, and nutritive properties. Dextrose is also used in nonfood applications in the chemical, drug, and pharmaceutical industries. In the baking industry, dextrose is used as a fermentable sugar to provide crust color and, also, to supply strength, develop flavor, and optimize texture. In the beverage industry, it is used as a source of fermentables in low calorie beer (qv) and as a sweetener in beverage powders. In the canning industry, it supplies sweetness, body, and osmotic pressure. It also contributes to better natural color retention in certain products. In the confectionery industry, it is used to supply sweetness and softness control and to regulate crystallization. Dextrose is also used to make tableted products. Flavor is often enhanced by the cooling effect obtained when dextrose hydrate dissolves in the mouth. In frozen desserts, it prevents oversweetness and improves flavor. Dextrose is also used in seasoning formulations for sausages and for color in hams, in peanut butter for mouthfeel and chewability, in jams and jellies for controlling sweetness and providing stability by controlling osmotic pressure, as a substrate for vinegar (qv) fermentation, and in prepared mixes for biscuits, pancakes, waffles, doughnuts, and icings.

In many cases, dextrose is used in conjunction with sucrose. Although dextrose by itself is somewhat less sweet than sucrose, the combination of the two may be as sweet as pure sucrose at the same concentration (22). Dextrose is also used in the pharmaceutical industry for intravenous feeding as well as for tableting and other formulations. In fermentation, dextrose is a raw material for biochemical synthesis of organic acids, vitamins, antibiotics, enzymes, amino acids, and polysaccharides (23). A principal industrial fermentation use of dextrose is for the production of fuel ethanol as an oxygenate or octane enhancer (24). Dextrose is hydrogenated to sorbitol for use in various food and nonfood applications. Reaction of dextrose with sorbitol and citric acid produces a low calorie dextrose polymer, which is used as a bulking agent in reduced-calorie foods (25). Other industrial applications of dextrose include use in wallboard as a humectant, in concrete as a setting retardant, in resin formulations as a plasticizer, in adhesives for flow control, and for the production of methyl glucoside.

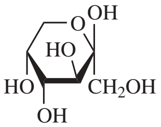
3. High Fructose Corn Syrups

High fructose corn syrups (HFS, HFCS, isosyrup, isoglucose) are concentrated carbohydrate solutions containing primarily fructose and dextrose as well as lesser quantities of higher molecular weight saccharides. A 42 wt% fructose syrup is produced by partial enzymatic isomerization of dextrose hydrolyzate. A 55 wt% fructose syrup is produced by a combination of enrichment and blending. Liquid products containing 80–95 wt% fructose are also manufactured. Pure crystalline fructose is produced in a dry form.

In nature, fructose (levulose, fruit sugar) is the main sugar in many fruits and vegetables. Honey contains ca 50 wt% fructose on a dry basis. Sucrose is composed of one unit each of fructose and dextrose combined to form the disaccharide. Fructose exists in polymeric form as inulin in plants such as Jerusalem artichokes, chicory, dahlias, and dandelions, and is liberated by treatment with acid or enzyme.

Fructose was first isolated in 1847 (26). In 1874, it was recognized that fructose had advantages over sucrose as a sweetener for diabetics (27). Based on the discovery of the alkaline conversion of dextrose to fructose in 1895 (28), a considerable number of investigations were conducted in an attempt to develop a commercial process (29). However, because of problems associated with color, off-flavor, degradation products, and low fructose yield, an alkaline conversion process was never commercialized. Enzymatic conversion of dextrose to fructose using glucose isomerase was first reported in 1957 and patented in 1960 (30,31). Research in this area continued for several years in Japan, resulting in a U.S. patent (32) and commercial production in Japan in 1966 (33). Japanese technology was then licensed by a U.S. company and production initiated in 1967 by a batch process (34). A 15 wt% fructose syrup was made first, followed in 1968 by a 42 wt% fructose product. In 1972, a continuous system was initiated using an immobilized enzyme process (35,36).

3.1. Properties. Fructose, a ketohexose monosaccharide, crystallizes as β-D-fructopyranose [7660-25-5] (**3**) and has a molecular weight of 180 and a melting point of 102–104°C. At equilibrium (25°C) the solubility of fructose in water is 80 wt%. In solution at 36°C, fructose undergoes rapid mutarotation to an equilibrium mixture of 3% α-D-fructopyranose [10489-81-3] (**4**), 57% β-D-fructopyranose, 9% α-D-fructofuranose [10489-79-9] (**5**), and 31% β-D-fructofuranose [470-23-5] (**6**) (37). In solution, the concentration of (**3**) varies from 77% at 0.5°C to 48% at 61°C (38). The crystalline form of fructose is 10–80% sweeter than sucrose and 50–100% sweeter than dextrose (13), depending on temperature, pH, concentration, and the presence of other additives.



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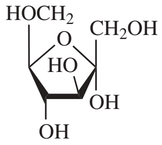

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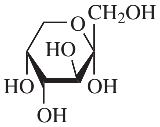

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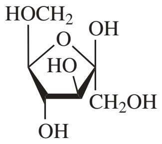

(**6**)

Because of the presence of fructose, HFS is sweeter than conventional corn syrups, although intensity of sweetness results from many factors. In general, 42% HFS is about 8% less sweet than sucrose, 55% HFS exhibits about the same sweetness as sucrose, and 90% HFS is about 6% sweeter than sucrose (39). Other properties of HFS include high solubility, which reduces the possibility of crystallization during shipment; humectant properties allowing for increased shelf life of bakery products; easier decomposition of fructose during baking resulting in improved color and flavor; and high osmotic pressure for containment of microbial growth.

3.2. Manufacture. HFS containing 42% fructose is produced commercially by column isomerization of clarified and refined dextrose hydrolyzate using an immobilized glucose isomerase. Enriched syrup containing 90% fructose is prepared by chromatographic separation and blended with 42% HFS to obtain 55% HFS.

Glucose isomerase is produced for commercial use from a variety of bacterial organisms, including *Actinoplanes missouriensis*, *Bacillus coagulans*, *Microbacterium arborescens*, *Streptomyces olivochromogenes*, *S. griseofuscus*, *S. murinus*, *S. phaeochromogenes*, and *S. rubiginosus* (40). The enzyme is immobilized and used in a continuous column operation to produce fructose from a dextrose feed. The high concentration of enzyme allows a short reaction time of 0.5–4 hours that minimizes problems associated with long batch reactions such as formation of color, off-flavors, and by-products. In addition, continuous use of the enzyme reduces enzyme cost to an economical level.

