

# Sweeteners from Starch: Production, Properties and Uses

*Larry Hobbs*

I. Introduction . . . . .	797
1. History . . . . .	797
2. Definitions . . . . .	799
3. Regulatory Status . . . . .	800
II. Production Methods. . . . .	800
1. Maltodextrins . . . . .	800
2. Glucose/corn Syrups . . . . .	802
3. High-fructose Syrups . . . . .	808
4. Crystalline Fructose. . . . .	813
5. Crystalline Dextrose and Dextrose Syrups . . . . .	813
6. Oligosaccharide Syrups . . . . .	816
III. Composition and Properties of Sweeteners from Starch . . . . .	817
1. Carbohydrate Profiles . . . . .	817
2. Solids . . . . .	818
3. Viscosity . . . . .	819
4. Browning Reaction and Color. . . . .	821
5. Fermentability. . . . .	822
6. Foam Stabilization and Gel Strength . . . . .	823
7. Freezing Point Depression. . . . .	824
8. Boiling Point Elevation . . . . .	824
9. Gelatinization Temperature . . . . .	824
10. Humectancy and Hygroscopicity . . . . .	825
11. Crystallization. . . . .	826
12. Sweetness . . . . .	827
13. Selection of Sweeteners. . . . .	828
IV. References. . . . .	829

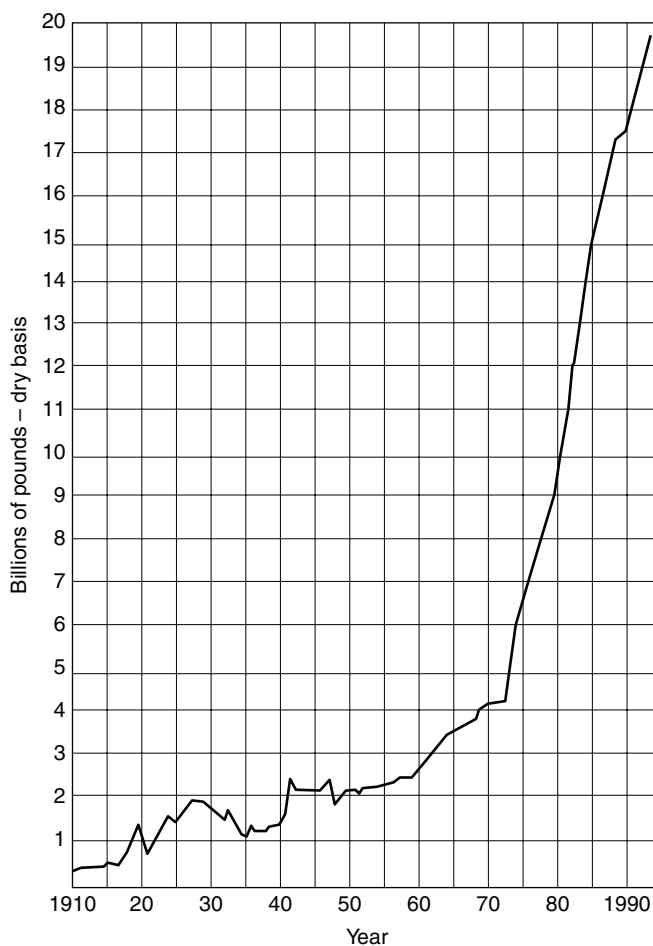
## I. Introduction

### 1. History

Commercial production of sugar in the Indus valley was reported during Alexander the Great's invasion in the period around 325 BCE, but cane sugar did not reach Europe

until the crusades.<sup>1</sup> Received at first as a novelty, Europeans developed a taste for sugar and demand for this new ingredient developed rapidly. During the sixteenth century, the Caribbean islands became major producers of this crop until the supply was disrupted during the Napoleonic Wars. With cane sugar supplies cut off by the British blockade, France turned to sugar beets. In 1811, G.S.C. Kirchoff, a Russian chemist, discovered that acid-catalyzed hydrolysis of starch produced a sweet substance.<sup>2</sup> By 1831, an American syrup plant capable of producing 30 gallons (115 liters) of syrup per day utilizing this new technology had been built; 150 years later, 140 American plants were producing starch from corn, wheat, potatoes and rice.<sup>3</sup>

Figure 21.1 provides a dramatic presentation of the growth of the industry since 1910.<sup>4</sup> The use of corn by the United States' corn refining industry increased to 1.4 billion bushels ( $39 \times 10^6$  tons,  $36 \times 10^9$  kg) in 1999, which was about 15% of the total crop harvested. From that production came 33 billion pounds ( $15 \times 10^9$  kg) of sweeteners, more than 2.5 times the amount produced in 1984 when the last edition of this book was published.<sup>5</sup>



**Figure 21.1** Corn sweetener shipments since 1910.<sup>4</sup>

In order to discuss the changes that have happened in the industry and the forces driving them, it is necessary to first define the types of sweeteners covered.

## 2. Definitions

*Dextrose equivalence* (DE) is a measure of the total reducing sugars calculated as D-glucose on a dry weight basis. The approved method for determining DE is the Lane–Eynon titration, which measures reduction of a copper sulfate solution. Unhydrolyzed starch has a DE value of zero, while the DE value of anhydrous D-glucose is 100. Glucose/corn syrups range from 20 to 95 DE.

*Maltodextrins* are the dried products or purified aqueous solutions of saccharides obtained from edible starch having a dextrose equivalency of less than 20. Outside the US, the products may be known as dextrans; only the US has an official definition of maltodextrins.

*Glucose syrups*, also known as *corn syrups* in the US, are purified aqueous solutions of nutritive saccharides obtained from edible starch having a dextrose equivalency of 20 or more.

*Dried corn syrups* or *corn syrup solids* are glucose/corn syrups from which most of the water has been removed.

*High fructose syrups* are purified aqueous solutions of nutritive saccharides obtained from edible starch in which a portion (at least 42%) of the dextrose (D-glucose) has been isomerized to fructose.

*Crystalline fructose* is crystalline product containing not less than 98.0% fructose and not more than 0.5% glucose.

*Dextrose monohydrate* is purified, crystalline D-glucose containing one molecule of water of crystallization per molecule of D-glucose.

*Anhydrous dextrose* is purified, crystalline D-glucose without water of crystallization.

*Baume* (Be) units arise from an arbitrary system of graduating hydrometers in degrees for determining the specific gravity of a solution. Within the corn refining industry, Baume is related to specific gravity by the following equation:<sup>6</sup>

$$\text{Baume (60°F/60°F)} = 145 \frac{145}{\text{true sp.gr.}} (60°F/60°F)$$

The modulus of 145 is the ratio of the total volume displaced in water by the hydrometer and the volume displaced by the unit scale length of the hydrometer stem. Corn syrups are commercially available with Baume values of 42, 43 and 44.

*Degree of polymerization* (DP) is the number of glucosyl (saccharide) units in an oligo- or polysaccharide. DP<sub>1</sub> refers to a monosaccharide, DP<sub>2</sub> refers to disaccharides and so on.

*Refractive index* (RI) is a measure of the refraction of light rays as they pass obliquely from one solution to another of different density. Refractive index is commonly used to measure the solids level of sweeteners. The refractive index of a sweetener is a function of the carbohydrate profiles, ash level, solids level and temperature of the solution.

*Retrogradation* is the reassociation of solubilized starch polymers in their native state or those in dextrans or in low-DE hydrolyzates resulting in an insoluble precipitate. Dextrans are depolymerized starches produced by heating a starch moistened with dilute hydrochloric acid or heating a moist starch in the presence of gaseous hydrogen chloride until a cold-water-soluble product is formed.

