Chapter 2
Sucrose, HFCS, and Fructose: History, Manufacture, Composition, Applications, and Production

John S. White

Key Points

- The most common nutritive (caloric) sweeteners in use today are sucrose and high fructose corn syrup (HFCS).
- Allegations that HFCS is especially obesigenic in comparison with other sweeteners promoted it from relative obscurity to national prominence and effectively positioned HFCS as the "unhealthy" sweetener; sucrose, which is comparable in so many respects, became the "healthy" sweetener by default. But is this polarizing characterization justified?
- This chapter will make the case that sucrose and HFCS are so similar in manufacturing, composition, caloric value, sweetness, and functionality as to make them interchangeable in many food formulations; and their consumption patterns and composition in the blood following digestion are also strikingly similar.
- Whether or not subsequent metabolism of the absorbed component sugars from sucrose and HFCS is different enough to affect disease risks and human health will be explored in the chapters that follow.

Keywords Caloric sweetener • Fructose • Glucose • High fructose corn syrup • High fructose syrup • HFCS • HFS • Isoglucose • Nutritive sweetener • Sucrose • Sugar • Sugars

Introduction

Sugars[1] are an important component of the modern diet, contributed not only by amounts naturally occurring in many fruits, vegetables, and nuts but also by sweeteners added to processed foods and beverages. Because these sweeteners contribute metabolizable energy to the diet, they are called "caloric" or "nutritive" sweeteners. This chapter is concerned with glucose–fructose sweeteners, those containing both sugars. The most important of these are sucrose and high fructose corn syrup (HFCS). Honey, fruit juice concentrates, and agave nectar are popular sweeteners fitting this

[1] "Sugars" (plural) is the descriptive term commonly applied to the category of mono- and disaccharides used to sweeten foods and beverages. "Sugar" (singular), used without a modifier, is a synonym for sucrose (common table sugar); sugar and sucrose will be used interchangeably in this chapter.

J.S. White, Ph.D. (✉)
White Technical Research, Argenta, IL 62501, USA
e-mail: white.tech.res@gmail.com

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description, but comprise only a small fraction of the total. Pure crystalline fructose will be included as a comparator; however, it should be understood that as a stand-alone ingredient, fructose is a specialty sweetener with unique functionality, but is also used in comparatively minor amounts.

Glucose is ubiquitous in the diet and plays a central role in the energetics and regulation of human metabolism. By itself, glucose is consumed in two forms: as the free sugar dextrose (a food industry synonym) and bonded to itself in polymers (starches in whole foods, purified starches, dextrins, maltodextrins, and regular corn syrups). Glucose also occurs in disaccharides bonded to other sugars, as in sucrose (bound to fructose) and the milk sugar lactose (bound to galactose). Finally, glucose exists in the free (unbonded) state with equivalent free fructose in most fruits, vegetables, and sweeteners (HFCS, honey, grape juice concentrate) or with surplus fructose in a few others (apple and pear juice concentrates and agave nectar). Regular corn syrup—mixtures of polymeric glucose of varying chain lengths, but *no* fructose—is sometimes grouped for statistical purposes with added sugars; however, its relative sweetness is quite low (about 40 % that of sucrose) and its functionality is quite different from HFCS. For this reason, glucose-only products will be mentioned just as comparators to fructose-containing sweeteners in this chapter; interested readers are referred to the excellent reference texts by Schenck and Hebeda [1] and Hull [2] for more specific information.

The so-called high intensity or low calorie sweeteners such as aspartame, sucralose, and stevia comprise a separate category of sweeteners that falls outside the scope of this chapter. More information on these "alternative" sweeteners can be found in the recently updated volume edited by Nabors [3].

The central question of this book—whether consumption of glucose–fructose sweeteners is excessive and constitutes a genuine threat to human health—will be addressed in the chapters that follow. The primary purpose of this chapter is to document the history, manufacture, composition, applications, and consumption of the primary fructose-based sweeteners: sucrose and HFCS. A secondary purpose is to demystify sugars by clarifying many of the misconceptions and inaccuracies so pervasive in contemporary scientific and popular literature.

Historical Perspective

Sugars have been a part of the human diet since the origin of man. During the hunter-gatherer period, sugars came mostly from wild fruits, vegetables, and nuts and consisted largely of glucose, fructose, and sucrose. These were supplemented on occasion whenever wild honey was chanced upon; honey consists mainly of variable amounts of glucose and fructose, with smaller amounts of sucrose and other sugars. Early agricultural communities farmed cereal grains such as rice, wheat, and maize (corn)—and later, tuberous potatoes—which provide considerable glucose when the starchy contents (high molecular weight glucose polymers) are enzymatically hydrolyzed in the normal course of digestion. As civilizations evolved, honey provided a means to sweeten the diets of the affluent on a more consistent basis, but was too scarce a commodity to be enjoyed by the masses. Although sugarcane was domesticated about 10,000 years ago, it wasn't until the last few centuries that sugar became widely available. The relatively recent development of HFCS provided a liquid sweetener alternative to sugar in the USA (and to a lesser extent in other countries), though sugar is still used at ten-times the level of high fructose syrups worldwide.

Sugar [4–10]

Sugar is derived from sugarcane or sugar beets and is produced in 123 countries around the world. Sugarcane produced 80 % of world sugar in 2009.

Domesticated sugarcane predates sugar beets by many thousands of years. It is a perennial true grass requiring a long growing season with exposure to abundant rain and sunlight. Not surprising, the earliest sugarcane species are thought to have originated in South Asia. *Saccharum edule* and *S. officinarum* were domesticated around 8,000 BC in New Guinea and *S. barbari* around the same time in India. *S. officinarum* survived as the dominant cultivar and sugarcane today is the most cultivated crop in the world. Sugarcane contains 12–13 % sucrose. In 2011, the top five sugarcane-producing countries in the world were (most to least) Brazil, India, China, Thailand, and Pakistan. Together they produced 1.3 *trillion* tonnes[2] (75 % of the annual sugarcane crop).

The sugar beet (*Beta vulgaris*) is descended from chard, the oldest known beet type, domesticated around 2000 BC by the Greeks and Romans for food and medicinal uses. Selective breeding in Italy produced the familiar bulbous taproot of red and white beets by 300 AD. Large-rooted mangel-wurzel beets were used as livestock feed in the 1700s in Germany, Holland, and England. They require long hours of moderate sunshine and lots of rain or irrigation for successful growth. These conditions are met throughout much of Northern Europe and in 12 states in the USA. Modern sugar beets contain 16 % sucrose. The top five sugar beet producing countries in the world in 2011 were the Russian Federation, France, the USA, Germany, and the Ukraine, with a combined production of 1.5 *million* tonnes (57 % of the annual sugar beet crop).

The history of sugar covers 10,000 years and its chronology closely follows military conquest, exploration, and colonial expansion. The following is a summary of milestones in its development as a dietary staple:

8000 BC	Sugarcane first domesticated in New Guinea; gradually spread to SE Asia, China, and India
2000	Chard, oldest known beet type, domesticated by Greeks and Romans as food and medicine
800	Early Chinese manuscripts contain first reference to sugar with descriptions of Indian sugarcane fields
500	Process to mold cooled sugar syrup into large flat bowls developed in India, enabling regional transport; Darius the First learns of sugarcane, "the reed which gives honey without bees," during his conquest of India
300	Alexander the Great brings "the sacred reed" along in his conquest of Western Asia; Greece and Rome begin to import sugar as a luxury sweetener and medicine
100–300 AD	Bulbous taproot of red and white beetroots developed through selective breeding as food source in Italy
400	Granulated sugar crystals from sugarcane juice developed during Golden Age of India by Imperial Guptas; sugar becomes a major trade item
500–600	Traveling Buddhist monks introduce sugar to China and Indian sailors expand sugar through trade with Indian Ocean partners; sugar plantations built in China based on Indian model
600s	Arabs acquire sugarcane among spoils of war after invading Persia; sugarcane spreads to Egypt, Rhodes, Cyprus, North Africa, Southern Spain, and Syria through further invasions, conquests, and increasing trade
700–1200	Muslim countries in Middle East and Asia adopt Indian sugar production methods during the so-called Arab Agricultural Revolution; returning Crusaders bring "sweet salt"; Venetian merchants produce sugar in Tyre for export to Europe
1300s	Improved press doubles juice yield, expanding sugarcane production to wider geographic areas; sugar sells at 2 shillings/lb in England (~$75/lb today), affordable only to the rich

[2] One tonne = 1,000 kg = 2,704.6 lb.