Two types of immobilization are used for immobilizing glucose isomerase. The intracellular enzyme is either immobilized within the bacterial cells to produce a whole-cell product, or the enzyme is released from the cells, recovered, and immobilized onto an inert carrier. An example of the whole-cell process is one in which cells are disrupted by homogenization, cross-linked with glutaraldehyde, flocculated using a cationic flocculent, and extruded (41). In a second example, a cell–gelatin mixture is cross-linked with glutaraldehyde (42). When soluble enzyme is used for binding, the enzyme is first released from the cell, then recovered and concentrated. Examples of this type of immobilization include binding enzyme to a DEAE-cellulose–titanium dioxide–polystyrene carrier (43) or absorbing enzyme onto alumina followed by cross-linking with glutaraldehyde (44,45).

HFS is produced from 93–96% dextrose hydrolyzate that has been clarified, carbon-treated, ion-exchanged, and evaporated to 40–50% dry basis. Magnesium is added at a level of 0.5–5 m*M* as a cofactor to maintain isomerase stability and to prevent enzyme inhibition by trace amounts of residual calcium. The feed may also be deaerated or treated with sodium bisulfite at a level of 1–2-m*M* SO_2 to prevent oxidation of the enzyme and a resulting loss in activity.

Hydrolyzate at about 55–61°C and 7.5–8.2 pH is passed through a fixed bed of immobilized isomerase at a controlled flow rate. Maximum fructose content at equilibrium is 50–55% dry basis; however, residence time is adjusted to attain 42–45% fructose because a greatly increased reaction time is required to attain higher levels. The enzyme can be used for as long as 10 weeks, during which time loss in activity is compensated for by regulating the residence time, ie, the flow rate through the column. Enzyme reactors are operated in parallel or in series and are replaced individually as isomerase is inactivated. The isomerized hydrolyzate at about 42 wt% fructose is adjusted to pH 4–5, carbon-treated to remove color and off-flavors, ion-exchanged to remove salts and residual color, and concentrated by evaporation to ca 71 wt% solids. Dextrose content in the 42% HFS product is 50–52%, thus storage at 35–41°C is recommended. At a lower temperature dextrose crystallization is a possibility and at a higher temperature color development may occur. Product is shipped in tank trucks or by railcars. If crystallization occurs, the syrup is heated to as high as 54°C to dissolve crystals prior to unloading.

Products containing higher levels of fructose are produced by chromatographic separation of 42 wt% HFS through a column of absorbent containing calcium or other cation groups. Fructose is retained to a greater degree than dextrose or oligosaccharides, and therefore a nonfructose stream is collected first as raffinate, followed by elution of fructose extract with water. In commercial operation, separation is achieved in a batchwise, semicontinuous, or continuous fashion. The continuous procedure involves a simulated moving bed in which feed and desorbent enter the column at different points while fructose and raffinate streams are withdrawn. Points of entry and withdrawal are changed periodically to correspond to flow through the column, and hence separation efficiency is maximized. In a typical operation, 42% HFS at a dry substance content of 50% is separated in a column at 50–70°C to generate a high fructose fraction and a by-product raffinate stream. The enriched fructose stream contains 80–90% fructose and 7–19% dextrose; the raffinate is composed of 80–90% dextrose and 5–10% fructose. Raffinate is recycled to isomerization columns for production of 42% HFS. Enriched HFS is blended with 42% HFS to produce a product containing 55% fructose and evaporated to 77% solids for shipment. Crystallization is not a concern because of the low dextrose level and storage temperature is generally maintained at 24–29°C. Other HFS products containing 80, 90, and 95% fructose (18, 9, and 4% dextrose, respectively) are also produced and evaporated to 77% solids (39) for shipment as an essentially noncrystallizable syrup.

Crystalline fructose differs from HFS in that it is >99.5% pure, contains less than 0.5% dextrose, and is dried to 99.5% solids. Aqueous, solvent, and mixed solvent processes have been proposed for fructose crystallization. The aqueous process is the primary mode of manufacture in the United States and elsewhere, although some aqueous–ethanol systems are also used in Europe and the Far East (39). In a typical process, a 90% fructose feed is added to an aqueous, alcohol, or combined solvent at 60–85°C and a pH of 3.5–8. Crystallization is accomplished by lowering temperature to 25–35°C and/or reducing pressure during 2–180 hours (39). Crystals are separated by centrifugation or filtration, impurities removed by washing, and the mass dried and screened. Shipment is by bags, totes, or railcars. A crystalline fructose syrup can be prepared by dissolving crystalline fructose in water to 77% solids (46).

3.3. Economic Aspects. Price index data are listed in Table 3. HFS price is influenced by the price of sugar, cost of corn, corn quality, and amount of excess wet-milling capacity. Prices exhibit a seasonal pattern having summer highs that are generally about 30% more than the yearly low price. The seasonal pattern results from increased consumption of soft drinks containing HFS during the summer months. Table 6 gives U.S. production, imports, and use including exports. See also Table 5 for other export data.

3.4. Analysis, and Specifications.

Methods of analysis are the same as those for dextrose. Specifications for HFS are the same as those for corn syrup.

3.5. Health and Safety Factors.

Health aspects are the same as those for dextrose HFS is presumed to be GRAS by the FDA (48).

There is controversy as to whether obesity is connected to the use of HFCS, especially in the consumption of soft drinks (49). See also Ref. 50 for further health information.

3.6. Uses.

High fructose syrup is used as a partial or complete replacement for sucrose or invert sugar in food applications to provide sweetness, flavor enhancement, fermentables, or humectant properties. It is used in beverages, baking, confections, processed foods, dairy products, and other applications.

The primary application of HFS is in soft drinks as emphasized by the rapid increase in usage of 55% HFS in the beverage industry since the 1980s. HFS containing 42% fructose was first used for this application in 1974. Because 55% HFS exhibits the same sweetness as sucrose, the use of a 50–50 blend of 55% HFS and sucrose was authorized by soft-drink producers in 1980 and 100% substitution was approved in 1984. HFS is also used in other applications such as baking where it acts as a source of fermentables and improves flavor, aroma, and texture. It is also used in ice cream to control crystallization and add body, in dairy products to provide body and improve mouthfeel and texture, in confectionery to control grain and humectancy, and in canned goods as a preservative and for adding sheen.