*Reversion* is the condensation reaction of reducing sugars to form di- and higher oligosaccharides.

### 3. Regulatory Status

Corn syrups, maltodextrins and D-glucose are affirmed as ‘generally recognized as safe’ (GRAS) in the US Code of Federal Regulations (CFR) 21, Section 184. High fructose corn syrup was affirmed as GRAS in 21CFR, Section 184.1866 on August 23, 1996.

## II. Production Methods

The pathways for production of the various sweeteners share many common steps. A generalized sweetener process is shown in [Figure 21.2](#).<sup>7</sup> Production of each of the sweeteners discussed will utilize one or more steps in this process.

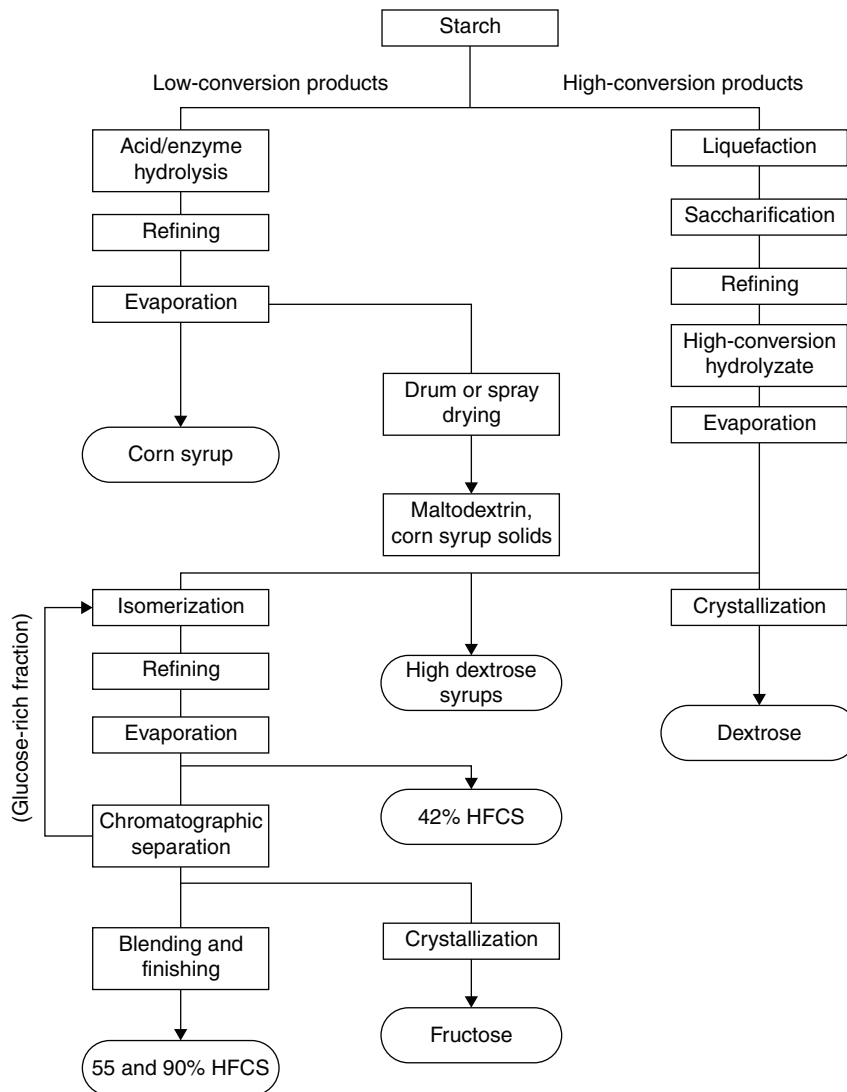
### 1. Maltodextrins

The GRAS affirmation contained in 21 CFR, Section 184.1444, defines maltodextrins as non-sweet, nutritive saccharide polymers consisting of D-glucosyl units linked primarily with alpha-1,4 bonds and having a DE less than 20. The document has been modified to include maltodextrins derived from potato starch as GRAS.<sup>8</sup> In 1992, more than 328 million pounds ( $149 \times 10^6$  kg) of maltodextrins and corn syrup solids were produced in the United States from various starch sources.<sup>9</sup>

Maltodextrins may be manufactured either by acid or by acid–enzyme processes. Maltodextrins produced by acid conversion of starch from dent corn contain a high percentage of linear fragments, which may slowly reassociate into insoluble compounds causing haze in certain applications.

Haze formation, which results from retrogradation, can be overcome by use of alpha-amylases. Alpha-amylases preferentially cleave the alpha-1,4-D-glucosidic bonds of amylose and amylopectin (see Chapter 7), leaving a higher proportion of branched fragments, decreasing the ability of the fragments to reassociate. Maltodextrins made from waxy corn starch also have a lower tendency to haze, because such starch is composed almost entirely of the highly branched molecule, amylopectin.

In a maltodextrin process using enzyme-catalyzed conversion, the starch slurry (30% to 40% dry solids) is first pasted at a temperature of 80–90°C, and is then treated with a ‘heat-stable’ bacterial alpha-amylase for liquefaction. When stabilized with calcium ions, alpha-amylases from *B. licheniformis* or *B. stearothermophilus* can withstand temperatures of 90–105°C for at least 30 minutes,<sup>10</sup> allowing sufficient process time to split the 1,4 bonds and form maltose and limit dextrans (see Chapter 7).



**Figure 21.2** General process flow for starch-derived sweeteners (corn/glucose syrups, high fructose syrups, dextrose, fructose, maltodextrins and syrup solids).<sup>7</sup>

The fragmentation reaction proceeds until there is a preponderance of maltohexoses and maltoheptoses and the liquor has a DE of 12–15.<sup>11</sup>

A number of maltodextrin production methods using multiple enzyme treatments have been described.<sup>12,13</sup> In one such process, a starch paste is first treated with acid and/or an alpha-amylase at 95–105°C for liquefaction, then cooled to 90–102°C, at which time addition of a second enzyme takes place. If desired, the slurry may be further cooled to 85°C for addition of a third enzyme.<sup>14</sup>

After conversion, the pH of the crude slurry is adjusted to about 4.5 and the solution is filtered to remove protein and fats. The clarified liquor is then refined in a

**Table 21.1** Typical carbohydrate profile of commercial maltodextrins<sup>5</sup>

Maltodextrin composition (% dry basis)				
DP	5 DE	10 DE	15 DE	20 DE
1	<1	<1	<1	<1
2	1	3	6	8
3	2	4	7	9
4	2	4	5	7
5	2	4	5	8
6	3	7	11	14
7+	90	78	66	53

process similar to that for glucose/corn syrups discussed in the next section. After refining and decolorization, the liquor is evaporated to a solids level of approximately 77% or dried to about 5% moisture.

Maltodextrin solutions are not evaporated to as low a solids level as is typical of most glucose syrups because the viscosity of the latter is extremely high (see Table 21.9). At the higher solids level of 43 or 44 Baume typical for corn syrups, maltodextrin solutions would be extremely difficult to pump. It should also be noted that, since the water activity of maltodextrins at a given solids level is so much higher than that of other syrups, some care must be exercised in the handling of these products to prevent microbial fermentation. Commercial maltodextrins, as shown in Table 21.1,<sup>15</sup> are used in applications where high viscosity coupled with a bland, neutral taste is desirable.