1400–1700	Spanish and Portuguese explorers looking for new land to grow profitable sugarcane take it to the Canary Islands, Hispaniola, and Central/South America; Flemish merchants establish Antwerp refining and distribution center to compete with Venetians; Dutch explorers introduce sugarcane from South America to the Caribbean islands
1700s	Widespread cultivation/processing makes sugar more affordable in Europe and America; Caribbean leads the world in low-cost production, facilitated by slave and indentured workforce; steam engine first used in Jamaica to power sugar mills and steam used to heat sugar extraction kettles
	Large-rooted "mangel-wurzel" beets used as livestock feed in Germany, Holland, and England; Marggraf discovers sucrose in beetroot; Achard builds first beet sugar factory in Cunern (in modern Poland); processing expands on small scale throughout Europe
1800–1850	Sugar becomes a food necessity, widely used in beverages, preserves, confections, desserts, and processed foods; Cuba becomes the richest Caribbean country due to abundant accessible land, lingering slavery and adoption of modern sugar cultivation/processing techniques; Edward Charles Howard's closed kettle vacuum pan reduces heat-catalyzed sugar losses via degradation reactions and reduces energy costs; Norbert Rillieux applies multiple-effect evaporation for further energy efficiencies; David Weston uses centrifugation to separate sugar from molasses
	Cane sugar shortage due to British blockades during Napoleonic Wars spurs beet sugar research
1850–1880	Beet sugar surpasses cane in Europe after slavery abolition depletes Caribbean workforce; first commercially successful American beet sugar factory is built in Central California
1900s	Sugar use becomes commonplace around the world; HFCS, a liquid sweetener alternative, takes nearly half of sugar's US market, but sugar remains globally dominant

High Fructose Corn Syrup (HFCS) [11–16]

The history of high fructose corn syrup is linked with sugar, in that HFCS owed its beginning to demand created by periodic upsets in the supply of sugar. During such times, caused by weather or political instability in cane-producing regions, sugar supplies became scarce and prices inflated, causing a hardship to food and beverage manufacturers. The mid-to-late-twentieth century was an especially tumultuous time for sugar production with two major price spikes (1975 and 1980) occurring within a span of 5 years; between 1960 and 2012, retail sugar prices increased sixfold. This created a window of opportunity for the corn wet milling industry, which had access to a plentiful and dependable raw material—cornstarch—and was seeking new ways to use it. Existing products such as regular corn syrups and dextrose lacked sufficient sweetness and functionality to successfully compete with sugar. A series of technical achievements serendipitously coalesced around the time of the most egregious sugar upsets to spur the development of a product with every bit as much sweetness and functionality as sucrose: high fructose corn syrup. History thus repeated itself, just as sugar supply issues created an opportunity for the budding beet sugar industry during the Napoleonic Wars 150 years earlier.

Although fructose is found in many fruits and vegetables and the primary added sugars, its use as a food ingredient is fairly recent. Crystalline fructose was available and used primarily in pharmaceutical applications prior to 1987. The A.E. Staley Manufacturing Company saw untapped opportunities for fructose in the food and beverage industry because of its unique sweetness and physical and functional properties, licensed crystallization technology from European beet sugar producer, Finnsugar, and began marketing it to food and beverage companies in the late 1980s.

The following timeline highlights events in the history of high fructose corn syrup that culminated in capturing nearly 50 % of the US sucrose market (see Chap. 9) for a more in-depth discussion):

6000 BC	Egyptians cement papyrus strips together with wheat starch adhesive
184 BC	Cato records an early grain starch process using steeping, pressing, filtration, sedimentation, washing, and drying
1500s AD	Wheat starch, first manufactured in Holland, finds use as laundry sizing and white hair powder
1765	Potato starch, more economical than wheat, begins in Germany
1807	First American wheat starch plant is built (NY); new uses expand global starch industry: textiles, paper, color printing, adhesives (dextrins, British gums), and food thickeners
1811	Russian chemist Gottlieb Kirchoff converts non-sweet starch into sweet glucose via acid hydrolysis
1844	Wm. Colgate & Co. switches raw material from wheat to corn; eventually becomes largest starch producer in the world
1864	Union Sugar Company (NY) treats cornstarch with enzymes to make corn syrup (mixture of glucose oligomers); less than half the sweetness of sugar but a good thickener, more reliably available, cheaper than cane sugar and heavily taxed molasses
1940	Sidney Cantor and Kenneth Hobbs patent alkaline isomerization of glucose to fructose for Corn Products Refining Company; process lacks commercial viability due to formation of excessive sugar degradation products
1957	Responding to erratic Cuban sugar production, Clinton Corn Processing Company (Clinton, IA) researchers Richard Marshall and Earl Kooi develop a process using microbial enzymes to partially isomerize domestic corn glucose to fructose; product is higher quality, domestic US corn is more reliable, but process isn't economically viable
1965	Japanese Agency of Industrial Science and Technology (AIST) fermentation scientist Yoshiyuki Takasaki isolates a heat-stable enzyme (xylose isomerase) from *Streptomyces* sp.
1966–1967	AIST uses small-scale Takasaki-Tanabe Enzyme Process to produce HFCS; AIST and Clinton form joint venture to scale up process; Clinton uses liquid enzyme in batch process to make the first commercial HFCS containing just 15 % fructose
1968	Using combined immobilized and liquid enzyme in batch process, Clinton produces HFCS with 42 % fructose ("first generation" HFCS); Clinton licenses process to A.E. Staley Manufacturing Company (Decatur, IL)
1972	Clinton produces 42 % HFCS from immobilized enzyme in the first continuous process
1974–1976	World shortages again spur research to find a suitable sugar replacement; Staley European partners, Amylum (Belgium) and Tunnel Refineries (UK), begin production of HFCS-42 (42 % fructose)
1978	Introduction of moving-bed chromatographic separation of fructose from glucose ("fractionation") enables production of HFCS with 55 % fructose ("second generation" HFCS)
1981–1983	Staley research team identifies trace differences between sucrose and HFCS; improved refining removes final barrier to full substitution of sucrose with HFCS in sugar-sweetened beverages
1984	HFCS approved at 100 % sugar replacement level in Coca-Cola and Pepsi
1987	Staley begins first large-scale crystalline fructose production under license from Finnsugar; process is adapted from sugar beet raw material to cornstarch

A key learning is that sugars have been a part of the diet for many thousands of years, though not in the amounts now consumed. The only bona fide challengers to cane sugar—beet sugar and HFCS—were developed in response to upsets in supply caused by the turmoil of war, weather, or politics.

Sweeteners in the Crosshairs: 1970 to the Present [17–23]

Sweeteners didn't attract much attention from nutrition critics until the 1970s. First published in 1972, updated in 1986, and republished in 2012, John Yudkin's book, *Pure, White and Deadly: How Sugar is Killing Us and What We Can Do to Stop It*, was one of the first to suggest nutritional differences between simple sugars and complex carbohydrates and propose that sugars have deadly effects at levels consumed in the Western diet. Yudkin's ideas fell out of favor as the relationship between cholesterol and cardiovascular disease promoted by rival Ancel Keys gained traction.

In the 1980s and 1990s, a series of scientific papers by Gerald Reaven (Stanford University) and Sheldon Reiser (USDA, Beltsville) focused attention on the fructose component of sucrose and HFCS as being especially problematic for heart disease and the metabolic syndrome. Many of the arguments put forward by Reaven, Reiser, and others were addressed in the 1993 Fructose Monograph edited by Allan Forbes and Barbara Bowman which concluded, "on the basis of currently available information, there is little basis for recommending increased or decreased use of fructose in the general food supply or in products for special dietary use."

Sugars remained out of the spotlight for a decade until publication of a commentary in the *American Journal of Clinical Nutrition* by Bray, Nielsen, and Popkin catapulted HFCS front and center. Their hypothesis that "the overconsumption of HFCS in calorically sweetened beverages may play a role in the epidemic of obesity" had two important consequences: (1) the hypothesis was accepted indiscriminately as fact by many in the lay public and scientific communities, thereby positioning HFCS as the "bad" sugar and (2) sucrose—not part of the hypothesis, though similar to HFCS in composition, calories, sweetness, functionality, consumption, and metabolism—was viewed as the "good" sugar. Though much data have been published since then demonstrating metabolic equivalence between the two sugars, the vilification of HFCS has been long-lived and its damaged reputation has proven difficult to repair.