HFS containing 90% fructose is used in low calorie or specialty foods because of its high sweetness and, therefore, reduced usage level and lower caloric value. Crystalline fructose is essentially pure and used at a level that provides sweetness at a lower caloric level than other sweeteners (qv). Initial use was in diet and nutritious foods but application has now been extended to many other food areas, such as powdered beverages, dry mix desserts, dairy products, and confections.

4. Corn Syrups

Corn syrups [8029-43-4] (glucose syrup, starch syrup) are concentrated solutions of partially hydrolyzed starch containing dextrose, maltose, and higher molecular weight saccharides. In the United States, corn syrups are produced from corn starch by acid and enzyme processes. Other starch sources such as wheat, rice, potato, and tapioca are used elsewhere depending on availability. Syrups are generally sold in the form of viscous liquid products and vary in physical properties, eg, viscosity, humectancy, hygroscopicity, sweetness, and fermentability.

4.1. Properties.

Corn syrups are defined as those starch hydrolysis products exhibiting a DE of 20–99.4. Lower DE products are classified as maltodextrins [9050-36-6] and higher DE products as dextrose. Syrups are often described in terms based on the type of production process, ie, acid conversion, acid–enzyme conversion, and enzyme–enzyme conversion; on the degree of hydrolysis (high conversion); or on a particular saccharide in the syrup (high maltose).

Examples of some of these syrups are shown in Table 7. The most adequate characterization is with respect to the concentration of individual saccharides. In many cases, it is the individual saccharides or groups of saccharides that determine syrup characteristics. Consequently, corn syrups exhibit many functional properties, including fermentability, viscosity, humectancy–hygroscopicity, sweetness, colligative properties, and browning reactions, which differ from the properties of other syrups.

Fermentability of corn syrups by yeast is important in certain food applications, eg, baking and brewing. The fermentable sugars present in corn syrup are dextrose, maltose, and maltotriose. Fermentability of maltose or maltotriose depends on the specific fermentation process and organism. In general, greater fermentability is obtained at higher DE levels.

Viscosity of corn syrup is a function of DE value, temperature, and solids concentration. Viscosity decreases with increasing DE and temperature but increases with increasing concentration. For a 43-DE corn syrup, viscosity at 1.42 sp gr (43° Be′) is 56,000mPa·s(= cP) at 27°C, 14,500mPa·s at 38°C, and 4,900mPa·s at 49°C. Corresponding values for a 55-DE syrup at the same density are 31,500, 8,500, and 2,900mPa·s.

The hygroscopic and humectant properties of corn syrups are of great importance in many applications. Depending on the type of syrup and on the specific conditions of temperature and humidity, the products may either resist or facilitate moisture loss or moisture absorption. The ability to attract moisture or retard its loss increases with increasing DE value. Prevention of moisture pickup is more characteristic of syrups having low DE values.

Sweetness is primarily a function of the levels of dextrose and maltose present and therefore is related to DE. Other properties that increase with increasing DE value are flavor enhancement, flavor transfer, freezing-point depression, and osmotic pressure. Properties that increase with decreasing DE value are bodying contribution, cohesiveness, foam stabilization, and prevention of sugar crystallization. Corn syrup functional properties have been described in detail (51).

4.2. Manufacture. Corn syrups are manufactured by acid, acid–enzyme, or enzyme–enzyme hydrolysis processes. Acid hydrolysis of starch is conducted by batch or continuous processes. Batchwise conversion is carried out in large cookers or converters, which are usually built of manganese–bronze and have capacities of ca 10 m^3 (10^4 L). A suspension of starch at 35–40 wt% dry solids is passed to the converter, hydrochloric acid is added to a concentration of 0.015–0.02 *N*, and the converter is steam-heated until a temperature of 140–160°C is reached. The mixture is held at temperature for a period of time, usually 15–20 minutes, to produce the desired degree of hydrolysis. Improved process control and therefore better product uniformity is achieved by a continuous process using indirect heating. In this type of process, acidified starch slurry is pumped at a constant rate through a series of heat exchangers at reaction conditions similar to those used in batch operations. In either process, hydrolyzate is neutralized to pH 4–5.5 by addition of soda ash, clarified by centrifugation or filtration, evaporated to ca 60 wt% solids, carbon-treated to remove color and acid degradation products, and concentrated to 77–85 wt% solids. Sulfur dioxide is added during evaporation to some grades of syrup to reduce color development.

The standard acid-converted syrup is typically about 42 DE, although higher and lower DE syrups are also produced by this process. Syrup DE is limited to about 30–55 because at lower DE residual starch may cause a haze problem and at higher DE excess color and off-flavor are produced owing to acid-catalyzed side reactions. Composition of 30–55-DE acid-converted syrups are shown in Table 7.

Syrups are also produced by acid–enzyme or enzyme–enzyme processes. Starch is first hydrolyzed by acid or by enzyme. The latter is similar to the method for liquefaction processes (see Fig. 1). Either treatment is followed by saccharification with one or more enzymes to the desired composition. Maltose syrup [69-79-4], for example, can be prepared from a 10–20-DE partially hydrolyzed starch substrate by saccharification using a maltose-producing enzyme at 50–55°C and pH 5. Maltogenic enzymes, eg, β-amylase extracted from germinated barley or fungal α-amylase derived from *Aspergillus oryzae*, are used to produce a hydrolyzate containing about 40–50 wt% maltose (Table 7). Higher levels of maltose, ie, 60–80 wt%, are produced by saccharification with a combination of a maltogenic enzyme and a debranching enzyme such as pullulanase. The pullulanase hydrolyses α-1,6 linkages during saccharification and provides additional substrate for the action of the maltogenic enzyme.

High conversion syrups of 60–70 DE containing intermediate levels of dextrose and maltose are also produced (Table 7). Saccharification is conducted with combination of glucoamylase and maltogenic enzyme at pH 4.8–5.2 and 55–60°C for several hours or days until the desired DE is reached. Maltose and high conversion syrups are refined and shipped in rail cars and tank trucks. Syrups are generally heated to ca 38°C to facilitate unloading. Some syrups, particularly those having a limited extent of hydrolysis, are reduced to dry form by spray-drying or roll-drying. These products are commonly called corn syrup solids and are shipped in moistureproof bags. Products of <20 DE are referred to as maltodextrins or hydrolyzed cereal solids (Table 5). These products are bland-tasting, free-flowing, and nonhygroscopic. Maltodextrins are prepared from regular or waxy corn starch by enzyme or acid processes to products of 10–20 DE, then clarified, refined, spray-dried to a moisture content of 3–5 wt%, and finally shipped in 45.4-kg bags. In some cases, a syrup of ca 75 wt% solids is produced.