## 2. Glucose/corn Syrups

Corn syrups are affirmed as GRAS in 21 CFR, Section 184.1865 and meet the further standards of identity in Sections 168.120 and 168.121. In 1999, more than 7 billion pounds ( $3 \times 10^9$  kg) of syrups were produced from starch in the US.<sup>16</sup> Figure 21.3 outlines a conventional glucose/corn syrup manufacturing process.<sup>17</sup>

Glucose/corn syrups may be manufactured by either an acid or an acid–enzyme process. Acid-catalyzed hydrolysis was the traditional method of corn syrup production and is still the most common method for producing sweeteners up to about 42 DE. Since acid-catalyzed hydrolysis of sweeteners to 55 DE or above creates products of reversion, such as gentiobiose, isomaltose and trehalose, which give unacceptable flavors to the syrup, these syrups are usually made by acid–enzyme processes.<sup>18</sup>

### Acid-catalyzed Hydrolysis

In an acid process the slurry, containing about 35–45% starch solids, is pumped into a pressure vessel called a ‘converter’ and acidified to a pH of about 2.0 with dilute hydrochloric acid at 140–160°C and a pressure of 80 psi (5.4 atm). Although acid-catalyzed hydrolysis is a rather (but not completely) random process,<sup>19,20</sup> carefully controlled hydrolysis produces syrups in the 25 to 45 DE range with very predictable carbohydrate profiles as shown in Table 21.2.<sup>21</sup>

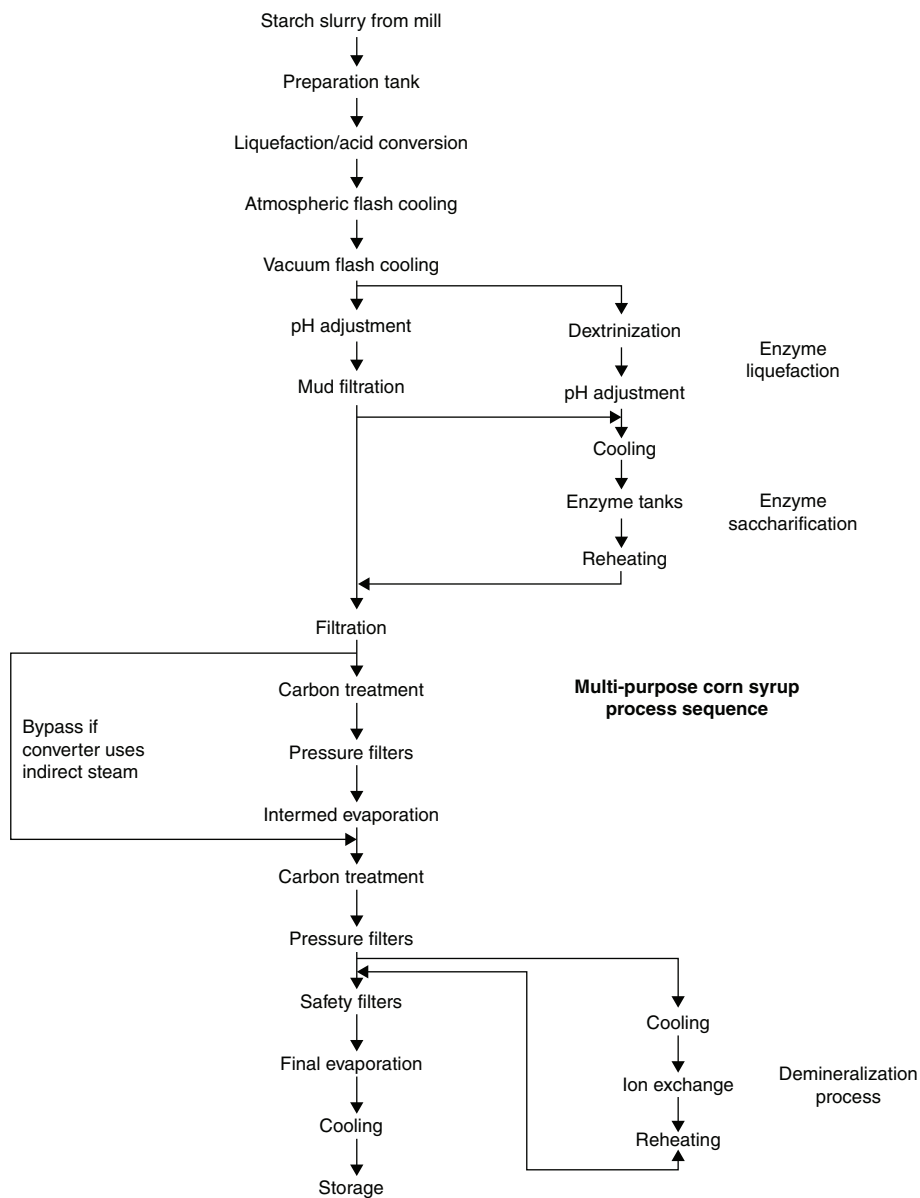


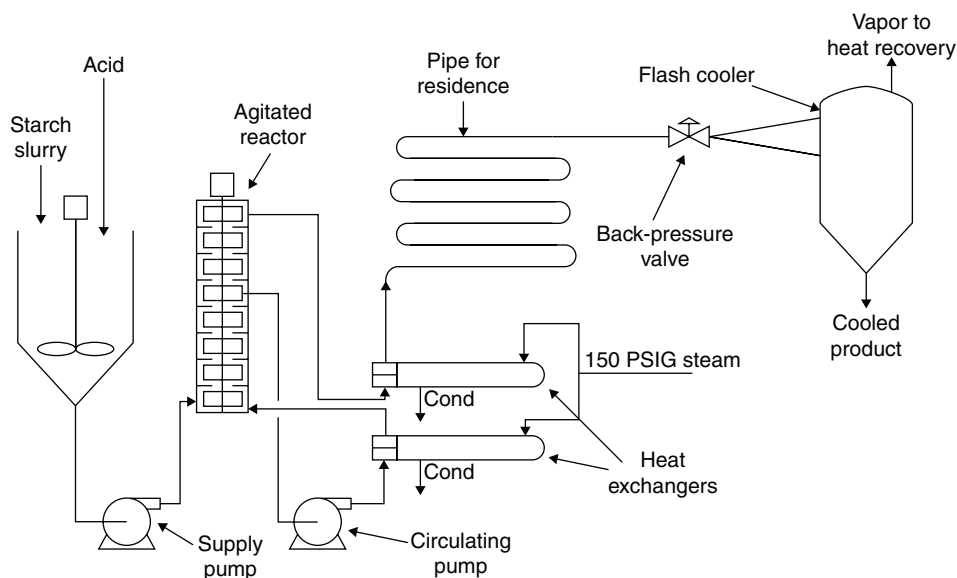
Figure 21.3 Typical corn/glucose syrup process.<sup>17</sup>

During hydrolysis, both 1,4 and 1,6 linkages are cleaved, converting the starch molecule to increasingly lower molecular weight products. A typical residence time in the converter is 5–10 minutes for low DE syrups; high DE syrups may require 15–20 minutes at the necessary temperature. It is important to keep the conversion time short to prevent unnecessary color development. A typical commercial acid converter system is shown in Figure 21.4.<sup>22</sup>