Direct challenges to fructose—from both sucrose and HFCS—resurfaced in the past decade from Bray, Peter Havel, Robert Lustig, Richard Johnson, and others. Bray reimagined Yudkin's book in the title of a recent paper and Lustig is a self-professed Yudkin acolyte. The current indictment of fructose is based largely on data of weak evidentiary value from epidemiologic and animal studies, or randomized controlled trials in humans using exaggerated experimental protocols comparing fructose and glucose in isolation or at doses well above those encountered in the human diet. The merits of these challenges are analyzed in the chapters that follow.

Manufacturing Processes [24–30]

One of the persistent misconceptions is that sugar is produced by immaculate process—it falls in shimmering white crystals from cane or beet into the sugar bowl—whereas HFCS production is highly industrialized using processing aids best relegated to the chemistry lab. In reality, both sweeteners are derived from complex botanical sources containing innumerable and potentially overwhelming color, odor, and flavor compounds that must be removed. Because food and beverage manufacturers demand highly purified sweeteners devoid of unwelcome contaminants and because process engineers only have access to a handful of refining techniques, the two manufacturing processes are

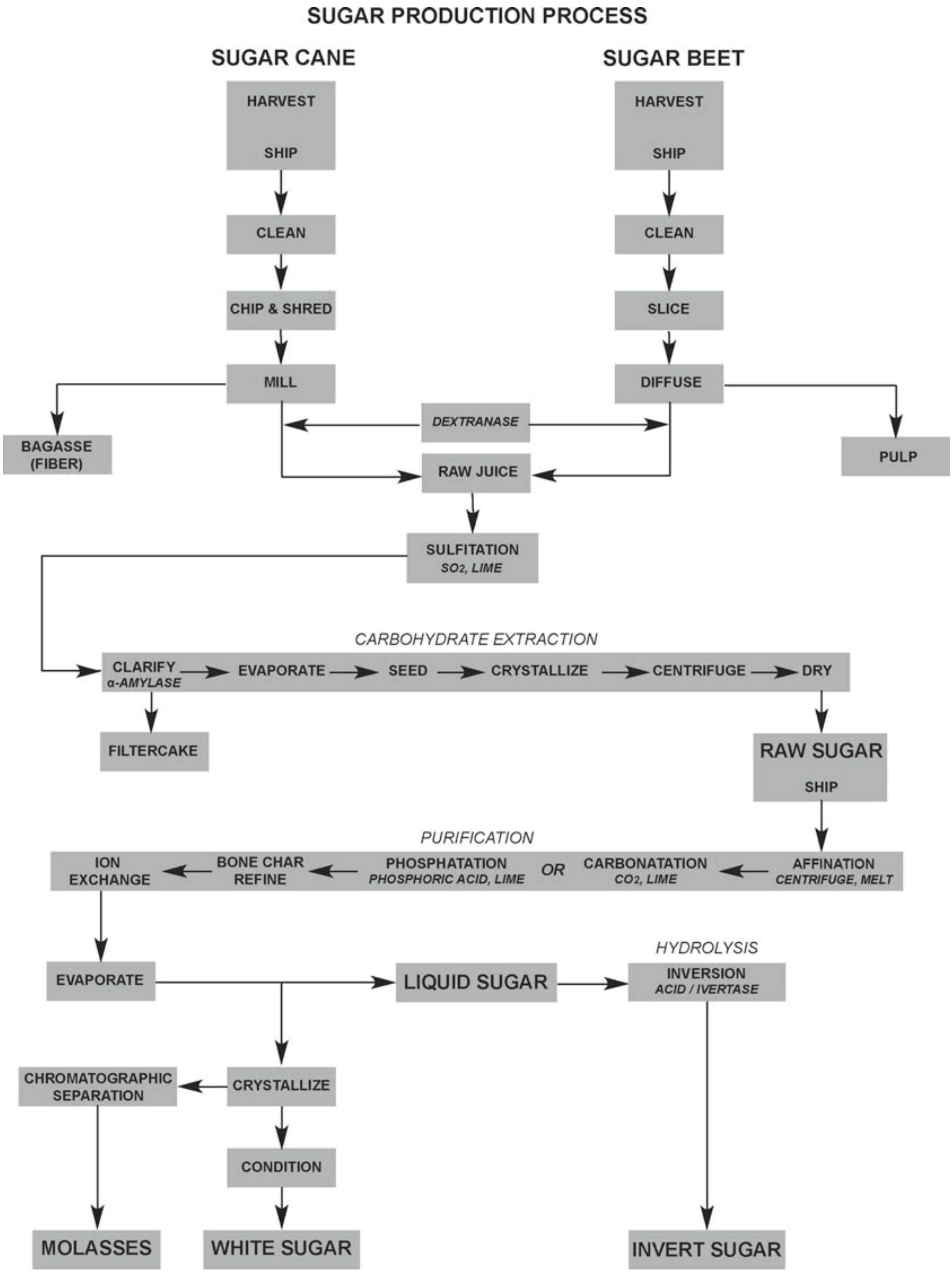

Fig. 2.1 Sugar (sucrose) production process

necessarily similar. Figures 2.1 and 2.2 show flow diagrams for production of sugar and HFCS, respectively. The process described for HFCS is called corn wet milling because of the water flow that carries raw materials through the manufacturing process to finished products. Several previous publications offer additional perspectives and detail the reader may find of interest [13, 31, 32].

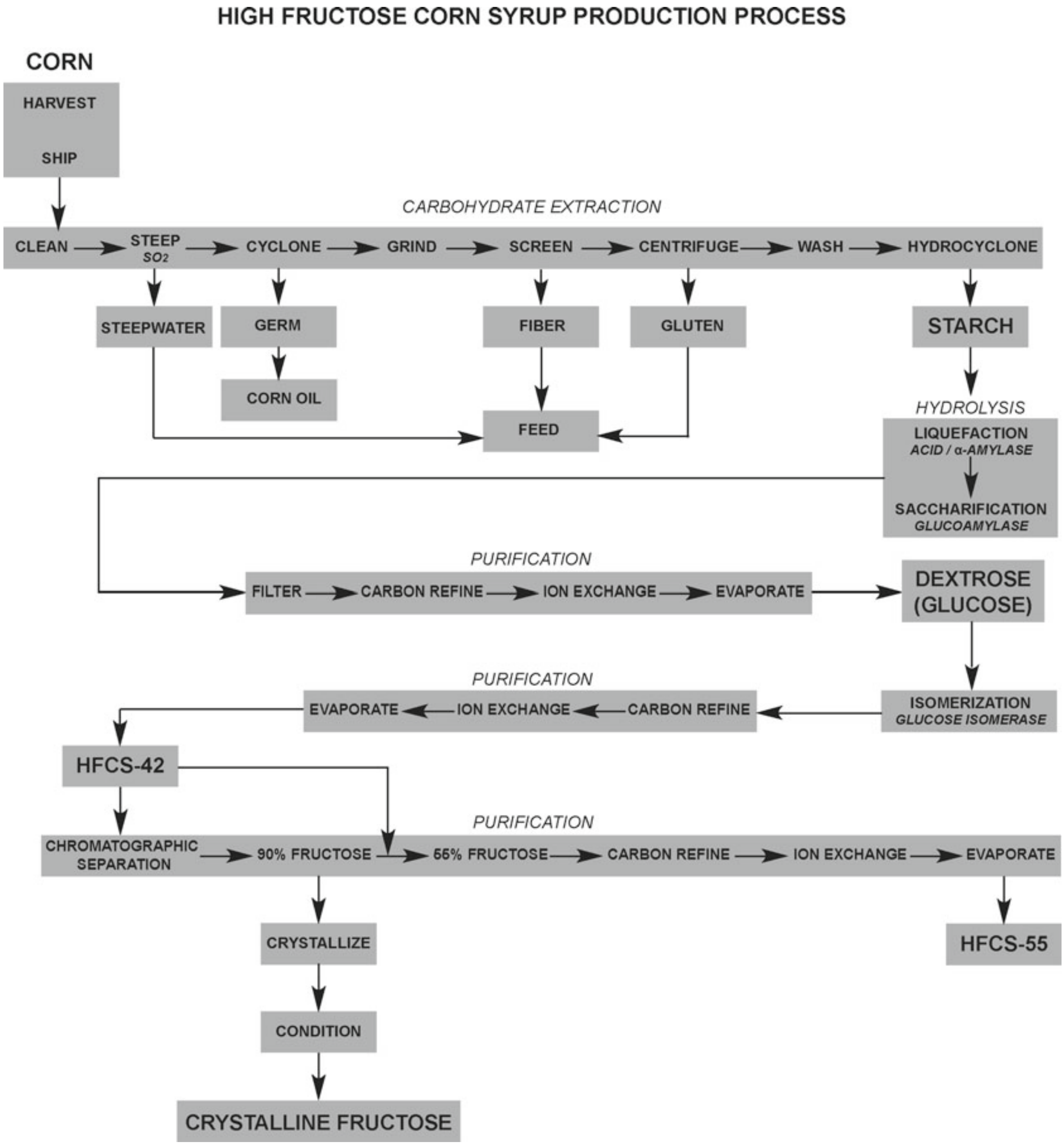

Fig. 2.2 HFCS production process

Sugar and HFCS manufacturing have the following process operations in common:

Harvesting and shipping of raw agricultural material to a processing facility occurs with all sweeteners.