4.3. Economic Aspects. Prices of corn syrup are listed in Table 3. Production capacity, demand, and corn prices affect corn syrup price.

4.4. Analysis, Specifications, and Health Factors. Corn syrups are usually sold with a specification of the Baumè measurement which is related to solids content. A typical value is 43.5° Be′, corresponding to 80.3 wt% solids for a 42-DE acid-converted syrup. Solids content for syrups at 41, 42, 43, 44, and 45° Be′ (sp gr 1.39, 1.41, 1.42, 1.43, and 1.45) are 75.0, 77.1, 79.1, 81.2, and 83.3 wt%, respectively. Higher DE syrups exhibit slightly higher solids levels at the same densities. DE is determined by copper reducing methods. Saccharide composition is determined by high performance liquid chromatography. Other analyses include color, iron, and pH. Specifications for glucose syrup and dried glucose syrup are available (52). Maltodextrin and corn syrup products are substances that are presumed to be GRAS by the FDA (53). Health and safety aspects are the same as those for dextrose.

4.5. Uses. The specific type of syrup employed depends on the properties desired in the final product. Syrup properties are important to varying degrees in different products, and changes in formulation can affect the choice of syrup required to supply the most desirable properties. In many cases, corn syrups are used as supplementary sweeteners when sucrose is the primary one.

In the confectionery industry, corn syrups are used extensively in nearly every type of confection, ranging from hard candy to marshmallows. In hard candies, which are essentially solid solutions of nearly pure carbohydrates, corn syrup contributes resistance to heat discoloration, prevents sucrose crystallization, and controls hygroscopicity, viscosity, texture, and sweetness. Maltose syrups, high conversion syrups, and acid-converted syrups (36 and 42 DE) are used for this application.

In the canning and preserving industries, corn syrups are used to prevent crystallization of sucrose, provide body, accentuate true fruit flavors, and improve color and texture. In the beverage industry, the predominant use is in the beer and malt-liquor areas. High conversion syrups are used to replace dry cereal adjuncts, provide fermentable sugars, enhance flavor, and provide body. These syrups contain controlled amounts of dextrose and maltose for proper fermentation.

Corn syrups used in baking are generally of the high conversion type. They are incorporated into cakes, cookies, icings, and fillings to increase the amount of moisture retained, retard crystal growth of other sugars, enhance tenderness, and increase shelf life. In yeast-raised goods, fermentability is of importance, and therefore only high DE syrups are used.

Corn syrups used in ice cream and frozen desserts are generally 36- or 42-DE acid-converted syrups. The syrup serves primarily to provide maximum flexibility in adjusting flavor, texture, body, and smoothness. It also aids in grain control and in the modification of meltdown and shrinkage characteristics of the frozen product.

Syrups of 25–30 DE are used as spray-drying aids in products such as coffee. High conversion syrup, maltose syrup, and 42-DE syrup are used in jams and jellies. Corn syrup is also used in table syrups, baby food, meat packing, breakfast foods, salad dressing, pickles, dehydrated powdered foods, medicinal syrups, textile furnishings, adhesives, and numerous other products and processes.

5. Maple Syrup

Maple syrup is prepared by concentrating (evaporation or reverse osmosis) sap from the maple tree to a concentrated solution containing predominantly sucrose. Its characteristic flavor and color are formed during evaporation. Maple syrup is produced from the sap of several varieties of mature maple trees, eg, the sugar maple (*Acer saccharum*) and black maple (*Acer nigrum*).

Collection of sap is made sometime between late fall and mid-spring, depending on weather conditions. The best time is when the temperature is ca 7°C during the day and below freezing at night. Sap generally contains 2–3 wt% solids, of which ca 96% is sucrose; the remainder is composed of other carbohydrates, organic acids, ash, protein, and lignin-like materials. A taphole is drilled into the tree and a spout is driven in the opening. Sap is collected in a bucket, in a bag, or alternatively in plastic tubes directed to a centralized collection tank by gravity or vacuum. Evaporation is conducted at atmospheric pressure until a boiling point of 104°C is reached to produce a syrup meeting governmental specifications of at least 66 wt% solids (54). A syrup concentrated to only 65 wt% solids has a thin taste, and one concentrated to $\geq$67 wt% crystallizes when cooled. A refractometer or hydrometer is used to measure concentration. Final specific gravity should be 1.35 (37.75° Baumè) at 15.6°C. Flavor and color develop during evaporation as a result of loss of water and reactions occurring between sugar and other components. Syrup is clarified, graded as to color, flavor, and density, and finally packaged in small containers for retail sale as table syrup. Typically the product contains 88–99 wt% sucrose and 0–12 wt% invert sugar. Maple syrup is also used in candy manufacture by blending with sucrose. Other applications include addition to cookies, ice cream, baked beans, baked ham, and baked apples.

Maple sugar is prepared by concentrating sap to a high solids content, ie, a boiling temperature of 116–121°C, and then allowing the supersaturated solution to crystallize or solidify during cooling. Maple cream or maple butter is made by stirring a supersaturated solution while cooling rapidly to produce a product of creamy texture.

5.1. Economic Aspects. In the U.S. 1.45×10^6 gal were produced in 2006. The main maple-syrup-producing areas are located in the northeastern and midwestern United States and eastern Canada. In the United States, leading producing states in 2006 were Vermont (accounting for 32% of total production), Maine (21%), New York (17.5%), and Wisconsin (17%) (54). Total production and value of maple syrup in the United States and Canada for 2003–2006 are listed in Table 8.

6. Molasses

Molasses, another type of syrup, is a by-product of the sugar industry. It is the mother liquor remaining after crystallization and removal of sucrose from the juices of sugar cane or sugar beet and is used in a variety of food and nonfood applications. Molasses, first produced from sugarcane in China and India centuries ago and later in Europe and Africa, was introduced as the by-product of cane-sugar production into Santo Domingo by Columbus in 1493. During Colonial times, molasses was very important to the American colonies for the production of rum. In 1733, the British Parliament passed the Molasses Act to tax molasses imported from foreign countries. This attempt to restrict trade was ignored by the colonies and was, in part, responsible for the American Revolution.