**Table 21.2** Composition of typical starch-derived sweeteners<sup>21</sup>

Designation	Ash	Saccharides, carbohydrate basis			
		DP <sub>1</sub>	DP <sub>2</sub>	DP <sub>3</sub>	DP <sub>4+</sub>
28 DE	0.3	8	8	11	73
36 DE	0.3	14	11	10	65
34 HM	0.3	9	34	24	33
43 HM	0.3	9	43	18	30
43 DE	0.3	19	14	12	55
43 DE (IE)	0.03	19	14	12	55
53 DE	0.3	28	18	13	41
63 DE	0.3	36	31	13	20
63 DE (IE)	0.03	36	31	13	20
66 DE	0.3	40	35	8	17
95 DE	0.3	95	3	0.5	1.5
95 DE (IE)	0.03	95	3	0.5	1.5
HFCS 42	0.03	95	3	0.7	1.3
HFCS 55	0.05	95.7	3	0.4	0.9
Crystalline fructose	0.05	100			

DP<sub>1</sub> = Monosaccharides (dextrose, dextrose + fructose in HFS, fructose in crystalline fructose)  
 DP<sub>2</sub> = Disaccharides, primarily maltose  
 DP<sub>3</sub> = Trisaccharides, primarily maltotriose  
 DP<sub>4+</sub> = Oligosaccharides, maltotetraose and higher saccharides  
 HM = High maltose  
 (IE) = Ion-exchanged



**Figure 21.4** Typical acid converter.<sup>22</sup>

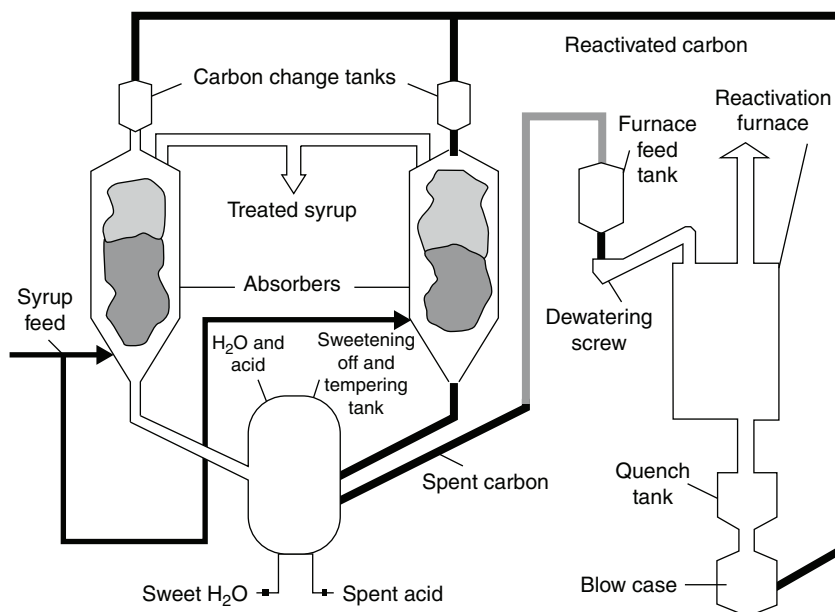


After conversion to the proper DE, the reaction is stopped in the neutralizer tank by raising the pH with soda ash (sodium carbonate) to 4.5–5.0. This pH is critical not only to optimize the conditions under which the proteins and fats can be removed, but also to reduce the risk of unnecessary color development. At this point, the liquor may be pumped to an enzyme tank for further enzyme-catalyzed conversion, or clarified, bleached and evaporated.

If the liquor is not to be enzyme-converted, it is pumped to ‘mud’ centrifuges and rotary drum filters which remove the suspended fats and insoluble impurities from the filtrate. Amino acids and peptides which may react with carbohydrates are also removed. Then the filtrate is passed through pulsed beds of activated carbon for clarification and bleaching. The temperature in the carbon column is maintained at 150–170°F (69–77°C) with a typical contact time of 90–120 minutes for optimum removal of impurities. Usually these columns contain packed granular carbon, although powdered carbon may also be used.

It has long been known that activated carbon removes color precursors and off flavors and is particularly effective in removing 5-(hydroxymethyl)-2-furaldehyde (HMF), a glucose decomposition product created during acid-catalyzed hydrolysis.<sup>23</sup> In typical systems, as shown in Figure 21.5, the carbon beds are used in a counterflow fashion in which the spent carbon is removed, regenerated in a furnace and repacked at the top of the column.<sup>24</sup> After the carbon beds, the liquor is passed through ‘check’ filters designed to remove escaping carbon fines.

Some syrups are ion-exchanged at this point in the process. Ion exchange is essential in the production of certain types of sweeteners, such as high fructose syrups. Not only does ion exchange improve the color and color stability of the syrup by



**Figure 21.5** Carbon treatment and regeneration system.<sup>24</sup>

removing components that could otherwise participate in a Maillard reaction with the reducing sugars, it also substantially reduces the ash level and improves the flavor.

Ion exchange resins are synthetic organic polymers containing functional groups that exchange mobile ions in a reversible reaction based on affinities. A cation exchange resin in the hydrogen ion form will exchange hydrogen ions for equally charged cations and become converted into a salt. Cation exchange resins in corn syrup manufacturing are typically strong acid exchangers with a sulfonic acid functional group. The anion exchange resins employed contain tertiary amino groups and act as weak bases.<sup>25</sup>

Typical ion exchange processes consist of 'trains' of three cation and three anion beds arranged in pairs. The first pair takes the heaviest load, while the second pair acts as the polishing unit and the third pair undergoes regeneration. As the resins become exhausted, ions start to leak through the primary units. At a predetermined level of exhaustion, the primary units are taken offline and the secondary units are moved to the primary position. The units that were in regeneration are put online as the secondary units and the exhausted primary units are regenerated (Figure 21.6).<sup>26</sup>

Following the carbon columns or the demineralizers, the pH of the filtrate is adjusted and the liquor is evaporated. The solids level of the filtrate prior to the evaporators is about 30% dry solids (DS). Typical evaporators are multiple-effect, falling-film evaporators in which the temperature is increased under precisely controlled conditions that prevent formation of unwanted flavors or color in the syrup. As shown in Figure 21.7, the flow is generally countercurrent, i.e. the hottest portion of the evaporation contains the syrup of lowest solids.<sup>11</sup> After evaporation, the syrup is pumped to large storage tanks where it is held under agitation and analyzed prior to shipment.