Carbohydrate extraction is achieved by physically disrupting the raw material to allow isolation of the carbohydrates within.

- Cleaned sugar beets are sliced and sugarcane is chipped, shredded, and milled. In a process called sulfitation, the disrupted material is soaked (steeped) in water to which lime and sulfur dioxide (SO_2) are added. Sulfitation serves to adjust pH, minimize subsequent color formation, and control microbial growth. "Mud" filtration improves clarity by removing unwanted insoluble materials.

Extraction is completed by an initial crystallization step. The raw sugar produced can be either processed onsite to higher purity grades or shipped to a remote refining plant.

- Physical disruption and SO_2 treatment are reversed in corn wet milling. Cleaned corn is steeped in SO_2 not only for pH/color/microbial control, but also to soften the hull for subsequent physical removal; the softened hull also allows diffusion of SO_2 into the kernel, which denatures the protein (gluten) matrix anchoring starch granules in place. Milling, grinding, and screening separate starch from hull and oil-containing germ. Mud centrifugation is also used in corn wet milling plants, where it removes protein (gluten) and other insolubles from starch, which is washed and centrifuged again to high purity.

Enzyme technology is used in both sugar and HFCS processing to reduce the size of high molecular weight carbohydrates and carry out molecular transformations of one sugar to another. Adjustments to pH and temperature are commonly made to accommodate enzyme optima, optimize reaction rates, and prolong enzyme lifespan.

- Sugar raw materials can contain dextrins and starches, both high molecular weight carbohydrates that create haze and impede filtration. The enzymes dextranase and alpha-amylase reduce the size of these molecules, thereby improving clarity and filtration. Total invert sugar is a syrup product very similar to HFCS that is made by purposely breaking (inverting) ~95 % of the chemical bonds in sucrose that link fructose and glucose together; medium invert sugar is a partial hydrolysis product of approximately 50 % sucrose and 25 % each glucose and fructose. While inversion can be accomplished with acid and heat, sugars degrade under these harsh conditions, creating unwanted color and flavor. A cleaner, more controllable molecular transformation is achieved when the enzyme invertase is used.
- Enzymes are used in corn wet milling for hydrolysis of high molecular weight starch and the molecular conversion of glucose to fructose. Hydrolysis takes place in two steps: liquefaction uses dilute mineral acid and/or alpha-amylase to reduce the polymer length of starch down to oligosaccharides and glucose; saccharification uses glucoamylase to hydrolyze remaining oligosaccharides to glucose.
- It has been known for more than a century that glucose can be converted to its structural isomer, fructose, by alkaline isomerization; however, this is a harsh process that leads to unacceptable decomposition of sugars. Use of enzyme technology overcame this obstacle and use of immobilized (reusable) glucose isomerase made the process commercially viable. Takasaki discovered that a xylose isomerase from *Streptomyces* sp. could convert glucose to fructose in the presence of magnesium activator. This was the first application of immobilized enzyme technology and remains one of the most successful.

Purification steps are needed to remove unwanted compounds to make sweetener products acceptable for foods and beverages.

- Sugar refiners used filtration through diatomite (diatomaceous earth) for many years to remove unwanted compounds, but now favor precipitation-flocculation methods such as carbonatation or phosphatation. These methods use carbon dioxide gas or phosphoric acid in combination with milk of lime (aqueous calcium hydroxide) to denature protein, absorb color compounds, and destroy monosaccharides (largely glucose and fructose) that interfere with crystallization and contribute additional color if left intact. A recent innovation is the use of process aids such as Talofloc® (a quaternary ammonium compound) to precipitate high molecular weight compounds. These methods may be followed by pH adjustment with soda ash and sulfitation. Following final filtration, the "light juice" is carbon treated and ion exchanged to remove residual color and non-saccharide compounds prior to final crystallization or enzyme hydrolysis; the commercial products white or invert sugar, respectively, are produced. Molasses is the colored, flavored, somewhat aromatic syrup residue after sugar crystals have been removed.

Table 2.1 Sugars comparison—compositions[a]

Component	Cane sugars				Corn sweeteners		
	Raw	Brown	White refined	Total invert	HFCS-42	HFCS-55	Crystalline fructose
Sucrose (%)	96–99	92.96	99.3	6			
Fructose (%)	0.2–0.3	2–3	0.006	47	≥42	≥55	≥99.9
Glucose (%)	0.2–0.3	1–2	0.007	47	53	42	0.1
Glucose Oligosaccharides (%)					5	3	
Physical form	Crystalline			Syrup	Syrup		Crystalline
Moisture (%)	0.3–0.7	1–2	0.015	22	29	23	0.1
Color[a]	900–8,000	2,000–9,000	35	40	≤25	≤25	≤30
Ash (%)	0.3–0.6	1–2	0.012	0.3	≤0.03	≤0.03	0.01
Sweetness Relative to sucrose[b]			100		92	99	117
Caloric value NME by weight (kcal/g)			3.9		3.7		3.6

Abbreviations: *Bx* Brix, *cps* centipoise, *ICU* international color units, *NME* net metabolizable energy, *ppm* parts per million, *RBU* reference basis units

[a]Color units: sucrose, ICU; HFCS and crystalline fructose, RBU

[b]Sweetness comparisons made at 10 % solids and room temperature relative to sucrose (sweetness = 100)

- In parallel with sugar refining, the corn wet milling process stream from liquefaction and saccharification is purified by filtration, carbon treatment, and ion exchange chromatography to remove gross particles, unwanted color and flavor, and charged compounds, yielding the commercial product dextrose. Subsequent inversion of the dextrose feed stream produces the commercial product HFCS-42 (42 % fructose) that is sold as-is or enriched for fructose (fractionated) using innovative moving-bed chromatographic separation. Fructose has a greater affinity than glucose for strong-acid cation exchange resin in the calcium salt form, effecting a practical separation of the two. Enriched (90 %) fructose is blended back with HFCS-42 to produce the higher-fructose commercial product HFCS-55, which then goes through the same purification sequence described above.

Crystallization is a powerful purification tool, wherein impurities are excluded from the growing crystal matrix.

- It is used to advantage in refining sugar, first in the production of raw sugar and later in the refinery process as the final purification step for white sugar.
- In another example of similarities to sugar manufacture, corn wet millers use crystallization to make crystalline fructose. A portion of the 90 % fructose stream produced during fractionation is diverted, seeded, and then sent to crystallizers.

A key learning is that sugar and HFCS/crystalline fructose manufacturing processes are more similar than most people realize. Non-sugar materials exist in sugar cane, sugar beets, and corn alike that must be separated from the sugars or they will overwhelm the food or beverage product in which they are used. Modern sugar and corn wet milling manufacturing plants use common physical and chemical refining methods; enzymes are used to reduce the size of large molecular weight molecules and to perform molecular transformations; carbon treatment and ion exchange resins are used to remove residual color, flavor and aroma compounds; and crystallization is used in both processes to produce dry, granular sweeteners.