6.1. Manufacture. Raw sugar is produced from sugarcane by a process that involves extraction of the sugar in water, treatment to remove impurities, concentration, and several crystallizations. After the first crystallization and removal of first sugar, the mother liquor is called first molasses. First molasses is recrystallized to obtain a second lower quality sucrose (second sugar) and a second molasses. After a third crystallization, the third molasses contains considerable nonsucrose material, and additional recovery of sucrose is not economically feasible. The third molasses is sold as blackstrap, final, or cane molasses. Raw sugar obtained from the above process is mixed with water to dissolve residual molasses and then separated by centrifugation. This process is called affination and the syrup is referred to as affination liquor. The sugar is dissolved in water, treated to remove color and impurities, and subjected to several crystallizations to obtain refined sugar. The mother liquor from the final crystallization is combined with affination liquor and crystallized to produce a dark sugar (remelts) which is recycled to raw sugar. The remaining mother liquor is called refiners molasses and is similar to final molasses but usually of better quality.

In beet sugar manufacture, the beet juice does not contain reducing sugars such as fructose and glucose, which are present in cane juice, but may contain raffinose. Because of the absence of reducing sugars, sucrose level in beet molasses is not reduced to the same extent as for cane. Final molasses from beet contains ca 60 wt% sucrose (dry basis) compared to 30 wt% sucrose (dry basis) in cane molasses. Treatment of diluted beet molasses with calcium oxide precipitates sucrose as tricalcium sucrate (Steffen process), which is recycled to the incoming hot beet juice. During recycling, raffinose accumulates in the final molasses and retards crystallization if not removed. Therefore, a portion of the final molasses, called discard molasses, is periodically removed.

Ion-exclusion chromatography is increasingly being used to remove sugar from beet molasses (55). As much as 90% sugar recovery is achieved by this technique, which involves passing diluted and clarified molasses through a column containing a strong acid cation exchange resin. Sucrose is absorbed on the resin and nonsucrose is recycled back to the sugar process. The resulting molasses contains 12–20% residual sugar (55) compared to traditional molasses that contains $\geq$50% sugar.

High test molasses (invert molasses) is produced from cane sugar when sucrose manufacture is restricted because of overproduction. The cane sugar at ca 55 wt% solids is enzymatically converted to invert syrup to prevent crystallization and evaporated to a syrup. The product is used in the same applications as blackstrap molasses.

Molasses from other sources include citrus and corn sugar (hydrol) molasses. Citrus molasses is produced from citrus waste and contains 60–75% sugars. Corn sugar molasses is the mother liquor remaining after dextrose crystallization and contains a minimum of 43% reducing sugars expressed as dextrose.

Molasses is shipped in drums, barrels, tank trucks, tank cars, barges, and sea vessels. Because of high viscosity, molasses must be heated in some situations to facilitate pumping. However, prolonged heating must be avoided to prevent caramelization.

6.2. Composition. Molasses composition depends on several factors, eg, locality, variety, soil, climate, and processing. Cane molasses is generally at pH 5.5–6.5 and contains 30–40 wt% sucrose and 15–20 wt% reducing sugars. Beet molasses is ca 7.5–8.6 pH, and contains ca 50–60 wt% sucrose, a trace of reducing sugars, and 0.5–2.0 wt% raffinose. Cane molasses contains less ash, less nitrogenous material, but considerably more vitamins than beet molasses. Composition of selected molasses products is listed in Table 9. Procedures for molasses analysis are available (56).

6.3. Uses. The primary use of molasses is in animal feed. Molasses, which provides a carbohydrate source, salts, protein, vitamins, and palatability, may be used directly or mixed with other feeds. The carbohydrate content of 24.6 L (6.5 gal) of blackstrap molasses is considered to be equal to 0.035 m^3 (one bushel) of corn as measured by the energy produced from 0.035 m^3 of corn and the amount of molasses required to produce the same amount of energy. When molasses is less expensive than corn, sales increase; when the reverse is true, sales decrease.

Molasses is also used as an inexpensive source of carbohydrate in various fermentations for the production lactic acid, citric acid, monosodium glutamate, lysine, and yeast (59). Blackstrap molasses is used for the production of rum and other distilled spirits.

Food applications utilize first and second molasses in baking (bread, cakes, cookies) for the molasses flavor. Molasses is also used in curing of tobacco and meats, in confections such as toffees and caramels, and in baked beans and glazes. A high speed consecutive, batch or continuous, low effluent process for production of ethanol from molasses, starches, or sugar has used recently (59).

6.4. Economic Aspects. U.S. molasses imports, are shown in Table 10. Production statistics are shown in Table 11 sources of imports to the United States are Australia, Dominican Republic, Guatemala, Mexico, and Poland (55). U.S. molasses price is regulated by supply and demand and the world sugar price. Price of beet molasses is generally higher than that of cane molasses owing to higher levels of sucrose and nitrogen.

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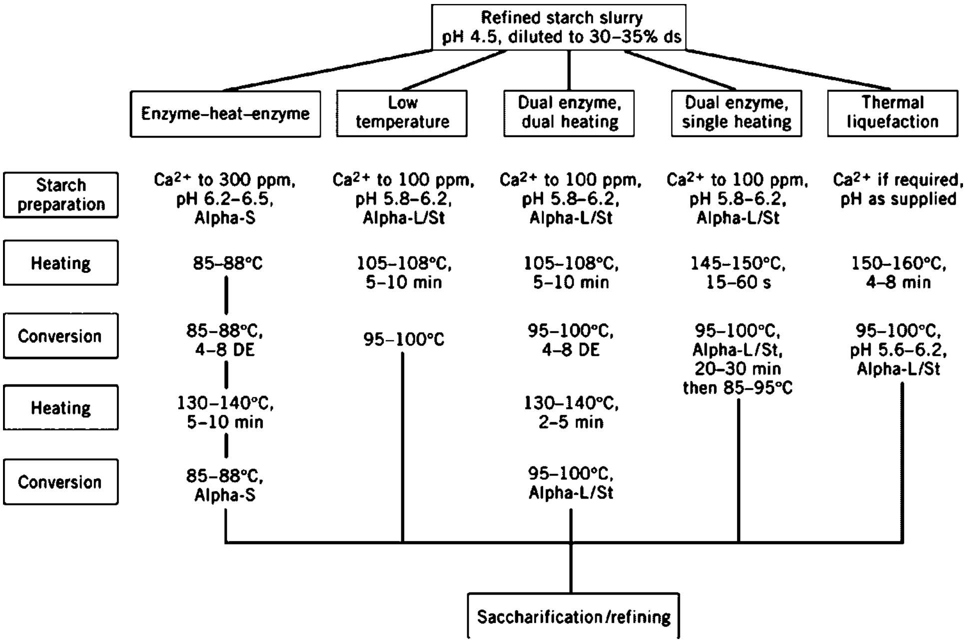

Fig. 1. Enzymatic liquefaction processes (9). Alpha-S is the α-amylase from *Bacillus subtilis;* alpha-L/ST are α-amylases from *B. licheniformis* or *B. stearothermophilus*, DE is dextrose equivalent, and ds is dry substance.