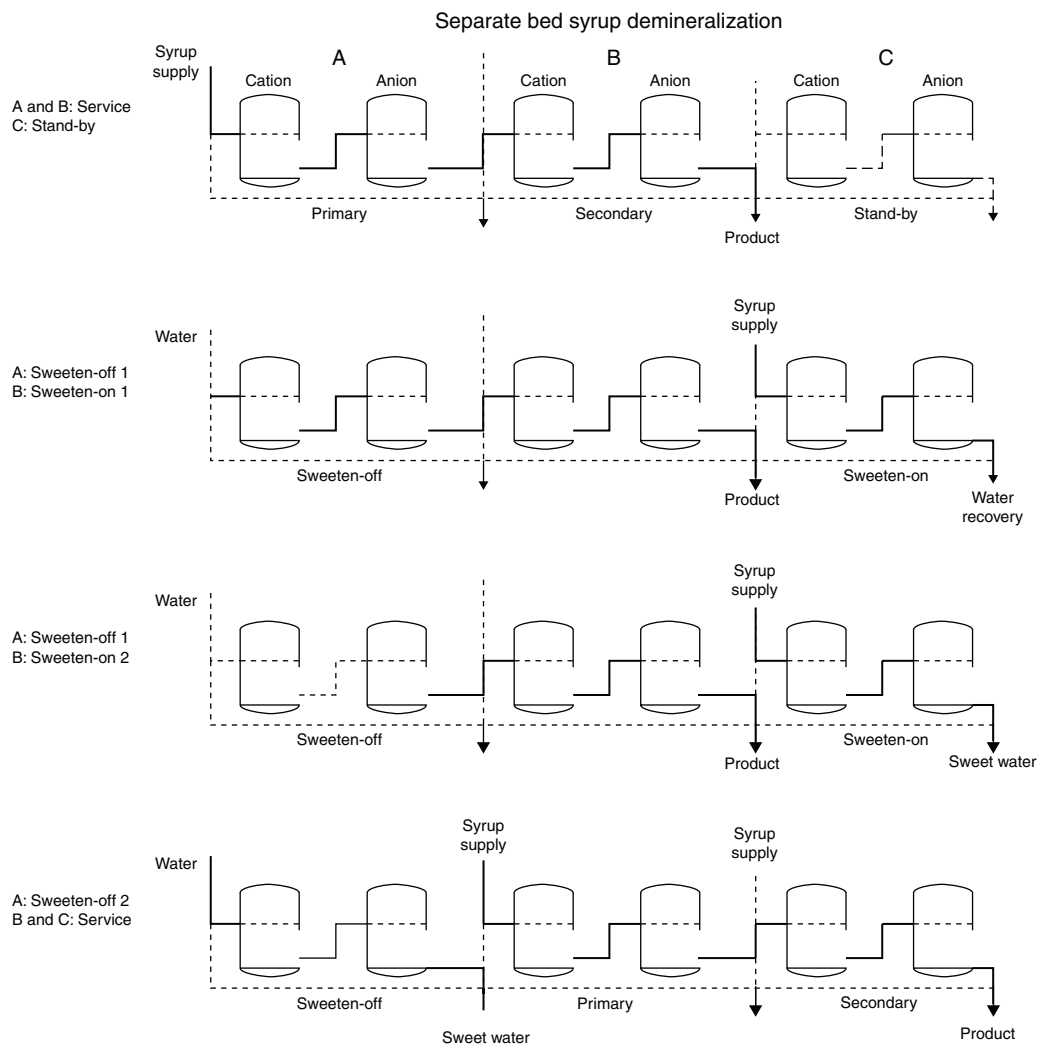
#### **Acid-Enzyme Processes**

As in the case of acid-catalyzed hydrolysis, the starch molecule is hydrolyzed to the desired starting DE in a converter, but further conversion is carried out with enzymes until the final DE or carbohydrate profile is reached. This is done by adding the appropriate enzymes to the acid-converted slurry and allowing them to react in a holding vessel called an 'enzyme tank.' Several enzymes may be used to achieve the desired carbohydrate profile.

The *alpha-amylases* (EC3.2.1.1) used are bacterial or fungal enzymes that hydrolyze alpha-1,4 linkages in both amylose and amylopectin, eventually producing dextrose and maltose. The reaction is initially rapid, then relatively slow<sup>27</sup> (see Chapter 7).

The *beta-amylases* (EC3.2.1.2) used are enzymes of barley and yeast that act on the non-reducing ends of starch molecules and produce maltose in the beta form from the starch polymers. These enzymes are used to produce high-maltose syrups. Although beta-amylase converts linear chains completely to maltose, the enzyme cannot cleave branch points and the yield of maltose from amylopectin<sup>11</sup> (see Chapter 7) is only 55% of the molecule.

*Glucoamylases* (EC3.2.1.3) are fungal enzymes which hydrolyze maltose to produce glucose (dextrose). These enzymes catalyze hydrolysis of alpha-1,3, alpha-1,6 and beta-1,6 linkages. Their primary reaction is on the 1,4-linked  $\alpha$ -D-glucopyranosyl units of

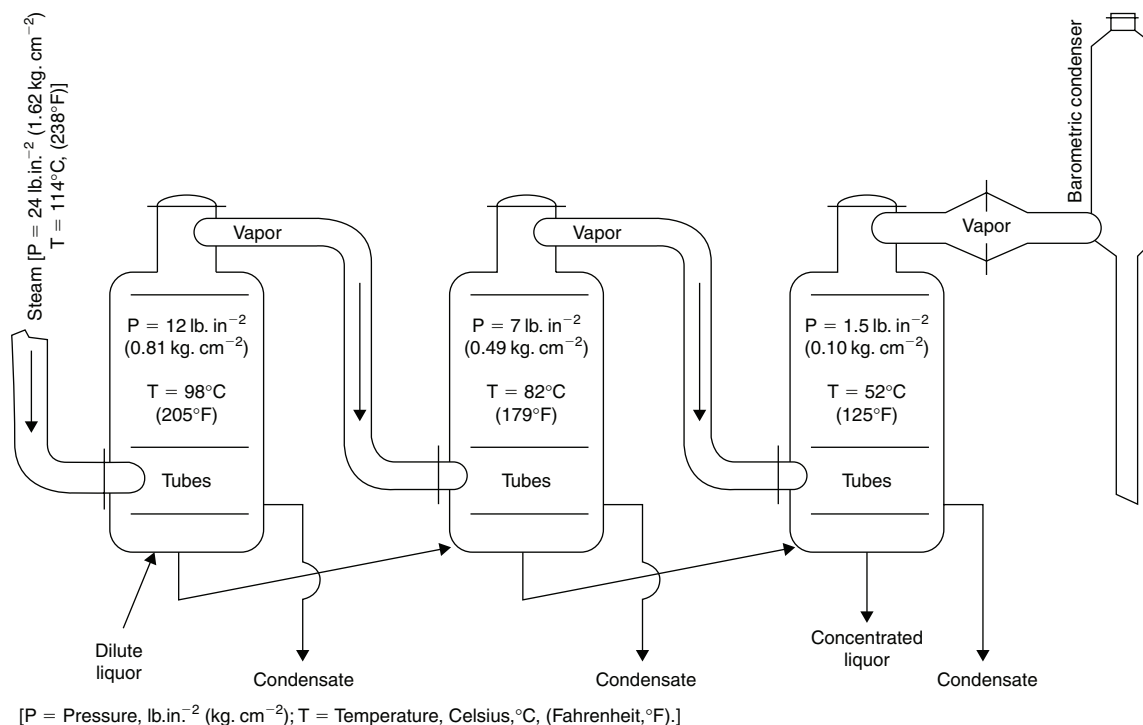


**Figure 21.6** Syrup demineralization sequence.<sup>26</sup>

non-reducing ends, releasing  $\beta$ -D-glucopyranose (see Chapter 7). When branch points are reached, the enzyme will cleave the 1,6 bonds, but at a much slower rate.<sup>28</sup>

*Pullulanase* (EC3.2.1.41) and *isoamylase* (EC3.2.1.68) are so-called debranching enzymes because they catalyze the hydrolysis of the 1,6 linkages without effect on the 1,4 linkages<sup>29</sup> (see Chapter 7). These enzymes are particularly useful in the production of extremely high maltose syrups with maltose levels of 50 to 90%.<sup>30</sup> Table 21.3 provides an overview of commercial enzymes used in the corn refining process today and typical operating requirements.

Proper pH and temperature control is critical during batch enzyme conversion processes, which usually last about 48 hours. In such processes, a number of enzyme tanks are filled sequentially from the converter at the adjusted temperature for treatment (140–150°F) and then dosed with the necessary enzymes. Progress of the reaction



**Figure 21.7** Multiple-effect evaporator<sup>11</sup>

is monitored by occasional checks of the DE or the carbohydrate profile until the desired conversion is reached.