Composition and Structure [32–38]

HFCS is commonly confused with either regular corn syrup (all glucose) or crystalline fructose (all fructose). That it is neither one has led to misconceptions about the sweetener. A comparison of selected cane and corn sweetener *compositions* is provided in Table 2.1. The cane sugars were chosen for their range of purities and physical forms; it should be kept in mind that cane and beet sugar manufacturers offer scores of product variations, but each one is sucrose-based. Although the corn wet milling industry makes a variety of corn sweeteners, only those containing fructose were chosen for this comparison.

A number of interesting contrasts and similarities can be drawn between cane and corn sweeteners; note that many of the same comparisons hold true for beet versus corn sweeteners:

- Cane sugars are sold in both crystalline and liquid forms. Invert sugar is a syrup product in which aqueous sucrose has been purposely hydrolyzed as described earlier into mixture of sucrose, glucose, and fructose. Invert sugar was popular prior to the advent of HFCS. Aqueous solutions of sucrose are also produced and these are called liquid sugar.

  HFCS is sold in the syrup form because it does not crystallize readily. Crystalline fructose is one of the several corn sweeteners available in dry form; an aqueous liquid fructose product—analogous to liquid sugar—is also made.
- All cane and HFCS products contain both glucose and fructose. For cane sweeteners in the crystalline form, the glucose and fructose are bound together as sucrose. For total invert sugar and HFCS, most of the glucose and fructose are in the free, monosaccharide form. Sucrose contains small amounts of residual free fructose and glucose, while HFCS contains small amounts of residual glucose oligosaccharides.
- Raw and brown sugar are highly colored, flavored, and aromatic products. Raw sugar is a crude product made early in the process that still carries considerable residue from cane or beets. Brown sugar derives its color, flavor, and aroma from compounds excluded from refined sugar during crystallization.

  Refined sugar, HFCS, and crystalline fructose are highly purified sweeteners with extremely low color, flavor, and aroma and are thus suitable for use in products with the most delicate flavors and colors. This is not surprising, since their manufacture incorporates many of the same purification processes.
- Relative sweetness is a means of ranking sweeteners in comparison with one another. By convention, comparisons are carried out using 10 % solutions (dry solids basis) held at room temperature by human sensory panels. Also by convention, sucrose is used as the standard and given a relative sweetness of 100; test comparators are awarded higher or lower numbers based on their perceived sweetness relative to sucrose.

  Crystalline fructose is the sweetest dietary sugar with a relative sweetness of 180. Reliance on this number has caused confusion in the literature, however, since when tested at 10 % solids—a condition more representative of its primary uses—fructose has a relative sweetness of 117, a number more in line with practical experience.

  HFCS-55 was strategically designed to have the same relative sweetness as sucrose so it could be easily substituted for sucrose in foods and beverages. HFCS-42 has a lower relative sweetness, directly attributable to its lower fructose content.

Chemical *structures* of sucrose and HFCS are shown before and after digestion and delivery to the bloodstream in Fig. 2.3. Another misconception about HFCS is that it is metabolized differently than sucrose. This misconception is due in large measure to a short-sighted focus on the dissimilar structures of the sugars *before* digestion rather than their similarities *after* digestion; the latter provide a far more accurate representation of the molecules that actually enter the metabolic pathways.

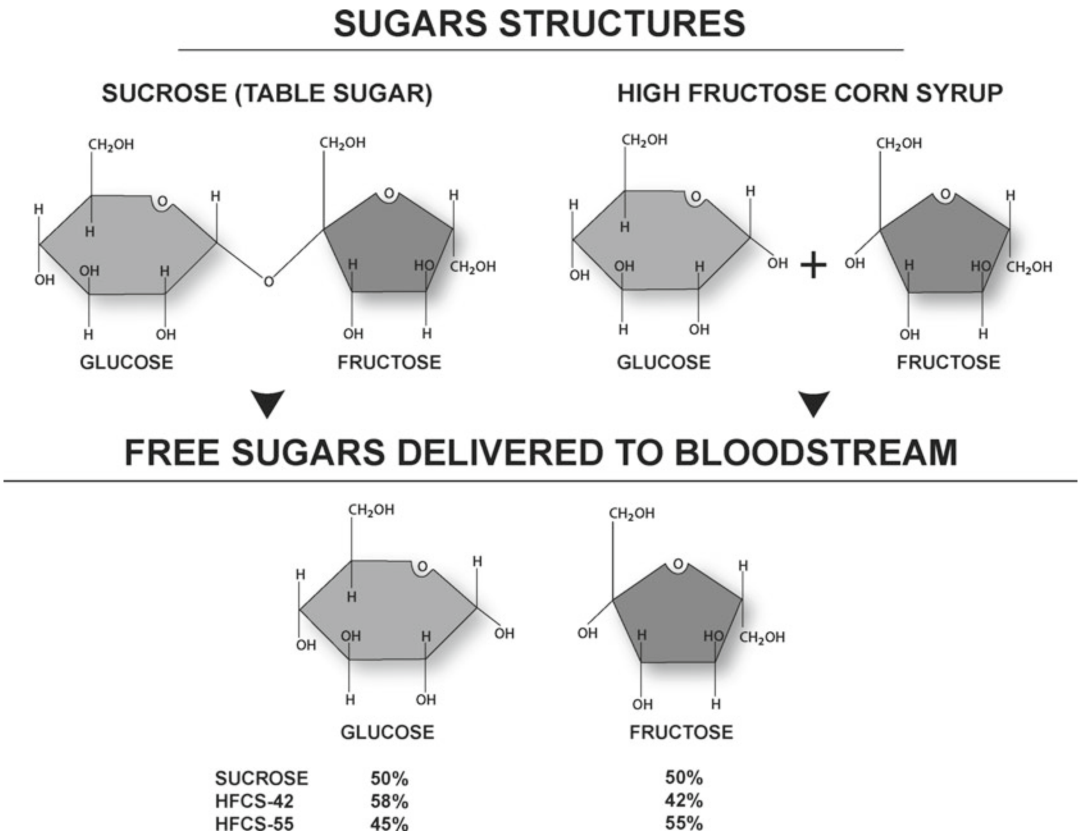

Fig. 2.3 Sucrose and HFCS structures before and after digestion and delivery to the bloodstream

Sucrose (α-D-glucopyranosyl-(1,2)-β-D-fructofuranoside) is a disaccharide comprised of equal parts of glucose and fructose. They are joined via glycosidic linkage between carbon-1 of glucose and carbon-2 of fructose. The glycosidic bond in sucrose is unusual in two ways: it eliminates the possibility of elongation by blocking subsequent bonding to other sugars; and it occupies the reducing ends of fructose and glucose, rendering sucrose a nonreducing sugar with particular functional implications, as we shall see later. During digestion, sucrose is rapidly and quantitatively hydrolyzed to free glucose and fructose by the enzyme, sucrase, situated in the lumen of the small intestine. Liberated glucose and fructose are transported into the portal blood via the action of enterocyte transporters SGLT-1, GLUT5, and GLUT2 (see Chap. 3 for additional detail).

The sugars in HFCS are primarily in monosaccharide form, so the action of sucrase is unnecessary. However, the residual glucose oligomers do require hydrolysis and are apt substrates for amylase enzymes found in the mouth and intestines. The product of amylase hydrolysis is monosaccharide glucose, so the complete digestive products of HFCS are free glucose and fructose. These free sugars interact directly with enterocyte transporters and arrive in the portal blood as monosaccharides, as did the products of sucrose hydrolysis. It is at this point—in the bloodstream after digestion—that the body loses the ability to distinguish the origin of the constituent glucose or fructose: sucrose and HFCS deliver the same sugars in similar ratios to the same tissues within the same time frame to the same metabolic pathways. Researchers promoting a difference between sucrose and HFCS have suggested the *incrementally greater* fructose in HFCS-55 may play a causal role in obesity and diabetes; however, there is no persuasive evidence from randomized controlled trials in support of this theory and a growing body of literature refuting it (see Chap. 11). And, of course, the theory ignores

Table 2.2 Sugars comparison—physical properties

	Fructose	Glucose	Sucrose
Sweetness relative to sucrose[a]	117	67	100
Glycemic index	14	103	65
Water activity (A_w) at 25 °C	0.634	0.891	0.844
Solubility @ 25 °C, g/g H_2O	4	1.04	2.07
Moisture binding, g H_2O/100 g solids			
@ Intermediate A_w (0.60)	18	11	3
@ High A_w (0.95)	380	207	188
Water control in frozen systems (W_g')			
Grams unfrozen H_2O/gram of solids	0.96	0.41	0.56

[a]Sweetness comparisons made at 10 % solids and room temperature relative to sucrose (sweetness = 100)

altogether the considerable use of HFCS-42 in foods and beverages, which delivers *incrementally less* fructose to the bloodstream than does sucrose (Fig. 2.3).