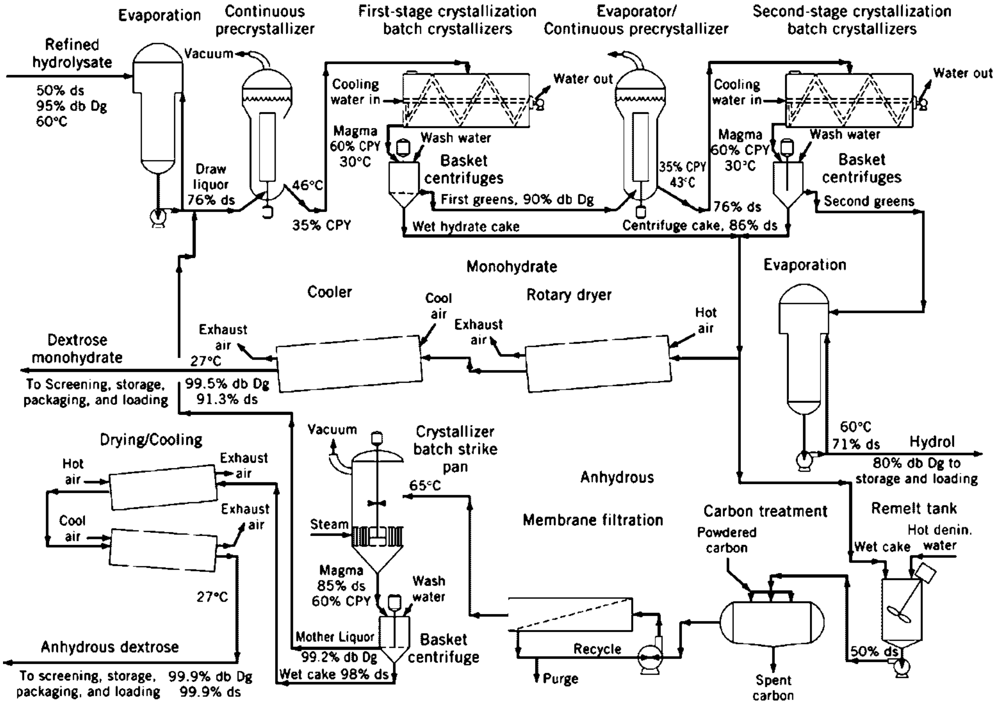

Fig. 2. Production of crystalline dextrose 7, where ds is dry substance; db, dry basis; Dg, D-glucose; and CPY, crystal-phase yield.

Table 1. **Physical Properties of D-Glucose**

Property	α-D-Glucose	α-D-Glucose hydrate	β-D-Glucose
molecular formula	$C_6H_{12}O_6$	$C_6H_{12}O_6 \cdot H_2O$	$C_6H_{12}O_6$
mp, °C	146	83	150
solubility at 25°C, g/100 g solution	62→30.2→51.2[a]	30.2→51.2[a,b]	72→51.2[a]
$[\alpha]_D$	112.2→52.7[a]	112.2→52.7[a,b]	18.7→52.7[a]
heat of solution at 25°C, J/g[c]	−59.4	−105.4	−25.9

[a] Initial value through solution equilibrium value. See text.

[b] Anhydrous basis.

[c] To convert J to cal, divide by 4.184.

Table 2. **Solubility of Dextrose in Water**[a]

Temperature, °C	Dextrose in solution, wt%
0	34.9
5	38.0
10	41.2
15	44.5
20	47.8
25	51.3
30	54.6
40	61.8
50	70.9
60	74.8
70	78.2
80	81.3

[a] Interpolated from data in Reference 6.

Table 3. **U.S. Producer Price Index for Corn Sweeteners[a] and Sugar, Monthly[b]**

Year	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.	OCt.	Nov.	Dec.	Annual
2000	98.9	98.0	97.8	98.0	97.9	97.9	97.8	98.0	98.0	97.6	99.2	100.3	98.3
2001	111.3	111.6	111.6	111.5	111.9	111.3	111.3	111.3	112.2	112.3	113.9	114.0	112.0
2002	116.5	120.1	119.7	119.8	117.4	119.6	121.2	121.0	127.4	127.9	125.9	126.5	121.9
2003	130.0	131.4	131.3	131.3	131.5	131.9	–	132.2	131.9	130.6	130.9	130.7	131.3
2004	131.9	132.0	131.9	131.7	131.6	131.7	131.8	131.5	131.6	131.5	131.6	131.6	131.7
2005	133.1	133.3	133.5	133.1	133.1	133.1	133.2	132.9	133.2	137.2	133.1	133.2	133.5
2006[c]	144.5	144.8	145.1	153.4	151.1	151.2	151.2	150.9	151.2	151.3	151.2	151.0	149.8

[a] Corn sweeteners (liquids and solids), incl. glucose, dextrose, and HFCS, June 1985 = 100. Based on a sample of domestic producers.

[b] Ref. 15.

[c] Prellminary, all indexes are subject to revision four months after original publishing.

Table 4. **U.S. Dextrose Supply and Use, by Calendar Year × 10^3 t**[a]

Year	Production	Imports	Total supply	Net change in stocks	Total use	Exports	Shipments to Puerto Rico	Non-food use	Food and beverage use
1995	676	14.5	690	10	679	46	2.7	152	479
1996	706	0.9	707	2.7	703	61	2.7	152	487
1997	676	0.9	677	−10	687	67	10.8	145	464
1998	663	0.9	664	−3.6	668	58	10.8	142	455
1999	641	0	641	−5.4	647	54	11.8	140	443
2000	642	0.9	642	0.9	641	51	5.4	153	431
2001	629	0.9	629	−4.5	634	56	6.3	145	425
2002	631	0.9	632	−2.7	634	69	1.8	134	429
2003	682	3.6	686	8	678	86	1.8	182	407
2004	674	1.8	676	2.7	673	73	2.7	156	442
2005	647	0.9	647	−9	657	83	4.5	142	428

[a] Ref. 16.