At completion of the enzyme conversion, the tanks are emptied in succession and the liquor is processed through filtration and carbon bleaching, as previously described, and evaporated to the proper solids level. The advent of enzyme-converted syrups lessens the importance of traditional methods of measurement, such as determination of DE. It is possible to have two syrups with the same DE and completely different carbohydrate profiles and performance characteristics, as shown in Table 21.4.<sup>31</sup>

### 3. High-fructose Syrups

Using immobilized enzyme technology, it is possible to produce high-fructose syrups containing 42%, 55% or 90% fructose. In 1999, US shipments of high-fructose syrups exceeded 24 billion pounds ( $11 \times 10^9$  kg) (dry basis).<sup>5</sup>

The typical process for producing a 42% high-fructose syrup is shown in Figure 21.8.<sup>32</sup> A starch solution at about 35% solids and a pH of about 6.5 is drawn into a steam jet at 180°F (82°C) in the presence of a calcium-stabilized, thermostable alpha-amylase. The slurry is maintained at this temperature through a series of loops for 3–5 minutes and then cooled to 95°C (200°F) in a secondary reactor, where further alpha-amylase additions occur. A holding time of up to 120 minutes in the secondary reactor produces a solution of approximately 12 DE. The pH is adjusted to about 4.3

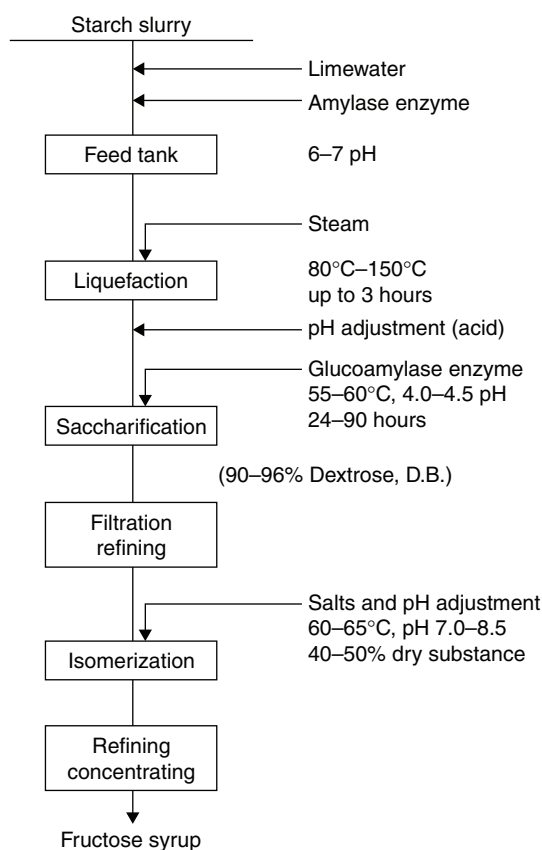
**Table 21.3 Enzymes used in corn milling processes**

Enzyme type	Enzyme activity	Enzyme dose, Dry substance, %	Temperature °F	Typical enzyme reaction conditions			Inactivated by	Notes		
				pH	Time, hours	Start DE				
High-temperature bacterial alpha-amylase	60 K-NOVO units/g	30-35	221	6.0-6.5	0.1	0	2	Calcium 50-70 ppm	pH < 4.5	Starch liquefaction
High-temp. bacterial alpha-amylase	60 K-NOVO units/g	30-35	203	6.0-6.5	1.5	2	12	Calcium 50-70 ppm	pH < 4.5	Starch liquefaction
Bacterial alpha-amylase	120 K-NOVO units/g	30-40	185	6.0-6.5	1.5	0	15	Calcium 50-70 ppm	pH < 4.5	Starch liquefaction
Bacterial alpha-amylase	120 K-NOVO units/g	35-45	170	5.8-6.2	6	15	22	Calcium 50-70 ppm	pH < 4.5	Destarching Acid conversion CSU
Fungal maltose alpha-amylase	40 000 SKB units/g	35-45	130-133	4.9-5.3	48	22	48	-	Heating to 175°F	High 42-DE syrup
Fungal maltose alpha-amylase	40 000 SKB units/g	35-45	130-133	4.9-5.3	48	22	48	-	Heating to 175°F	High 48-DE syrup
Glucosylase	150 NOVO AG units/mL	30-35	136-140	4.0-5.0	48	15	95	-	Heating to 175°F	Dextrose syrup from acid liquid
Glucosylase	150 NOVO AG units/mL	30-35	136-140	4.0-5.0	48	15	98	-	Heating to 175°F	Dextrose syrup from acid liquid
Malt beta-maltose amylase	1500°F Lintner	35-45	130-133	4.9-5.3	48	22	48	-	Heating to 175°F	High 42-DE syrup
Malt beta-maltose amylase	1500°F Lintner	35-45	130-133	4.9-5.3	48	22	48	-	Heating to 175°F	High 48-DE syrup
Fungal alpha-amylase	40 000 SKB units/g	35-45	130-133	4.9-5.3	48	22	48	-	Heating to 175°F	High 48-DE syrup
+										
gluco-amylase syrup	150 NOVO AG units/mL	35-45	130-133	4.9-5.3	48	22	48	-	Heating to 175°F	62-DE acid-enzyme
Glucose isomerase	150 I/GIC units/g	35-45	140-150	7.5-8.5	-	95% dextrose	-	Magnesium Calcium 0.0004M	Deaerated <1 ppm	Demineralized

**Table 21.4** Saccharides, total carbohydrate basis<sup>31</sup>

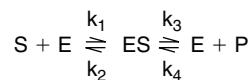
Designation	DE	DP <sub>1</sub> , %	DP <sub>2</sub> , %	DP <sub>3</sub> , %	DP <sub>4+</sub> , %
43 DE	43	19	14	12	55
43 HM (high-maltose)	43	9	43	18	30

DP<sub>n</sub> = degree of polymerization

**Figure 21.8** High-fructose syrup process.<sup>32</sup>

and glucoamylase is added. Then the product is pumped to saccharification tanks where the enzyme reacts for 24–90 hours. The glucoamylase reaction produces liquor containing 94% dextrose, which is then filtered to remove residual protein and fats before being passed through beds of activated carbon, as was described for the corn syrup process. Following carbon purification, the hydrolyzate is demineralized through anion and cation exchange resins prior to being isomerized.

The conversion step to high-fructose syrup takes place in a reactor containing immobilized glucose isomerase. Although nonenzymic processes to isomerize glucose to fructose have been developed,<sup>11</sup> these processes result in undesirable by-products of ash, color, and flavor, and other faults.



Where S, E, ES and P are substrate, enzyme, enzyme-substrate complex, and product respectively.  $K_1$ ,  $K_2$ ,  $K_3$ , and  $K_4$  are the rate constants. The mechanism can be described by the rate equation:

$$V = \frac{E[(K_3S)/KS - (K_2P)/KP]}{1 + (S/KS) + (P/KP)}$$

Where V is the rate of product formation and KS and KP are the Michaelis constants for substrate and product, respectively.

**Figure 21.9** Michalis–Menten kinetics.

Considerable effort based on research work initiated in the 1950s resulted in enzyme technology able to convert glucose to fructose on a commercial scale.<sup>32–34</sup> Current production of high-fructose syrups generally uses immobilized, rather than soluble, enzymes. Sources of the enzyme include *Streptomyces*, *Bacillus*, *Actinoplanes* and *Arthrobacter* species.