Sucrose, HFCS, and crystalline fructose provide comparable energy[3] to the body: caloric values are 3.9 kcal/g, 3.7 kcal/g, and 3.6 kcal/g, respectively (Table 2.1). This is to be expected, given their similar compositions. Those promoting a difference between sucrose and HFCS have argued that sucrose actually provides less energy than HFCS to the body, pointing to the sucrose enzymatic hydrolysis step as an important distinction with a cost to the body in energy to make and sustain sucrase. However, this argument is supported neither by the overlooked counterargument that residual glucose oligomers in HFCS require *many* enzymatic hydrolysis steps per molecule—also at a cost to the body in energy—nor by the comparative NME data in Table 2.1, which take into account energy losses in such processes.

Physical Properties and Functionality [12, 13, 39]

A common misconception about all sugars is that their only purpose is to sweeten foods and beverages. In fact, they are highly functional ingredients capable of performing multiple duties in products. The physical properties of individual sugars comprising cane and corn sweeteners in Table 2.2 provide a basis for understanding performance differences that exist between sugar and HFCS in foods and beverages. In some cases, the functional differences are so slight that neither sweetener offers an advantage; in others, the functional differences are significant enough to offer food formulators a clear advantage.

- *Relative sweetness*. As stated earlier, fructose is the sweetest dietary sugar and is nearly 1.2 times as sweet as sucrose. Glucose is less sweet at a relative sweetness of 67. The relative sweetness of HFCS (Table 2.1) is a product of the individual sweetness contributions from glucose and fructose (Table 2.2). Thus, HFCS-55 is sweeter than HFCS-42 because it contains a higher proportion of more-sweet fructose and lower proportion of less-sweet glucose.

  Flavor enhancement is related to the unique sweetness perception profiles of each sugar. Because its sweetness perception profile is bell-shaped and broad—slow to develop and slow to decay—sucrose imparts a pleasing sweetness to foods and beverages. However, its broad profile can mask flavors that are perceived at the same time; sometimes, this is an asset, like the masking

[3] Ingested or gross energy is the maximum amount measured after complete combustion to carbon dioxide and water in a bomb calorimeter. When the energy lost to microbial fermentation of incompletely digested food, formation of urinary waste products, and body surface and internal waste heat production are subtracted, the actual energy content of food remains—the net metabolizable energy (NME).

of unpleasant flavors in pharmaceutical elixirs, and sometimes a liability when flavor characteristics important to a product are muted. The sweetness perception profile of HFCS is the sum of those of its constituent sugars, fructose, and glucose. The sweetness of fructose is perceived and decays quickly in a sharp peak 20 % higher than sucrose; glucose sweetness perception lags fructose but precedes sucrose in a peak 30 % lower than sucrose. Because perception of the sugars in fructose-only or HFCS-sweetened products decays faster than sucrose, these sweeteners are said to enhance the flavors of fruits and spices that are masked to a degree by sucrose

- *Glycemic index* is a measure of how quickly blood sugar (glucose) rises after eating a specific food or ingredient. Since oral glucose gives the highest blood sugar response, it is used as the standard and assigned a value of 100. At a GI of 14, fructose is at the opposite end of the scale and among the lowest GI ingredients. Sucrose, comprised equally of glucose and fructose, has a GI of 65, close to the midpoint between glucose and fructose as might be predicted. Based on sugars composition, HFCS-55 would be predicted to have a GI slightly below and HFCS-42 a GI slightly above sucrose. Because of its low GI, fructose was initially promoted as a more healthful sweetener than sucrose for diabetics. The spate of recent research suggesting fructose provokes undesirable health effects tempered this early enthusiasm, despite the tenuous nature of the claims.
- *Moisture binding and water activity* measure the ability of a substance to bind and hold moisture. These physical properties contribute to functional attributes called hygroscopicity and humectancy. Monosaccharide fructose is superior to glucose and sucrose in both attributes, giving crystalline fructose and HFCS the following functional advantages: controlling moisture to prevent separation in yogurt and sauces; extending shelf life of baked goods by retarding staling and microbial growth; and retaining moisture in dry products like granola and breakfast and energy bars. These moisture-holding abilities make it very difficult to crystallize fructose and, consequently, HFCS. While this characteristic makes HFCS unsuitable for use in baked goods requiring sugar recrystallization to help product structure, it made possible the development of soft-texture cookies where crystallizability is a detriment.

  Fructose and HFCS also provide superior water control in frozen systems like ice creams, confections, frozen baked goods, and juices. They control moisture migration and ice crystal growth in freezers, thereby minimizing water/ice separation and fruit tissue damage.
- *Colligative properties* are dependent on the ratio of the number of solute particles to the number of solvent particles for a given mass of solute—for this discussion, the ratio of sugar to water. Boiling point elevation, freezing point and vapor pressure depression, and osmotic pressure are colligative properties important to the food industry.

  Fructose has twice the solubility and half the molecular weight, so has enhanced colligative properties versus sucrose. Glucose has not only half the solubility but also half the molecular weight, so will exhibit comparable colligative properties to sucrose. Since HFCS is a blend of fructose and glucose, its colligative properties fall between those of fructose and sucrose. Thus, fructose and HFCS offer food scientists additional means of balancing freezing points to tailor ice cream scoopability and dispensing, maintain flowablility of frozen juices, and control microbial growth through amplified osmotic pressure in finished products.
- *Reducing sugars* are those able to function as chemical reducing agents, as identified in analytical tests like Tollens', Fehling's, or Benedict's. Reducing sugars and amino groups in proteins participate in Maillard nonenzymatic browning reactions to produce the appealing flavors, aromas, and surface browning in baked, cooked, and heated foods. Monosaccharide glucose and fructose are reducing sugars, both as individual ingredients and as components of HFCS. However, the reducing ends of glucose and fructose are bonded together in sucrose, making it a nonreducing sugar. For this reason, HFCS offers superior browning, flavor and aroma development in heated foods and beverages, and candies like toffees, caramels, and fudges.
- *Physical form* is important in some applications. Crystalline sucrose is well suited to dry mix products, while liquid sweeteners like HFCS are preferred for beverages. But consideration is also given to formulating sugar-sweetened beverages (SSB) with mono- versus disaccharides. The glycosidic

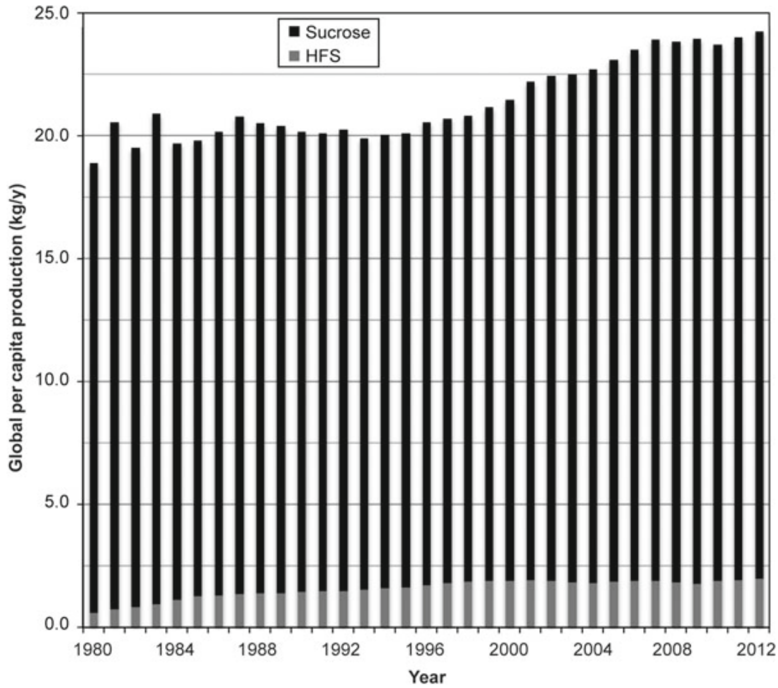

Fig. 2.4 Global per capita production of sugar (sucrose) and HFS

bond in sucrose is labile and readily hydrolyzed (inverted) over time in acidic products like SSB (pH ~3.5). Sucrose in SSB begins inverting immediately after bottling at a rate accelerated by increasing storage temperatures, changing the character of the original formulation over time. One reason SSB manufacturers turned to HFCS in the 1980s was because its composition—and product quality—remains unchanged from bottling through consumption.