Table 5. **U.S. Corn Sweetener Exports to all Countries, Fiscal Years 1992–2007**[a]

	Dextrose	Glucose syrup	HFCS-42[d]	Crystalline fructose[d]	HFCS-55 and above - syrup[f]	HFCS-55 and above - solid[g]	Total HFCS and Cry.Fr.	Total corn sweeteners
			Metric tons, dry basis					
1995	43,354	39,415	21,363	23,360	41,907	15,900	102,529	185,298
1996	57,409	70,165	22,879	36,492	57,891	23,810	141,071	268,644
1997	69,747	68,973	23,709	43,928	192,587	17,807	278,031	416,752
1998	57,812	81,676	30,876	51,692	227,911	23,885	334,365	473,853
1999	54,787	76,521	39,408	54,387	209,450	12,834	316,079	447,387
2000	52,659	88,377	29,989	62,162	174,214	27,071	293,437	434,473
2001	52,810	101,529	24,327	47,373	147,388	14,138	233,227	387,566
2002	65,594	108,516	15,705	43,335	87,017	12,085	158,142	332,252
2003	81,786	130,621	15,486	43,409	62,392	21,780	143,067	355,474
2004	76,410	117,920	14,116	55,553	56,576	12,270	138,514	332,844
2005	83,790	151,095	24,777	120,255	92,939	6,006	243,976	478,862
2006	93,146	209,705	47,287	126,634	254,539	7,868	436,328	739,179
2007[h]	14,163	45,786	5,803	14,032	46,428	742	67,010	126,959
			Dollars × 10^6					
1995	23.432	20.156	9.832	18.227	18.875	11.322	58.256	101.845
1996	31.532	28.576	13.122	28.410	25.876	13.383	80.792	140.901
1997	39.641	26.784	12.612	32.138	83.415	15.896	144.061	210.487
1998	33.188	31.213	10.855	39.064	92.339	20.049	162.308	226.711
1999	29.878	32.368	12.871	34.505	74.405	20.005	141.788	204.036
2000	27.620	36.797	9.818	39.909	58.115	27.761	135.604	200.022
2001	26.120	41.305	9.450	32.998	52.886	22.666	118.001	185.427
2002	31.045	47.629	6.699	29.181	36.282	32.216	104.379	183.054
2003	38.589	50.663	6.063	31.800	29.462	36.871	104.198	193.452
2004	38.040	47.570	5.610	44.077	26.900	40.159	116.747	202.357

2005	41.723	51.022	8.676	67.744	42.485	20.881	139.789	232.534
2006	51.947	74.871	18.578	76.603	91.162	25.032	211.377	338.196
2007[h]	7.927	16.992	1.895	10.953	15.417	2.619	30.886	55.807
			cents per pound					
1995	24.5	23.2	20.9	35.4	20.4	32.3	25.8	24.9
1996	24.9	18.5	26.0	35.3	20.3	25.5	26.0	23.8
1997	25.8	17.6	24.1	33.2	19.6	40.5	23.5	22.9
1998	26.0	17.3	15.9	34.3	18.4	38.1	22.0	21.7
1999	24.7	19.2	14.8	28.8	16.1	70.7	20.3	20.7
2000	23.8	18.9	14.9	29.1	15.1	46.5	21.0	20.9
2001	22.4	18.5	17.6	31.6	16.3	72.7	22.9	21.7
2002	21.5	19.9	19.3	30.5	18.9	120.9	29.9	25.0
2003	21.4	17.6	17.8	33.2	21.4	76.8	33.0	24.7
2004	22.6	18.3	18.0	36.0	21.6	148.5	38.2	27.6
2005	22.6	15.3	15.9	25.6	20.7	157.7	26.0	22.0
2006	25.3	16.2	17.8	27.4	16.2	144.3	22.0	20.8
2007[h]	25.4	16.8	14.8	35.4	15.1	160.0	20.9	19.9

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[a] Ref. 15, Source: HS Export Data. Foreign Trade Division. Bureau of Census.

[b] HTS 1702.30.0020. Dry basis is commercial weight multiplied by 0.92.

[c] HTS 1702.30.0040. Dry basis is commercial weight multiplied by 0.803.

[d] HTS 1702.40.0000. Dry basis is commercial weight multiplied by 0.71.

[e] HTS 1702.50.0020. No conversion.

[f] HTS 1702.60.0050. Dry basis is commercial weight multiplied by 0.77.

[g] HTS 1702.60.0060. Dry basis is commercial weight multipled by 0.77.

[h] Through November.

Table 6. **U.S. High Fructose Corn Syrup (HFCS) Supply and Use, Calendar Year × 10^3 t**[a],[b]

Calendar year	Supply					Use		
	Domestic production						Domestic disappearance	
	HFCS-42	HFCS-55	Total	Imports	Total supply	Exports	HFCS-42	HFCS-55
1995	2,771	4,268	7,039	72	7,111	94	2,790	4,226
1996	2,791	4,609	7,400	112	7,512	203	2,808	4,502
1997	2,891	4,981	7,872	105	7,977	250	2,926	4,800
1998	2,990	5,311	8,301	106	8,407	352	3,010	5,045
1999	3,196	5,343	8,539	110	8,648	318	3,217	5,114
2000	3,192	5,258	8,451	110	8,560	291	3,220	5,049
2001	3,172	5,207	8,371	134	8,513	210	3,226	5,074
2002	3,302	5,137	8,439	123	8,562	132	3,352	5,079
2003	3,295	5,006	8,301	131	8,432	144	3,344	4,938
2004	3,321	4,046	8,221	142	8,364	145	3,343	4,875
2005	3,339	5,630	8,371	142	8,513	295	3,397	4,821
2006	3,364	5,142	8,506	158	8,664	516	3,417	4,930

[a] Source Ref. 47.

[b] Includes Puerto Rico.