The advantage of fixed bed systems is that the relatively high activity per unit weight allows manufacturers to process large quantities of product through relatively small reactors in short times. The short residence time in these reactors also reduces development of undesirable color and flavor compounds.

The isomerization of glucose to fructose has been extensively studied and the mechanism is well-documented.<sup>35–37</sup> The reaction is essentially first order and reversible, following Michalis–Menten characteristics shown in Figure 21.9.

Glucose isomerase requires divalent cations, such as  $\text{Co}^{++}$ ,  $\text{Mg}^{++}$  or  $\text{Mn}^{++}$  for catalytic activity and is inhibited by the presence of  $\text{Cu}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Ag}^{++}$ ,  $\text{Hg}^{++}$ ,  $\text{Ca}^{++}$  and  $\text{Zn}^{++}$  ions. Therefore, proper demineralization of the liquor prior to isomerization is essential. Depending on the source of the enzyme, optimum operating conditions include a pH range of 6.5 to 8.5 and a temperature of 40–80°C. Residence time in the reactor is usually less than four hours. Enzyme decay is exponential; therefore the typical system will contain a number of reactors containing enzyme in varying stages of output. A typical half life of such a column may be as long as 200 days.

The fructose level of the output of each of these columns can be controlled by varying the reaction time (flow rate), temperature and pH. Once conversion is complete the liquor is pumped through beds of activated carbon and then evaporated to the proper solids level, generally 71% or 80% dry solids as previously described.

Forty-two percent high-fructose syrup produced by this method is used in many applications as a replacement for liquid sucrose. However, in some applications, 42% high-fructose syrup is not sweet enough and a higher level of fructose is necessary. Although it is possible to create enriched fructose syrups by forming complexes with borate compounds during isomerization<sup>38</sup> and by liquid–liquid extraction,<sup>39</sup> commercial production of such products generally involves adsorption–separation technology. This technology employs the relative differences in the affinity of dextrose and fructose for strong acid

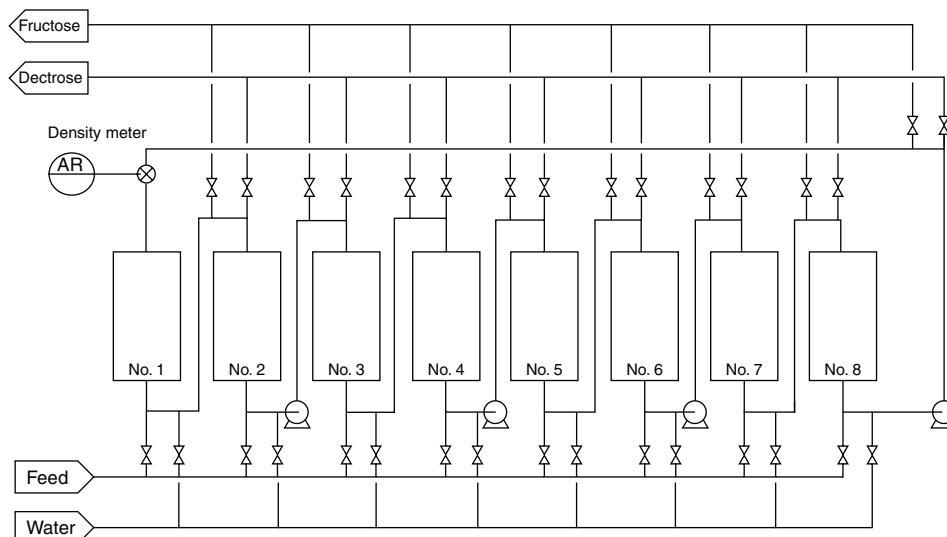


Figure 21.10 Adsorption separation columns.<sup>41</sup>

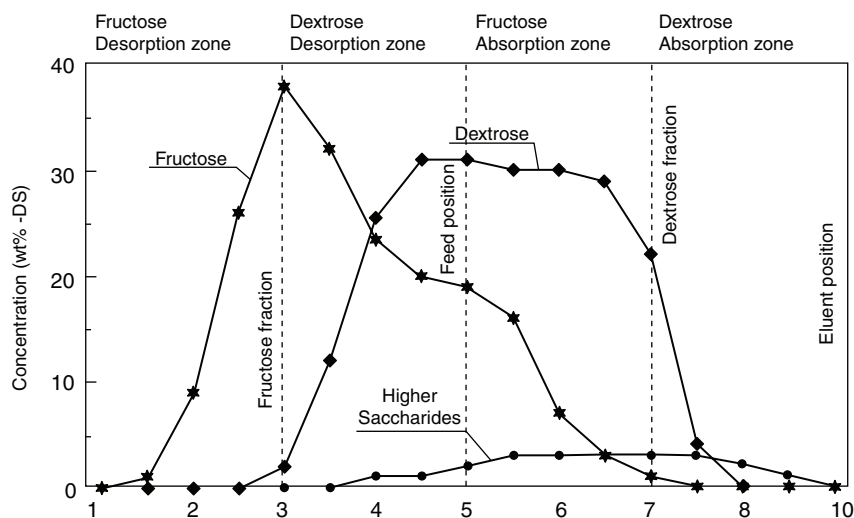


Figure 21.11 Separation of glucose and fructose on adsorption columns.<sup>41</sup>

ion exchange resins in the  $\text{Ca}^{++}$  salt form. By controlling the feed and elution rate of the components or by monitoring elution of certain components in the direction of flow<sup>40</sup> it is possible to separate the sugars in a continuous process in a large column.

The 42% fructose syrup from the isomerization column is first demineralized to remove trace components picked up during isomerization, and is then pumped into the separator at 36–60% solids. The relative difference in affinity of the resin for fructose and dextrose allows separation of the carbohydrates into two enriched streams. A typical system, shown in Figures 21.10 and 21.11, is based on the concept



of a simulated moving bed.<sup>41</sup> As the 42% fructose feedstock is pumped through the bed, the fructose portion is selectively absorbed relative to dextrose, resulting in separation of the two carbohydrates.

Through a series of automatic valves, it is possible to draw off a stream of enriched dextrose, as well as one of enriched fructose. Some consideration must be given to the fact that the higher is the purity of this stream, the lower are the solids and the greater is the evaporation cost. Typical purity of the separated streams of dextrose and fructose is 85% to 90%. The dextrose fraction ('raffinate') is returned to the front of the system to be reisolomerized, while the enriched fructose fraction is blended with a 42% fructose stream to produce 55% high-fructose syrup. The enhanced fructose phase may also be isolated as a separate product stream to make 90% high-fructose syrup or crystalline fructose.