A key learning is that there are differences in physical properties between sucrose, HFCS, and their constituent sugars, glucose and fructose. These differences have predictable functional consequences that food formulators need to be aware of when choosing a sweetener for a particular application. That being said, there is considerable overlap in sweetener functionality; enough that sucrose and HFCS can be substituted for one another in many applications with only minor formulation changes.

Production [40–47]

In the following section, HFCS (high fructose *corn* syrup) will refer to sweeteners made in the USA and HFS (high fructose syrup—made from corn, wheat, rice, or tapioca starch) will refer to these sweeteners made around the globe, irrespective of starch raw material.

Global per capita production of sucrose and HFS is illustrated in Fig. 2.4. Although HFCS is currently getting the lion's share of attention from critics in the USA, we live in a world dominated by sucrose. Figure 2.4 does not support the hypothesis that worldwide proliferation of HFS-55 is increasing dietary fructose, and the primary cause of rising rates of diabetes and other health disorders. In the 45 years since HFCS was introduced in the USA, the global market share for HFS has never exceeded 9 % versus sucrose and, in fact, per capita global production has been stagnant for the past 15 years. Sucrose per capita production, on the other hand, while sluggish during HFCS growth years, has grown at a steep rate since 1993. Importantly, this hypothesis ignores HFS-42, containing *less*

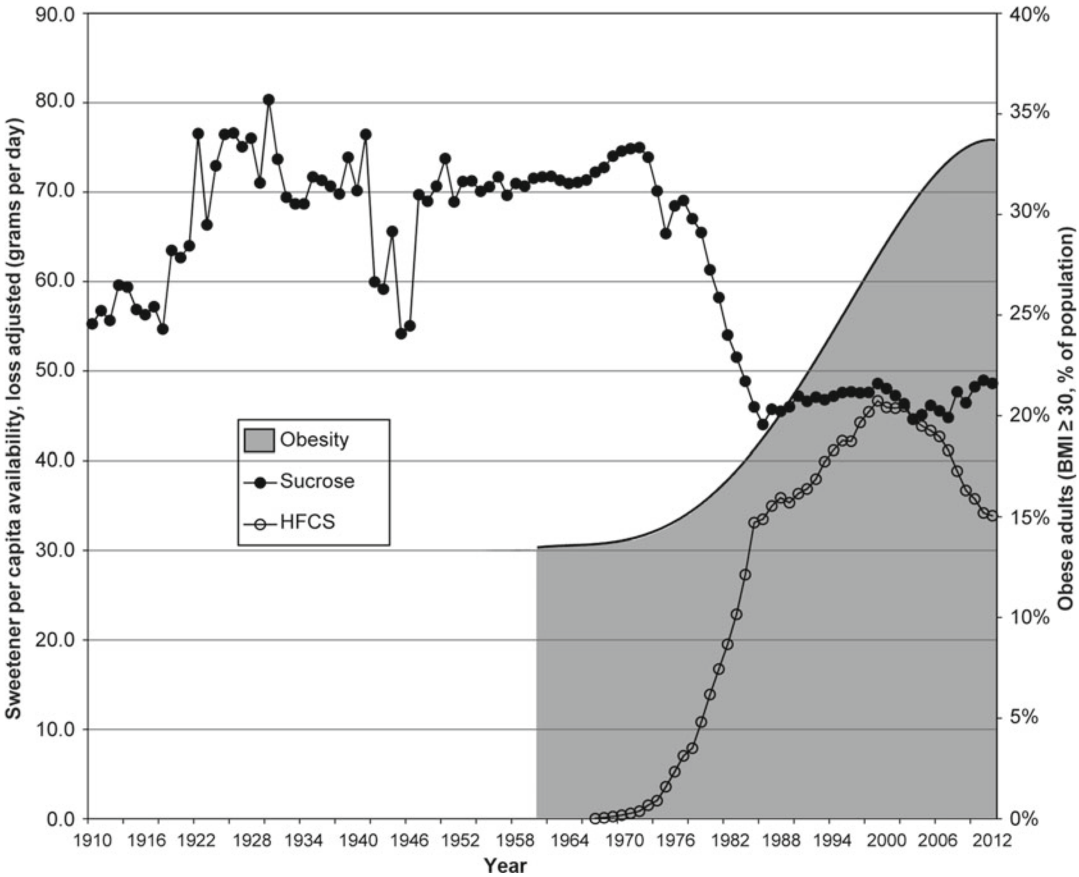

Fig. 2.5 US historical trends in sugar (sucrose) and HFCS per capita availability versus rates of obesity in adults

fructose than sucrose; HFCS-42 comprises a significant volume in the USA and is the *only* form of HFS produced in the EU [48]. And when perspective is broadened beyond sweeteners, it becomes apparent that sugars intake from all dietary sources (e.g., starches, dairy, fruits/vegetables, glucose-based ingredients) are dominated by glucose—which exceeds dietary fructose by a ratio of 5-to-1 [23]—further diminishing the plausibility of a unique role for HFCS-specific fructose in human health outcomes.

As noted earlier, Bray et al. focused astonishing attention on HFCS with their correlation-based hypothesis linking it in SSB with the US epidemic of obesity, thereby creating a persistent misconception that HFCS is uniquely obesigenic. Bearing in mind that correlation is not causation, it is useful to ask—10 years later—whether the correlation still exists. Bray's correlation relied on data between 1960 and 2000, a period when HFCS use was expanding. A very different picture emerges when current data are also considered. Figure 2.5 is a graph of US historical trends in refined sugar (sucrose) and HFCS availability versus rates of obesity in adults, from USDA–Economic Research Service per capita consumption data adjusted for loss and the WHO Global Database on BMI. Availability is derived from production data and is a rough measure of consumption. Several important observations can be made from this graph:

- Sucrose availability was relatively stable from the 1920s until sales of HFCS started to rise in the early 1970s, apart from shortages during World War II. The rise in HFCS use was mirrored on a 1-for-1 basis by a decline in sucrose. Why? Because HFCS and sucrose functioned similarly in foods and beverages.
- HFCS consumption peaked in 1999, at the tail end of Bray's data window, and has been in rapid decline for over a decade. It is worth noting that consumption rates in 2012 were similar to those

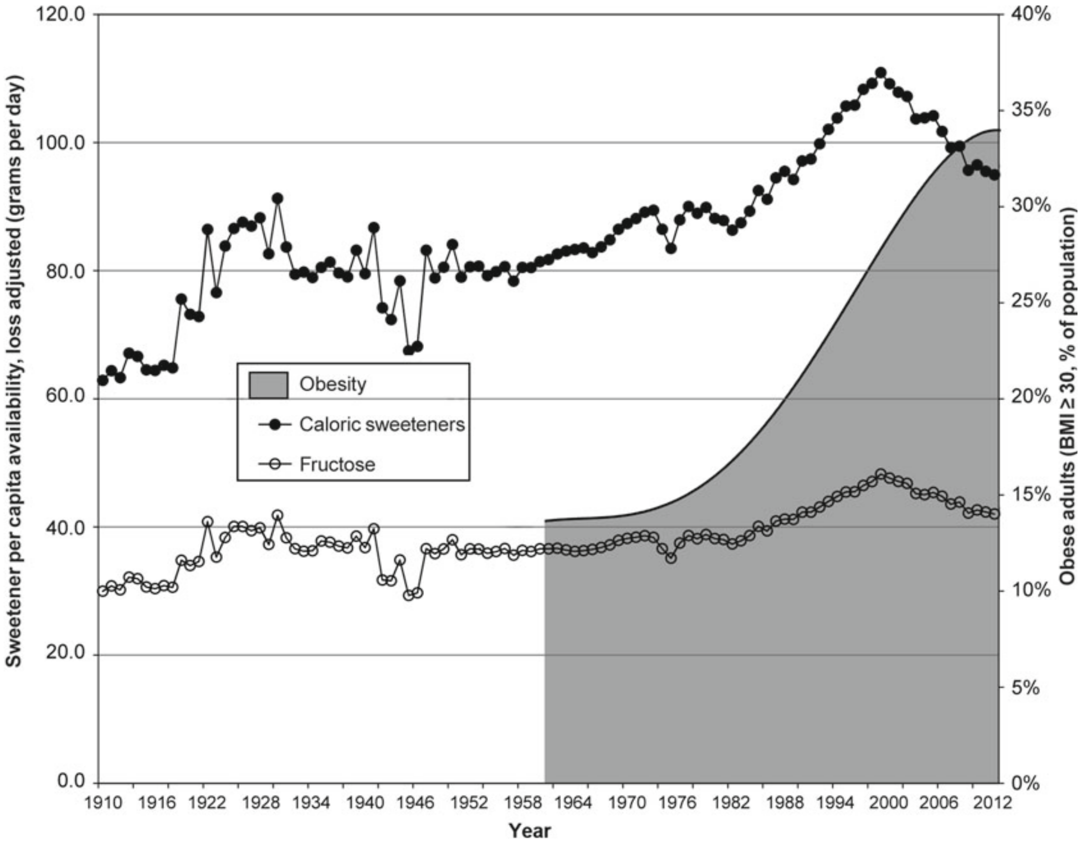

Fig. 2.6 US historical trends in fructose and caloric sweetener per capita availability versus contemporary rates of obesity in adults