Table 7. **Composition of Corn Syrups and Maltodextrins**

	Amount of constituent[a], wt %				
Type	DE	DP-1	DP-2	DP-3	DP$_{-4+}$
acid-converted syrup	30	9	10	12	69
	36	14	12	10	64
	42	19	14	12	55
	55	31	18	13	48
high maltose syrup	42	6	44	13	37
	48	9	52	15	24
	50	3	75	13	9
high conversion syrup	64	37	31	11	21
	70	43	30	7	20
maltodextrin	10	0	3	4	93
	15	1	5	7	87
	20	1	8	9	82

[a] DP refers to degree of polymerization, where DP-1 is dextrose, DP-2 is a disaccharide, etc. DE = dextrose equivalent.

Table 8. **Production, Price, and Value of Maple Syrup 2003–2005**[a]

State	Production, gal × 10^3,				Average gallon equivalent price of all sales $[b]			Value of production, $ × 10^3		
	2003	2004	2005	2006	2003	2004	2005	2003	2004	2005
Connecticut	10	11	10	10	48.60	51.70	50.00	486	569	500
Maine	285	290	265	300	22.50	19.40	21.50	6,413	5,626	5,698
Massachusetts	37	50	40	40	41.90	46.30	51.20	1,550	2,315	2,048
New Hampshire	60	83	57	64	43.00	35.40	41.30	2,580	2,938	2,354
Vermont	420	500	410	460	27.80	27.30	27.80	11,676	13,650	11,398
Total New England	**812**	**934**	**782**	**874**	**27.96**	**26.87**	**28.13**	**22,705**	**25,098**	**21,998**
Michigan	59	80	58	78	31.20	38.00	36.00	1,841	3,040	2,088
New York	210	255	222	253	26.80	28.20	31.70	5,628	7,191	7,037
Ohio	51	78	69	78	35.10	32.00	36.00	1,790	2,496	2,484
Pennsylvania	52	60	61	66	27.40	29.00	31.50	1,425	1,740	1,922
Wisconsin	76	100	50	100	29.10	32.30	32.40	2,212	3,230	1,620
Total United States	**1,260**	**1,507**	**1,242**	**1,449**	**28.30**	**28.40**	**29.90**	**35,601**	**42,795**	**37,149**
New Brunswick	191	210	248		26.56	28.75	29.01	5,073	6,037	7,194
Nova Scotia	36	26	25		28.72	30.85	33.96	1,034	802	849
Ontario	262	262	262		30.41	31.30	33.77	7,968	8,201	8,848
Quebec	6,822	6,551	6,822		14.86	14.94	18.19	101,344	97,886	124,109
Total Canada[c]	**7,312**	**7,050**	**7,359**		**15.78**	**16.02**	**19.16**	**115,417**	**112,925**	**141,000**

[a] Ref. 55.

[b] Average gallon equivalent price in United States dollars is a weighted average across retail, wholesale, and bulk sales. This price is lower for States, such as Maine, with more bulk sales. The average gallon equivalent price is not the average retaiil price paid for a gallon of syrup.

[c] Canadian dollars to United States dollars exchange rates were valued at or near the closest date to July 1 for each year. Exchange rates were 0.74118 for 2003. 0.750469 for 2004, and 0.805283 for 2005. Canadian imperial gallons were converted to United States gallons (one imperial gallon times 1.2021778 equals one United States gallon.)

Table 9. **Composition of Various Types of Molasses, wt %**

Molasses type	Solids	Total sugars as invert	Crude protein	Total ash
cane				
Louisiana	80.8	59.5	3.0	7.2
refiners	75.4	55.9	2.1	8.6
high test (Cuba)	80.4		0.7	1.4
beet (Wisconsin)	78.6	52.7	11.4	9.3
corn	74.9	50.3	0.4	8.9
citrus	71.4	42.4	4.7	4.8

Table 10. **Total Monthly Imports of Molasses, by Tariff Code, × 10^{3a}**

Year	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.	Oct.	Nov.	Dec.	Calendar	Fiscal
1995	43,663	57,170	90,002	96,365	60,062	44,142	85,265	44,151	46,268	53,869	72,191	60,176	753,321	827,147
1996	41,157	87,445	77,009	100,709	76,971	93,053	82,266	52,870	127,492	83,499	41,783	126,375	990,630	925,207
1997	66,245	85,444	82,829	90,829	147,276	58,916	69,619	116,020	102,723	64,876	61,148	80,094	1,026,018	1,071,558
1998	91,628	112,779	136,014	127,926	91,483	81,868	54,363	27,486	101,510	112,317	61,220	74,277	1,072,871	1,031,175
1999	40,010	56,175	97,594	63,714	86,061	60,754	69,632	81,867	58,931	23,534	55,153	73,411	766,835	862,551
2000	90,662	98,536	106,504	69,593	52,059	70,499	22,881	78,789	43,807	104,573	22,507	60,093	820,502	785,427
2001	126,147	51,622	102,224	91,375	87,277	101,686	84,396	75,744	86,537	142,908	72,048	45,570	1,067,536	994,182
2002	39,648	116,767	113,561	146,659	110,557	43,146	76,929	102,824	95,340	73,015	132,548	84,091	1,135,084	1,105,956
2003	117,884	104,397	132,850	118,344	189,691	113,580	94,281	104,481	91,148	82,038	90,845	44,396	1,283,936	1,356,311
2004	135,203	122,992	129,270	117,853	134,615	119,754	83,771	83,738	102,094	79,293	52,091	56,281	1,216,955	1,246,570
2005	50,055	206,426	195,909	87,580	150,181	100,377	53,118	52,378	96,252	95,159	80,455	101,093	1,268,981	1,179,939
2006	162,204	142,207	124,617	66,449	117,260	75,650	37,914	73,683	34,197	60,309	62,084	163,475	1,120,051	1,110,890

[a] Ref. 57.

Table 11. **Product Statistics Including Molasses 2002**

NAICS product code	Description	Unit of measure	Number of companies	Quantity of shipments	Value of shipments ($1,000)
3119994	sweetening syrups and molasses		0	X	513,167
31199941	sweetening syrups and molasses		0	X	454,790
3119994111	sweetening syrups and molasses, containing corn syrup	620	38	S	299,944
3119994121	sweetening syrups and molasses, not containing corn syrup	620	23	S	154,846
3119994Y	sweetening syrups and molasses, nsk		0	X	58,377
3119994YWV	sweetening syrups and molasses, nsk		0	X	58,377

[a] Data based on the 2002 Economic Census.