last seen in 1987. Although comparable sucrose and HFCS were consumed a decade ago, Americans today consume nearly 1.5-times more sucrose than HFCS.

- Obesity rates continued to rise over the past decade. There no longer is a correlation between HFCS use and obesity rates.

A key learning is that data for the past 13 years do not support the HFCS-obesity hypothesis of Bray et al. Contemporary scientific papers all too often present a distorted picture of sweetener consumption by quoting literature sources that are badly out of date.

The HFCS hypothesis has now morphed into the fructose hypothesis. Once it was demonstrated that HFCS and sucrose are metabolically and otherwise equivalent and that a correlation between HFCS and obesity no longer exists, the HFCS hypothesis became untenable and antagonists broadened their target to include fructose from all dietary sources. The fructose hypothesis has two essential justifications:

> (1) Significant diseases related to intermediary metabolism—obesity, diabetes, cardiovascular disease, hypertension, cancer, nonalcoholic fatty liver disease, and metabolic syndrome—are increasing among Americans in step with disproportionate fructose increases in the human diet; and (2) Cause-and-effect evidence uniquely links the metabolism of fructose to these diseases in humans at typical U.S. dietary exposure levels and intake patterns [23].

The first justification in the fructose hypothesis is challenged in Fig. 2.6; the second is the subject of other chapters in this book. Figure 2.6 is a graph of US historical trends in fructose and caloric

Table 2.3 Sugars comparison—uses

	Percent of sweetener use	
Food category	Sucrose	HFCS
Bakery and Cereal	41	6
Beverages	9	72
Confectionery	19	1
Dairy	12	5
Processed foods	7	10
Other food uses	12	6

sweetener availability versus rates of obesity in adults, from USDA–Economic Research Service per capita consumption data adjusted for loss and the WHO Global Database on BMI. The following important observations can be made:

- Historical availability data show an upward trend in per capita consumption of all caloric sweeteners over the past 50 years. The upward trend peaked in 1999, the same year as HFCS, and caloric sweetener use has been in steep decline since then. This trend is supported by the NHANES study of Welsh et al., which confirmed the decline in intake of added sugars in children of all ages and people of all ethnicities since 1999.

  White recently observed that per capita energy intake in the USA increased by 449 kcal/day between 1970 and 2010, but that increased energy from caloric sweeteners was minor, accounting for only 34 kcal/day; the bulk of the increase came from flour/cereal products and added fats, which accounted for more than 90 % of the increase [23].
- The fructose hypothesis claims that fructose has increased disproportionately in the human diet, but this appears not to be so. Fructose intake rose between 1985 and its peak in 1999, but has since been in decline along with total caloric sweeteners and HFCS. Over the past 90 years, fructose intake has averaged 39 ± 4 g/day/person, a variation of just 16 kcal/day. In fact, fructose consumption in 2012 was equivalent to levels in the early 1920s, nearly a 100 years ago.

A key learning is that fructose and added sugars consumption has *not* increased disproportionately in the diet, as argued in the fructose hypothesis. Rather, fructose intakes have been remarkably constant despite the ebb and flow in dietary trends and sweetener ingredients.

Uses [49–51]

USDA-ERS tracks US deliveries of commodity ingredients to specific segments of the food industry. These data are used in Table 2.3 to compare the top use categories for sugar and HFCS in foods and beverages. It is not surprising that the top use for sugar is in bakery items and cereals. Sucrose plays a critical role in structure setting of baked goods through recrystallization and is also used in many bakery fillings and toppings. The sweet coating on cereals is made by applying a dilute sugar slurry (with or without flavorings) to wet cereal and then drying it to recrystallize the sugar, creating a visually appealing and sweet tasting cereal coating. Substantial sugar is used in the confectionery industry, largely for reasons of recrystallization in products like hard candies, chocolates, fudge, tablets, jellies, marshmallows, and taffy. In those confections where crystallinity is undesirable, like caramels or fondants (partially crystallized), the addition of corn syrup (glucose polymers) prevents this from occurring. Sugar is used in ice creams in combination with other sugars (HFCS, corn syrup, etc.)

for sweetening and to control freezing point. Note that the beverage category is one of the lowest for sugar, where its use has largely been supplanted by HFCS.

By contrast, more than 70 % of HFCS use is in beverages and for good reason. HFCS offers the same sweetness as sugar in a syrup form that is more stable in low pH beverages and requires less labor to handle: it can be offloaded from delivery vehicles and moved around a manufacturing plant by pump, is already pre-dissolved so is readily mixed with other ingredients, requires no dumping of bags, and has fewer sanitation issues. Appreciable HFCS is also used in processed, bakery and cereal products, which take advantage of its solubility (resistance to crystallization), food preservation (moisture retention and microbial control), flavor and color development/enhancement, texture softening and viscosity (at high solids). It is used in dairy applications for its fermentable sugars (yogurt), to sweeten flavored milk and with sucrose and corn syrup to balance freezing point in ice cream, frozen confections, and juices. Note that very little HFCS is used in the confectionery industry because of its resistance to crystallization, a primary sweetener requirement. However, its tendency to develop color is useful in the manufacture of fudge, caramel, and toffee.

A key learning is that sugar and HFCS are similar in many ways. Certainly, given a choice, there can be advantages to using one sweetener over another for some applications, but in many cases the advantages are subtle. Pragmatically speaking, HFCS captured nearly half of the US sugar market 40 years ago; sugar is certainly functional enough to take market share back again if the opportunity presented itself. And this is already occurring on a very limited scale: a few food and beverage manufacturers wishing to cash in on HFCS hysteria have reformulated a small number of products with sucrose. Front-of-package labeling plays to the misconception that HFCS is nutritionally inferior to sugar. However, market analysis shows that reformulation to sugar has not positively affected sales the way manufacturers intended—for the majority of reformulated products, sales trends have continued in the direction they were moving before reformulation. The reason is found in unaided consumer surveys, which reveal that less than 5 % of the buying public has sufficient top-of-mind concern to seek out HFCS-free products [52, 53].

Conclusions

This chapter has documented the history, manufacture, composition, consumption, and applications of sugar and HFCS, the primary fructose-based sweeteners. When popular misconceptions are dispelled, it becomes clear that HFCS and sugar share much in the way of botanical origins, manufacturing processes, constituent sugars, post-digestion composition, consumption patterns, physical properties, caloric value, sweetness and functionality in foods.

HFCS, added sugars, and fructose have not increased disproportionately in the food supply in the past 40 years; in fact, their consumption has been in decline for more than a decade. These data support neither the HFCS nor the fructose hypotheses seeking to link these nutritive sweeteners with rising rates of obesity, diabetes, cardiovascular disease, hypertension, cancer, nonalcoholic fatty liver disease, and metabolic syndrome.

The polarizing characterization of HFCS and sugar as opposites has made sensational media fodder, but is simply not justified as detailed in this chapter. Far better for the general public—and scientific community—to recognize that HFCS and sugar are simply two sweeteners cut from the same cloth with very similar composition, sweetness, caloric value, and functional properties. Nutritive sweeteners contribute richly to the palatability and flavor of the foods we eat, but as with all caloric ingredients, care must be exercised to take them in moderation.

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