#### 4. Crystalline Fructose

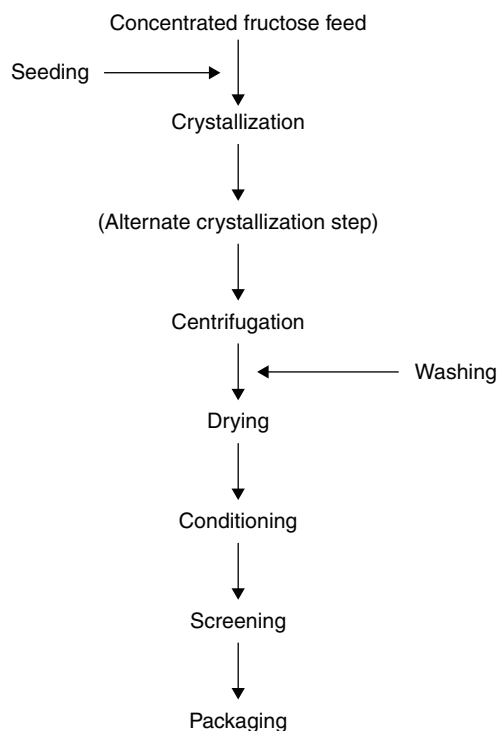
If the ratio of fructose to non-fructose materials is high enough, it is possible to crystallize the fructose. In one such process, the fructose must have a purity of at least 90% to achieve sufficient saturation.<sup>42</sup> The liquor is seeded with crystals of dry fructose and cooled to crystallize the pure fructose. The resulting crystals are washed and separated from the mother liquor by centrifugation, then dried, producing crystalline fructose material that is 99.5% pure. Since fructose is only moderately soluble in alcohol, processes improving the crystallization of fructose by adding ethanol or methanol to the solution have also been described.<sup>43</sup> Crystalline fructose may exist as anhydrous  $\beta$ -D-fructopyranose. Crystals of the dihydrate of fructose require careful handling, because of their ability to dissolve in their own water of hydration. A typical crystalline fructose process is outlined in Figure 21.12.<sup>44</sup> Because of its extremely hygroscopic nature crystalline fructose should be stored under conditions below 50% relative humidity. Figure 21.13<sup>45</sup> shows the equilibrium water content of fructose and sucrose.

#### 5. Crystalline Dextrose and Dextrose Syrups

Several processes of separating and crystallizing dextrose by repeated seeding, washing and crystallization were developed during the 1800s and early 1900s,<sup>46</sup> but these methods were time consuming and costly. Today, commercial processes begin with the solution produced by liquefaction of the starch in a jet cooker, as previously described.

Saccharification produces a 94% dextrose liquor, which can be processed in several ways. To make a dextrose syrup, the fats and protein are removed from this liquor, as in the high fructose process. The syrup is then carbon bleached, demineralized and evaporated to 71% solids. The 94% dextrose liquid may also be further refined to 99% dextrose by adsorption-separation chromatography prior to being bleached, demineralized and evaporated.

Either anhydrous dextrose or dextrose monohydrate can be obtained by crystallization. Monohydrate crystallizers are large horizontal, cylindrical batch tanks or



**Figure 21.12** Fructose crystallization process.<sup>44</sup>

continuous systems in which the crystal mass is continuously removed, leaving about 20–25% of the batch to seed the next. During crystallization, the syrup (75% solids, 95% dextrose) is cooled carefully and in a controlled manner below 50°C. Since crystallization of dextrose is an exothermic reaction, constant cooling is essential to maintain the proper level of supersaturation. When the magma of crystallized dextrose ( $\alpha$ -D-glucopyranose) monohydrate is formed, the material is washed and centrifuged in basket centrifuges to remove the mother liquor ('first greens'). The first greens may be reprocessed to yield a second crop of crystals. The mother liquor from this step is known as 'second greens' or hydrol. Both hydrol streams are combined to improve the yield. The remaining monohydrate crystals are dried in a stream of hot air and packaged. A typical batch crystallizer and basket centrifuge are shown in Figures 21.14 and 21.15.<sup>47</sup>

Anhydrous dextrose is produced by dissolving the monohydrate in hot purified water and refining it again. During the crystallization step, proper temperature control is essential to ensure formation of nuclei in the anhydrous dextrose ( $\alpha$ -D-glucopyranose).<sup>48</sup> These nuclei are grown under controlled conditions, separated from the mother liquor, and washed and screened as before. The mixture is then evaporated under reduced pressure with heat and agitation and dried to a moisture level of 0.1%, resulting in a free-flowing powder. These crystals are separated and packaged as in the case of the monohydrate. A typical process for both anhydrous and monohydrate production is shown in Figure 21.16.<sup>48</sup>

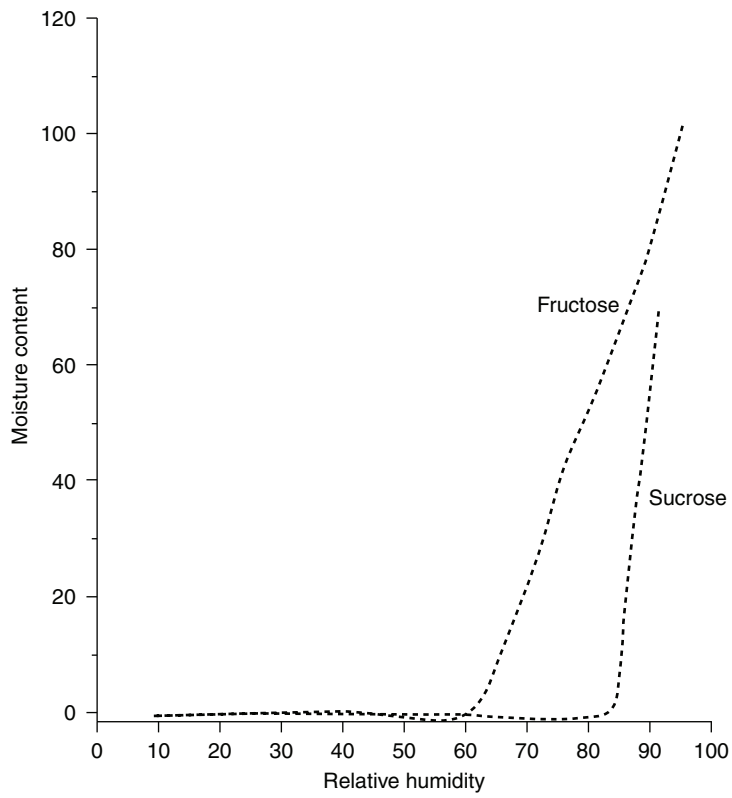


Figure 21.13 Equilibrium water content of fructose and sucrose.<sup>45</sup>

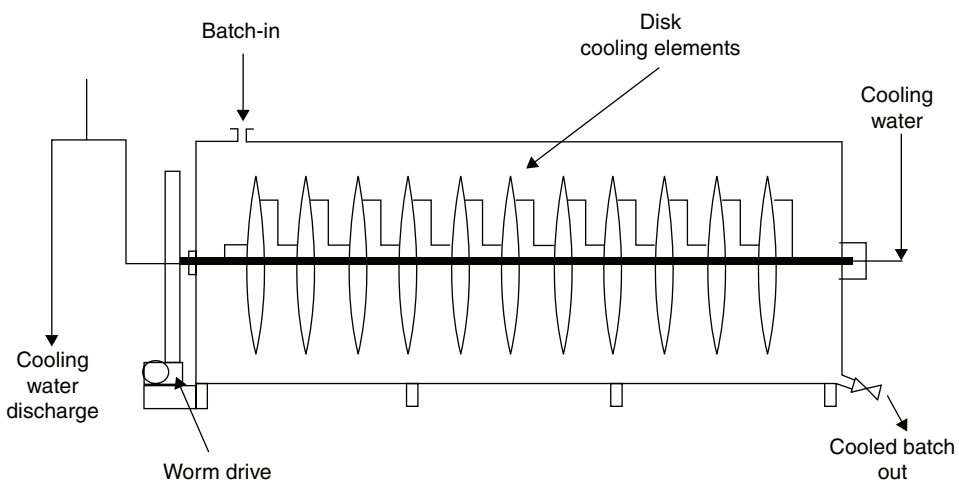


Figure 21.14 Batch crystallizer.<sup>47</sup>

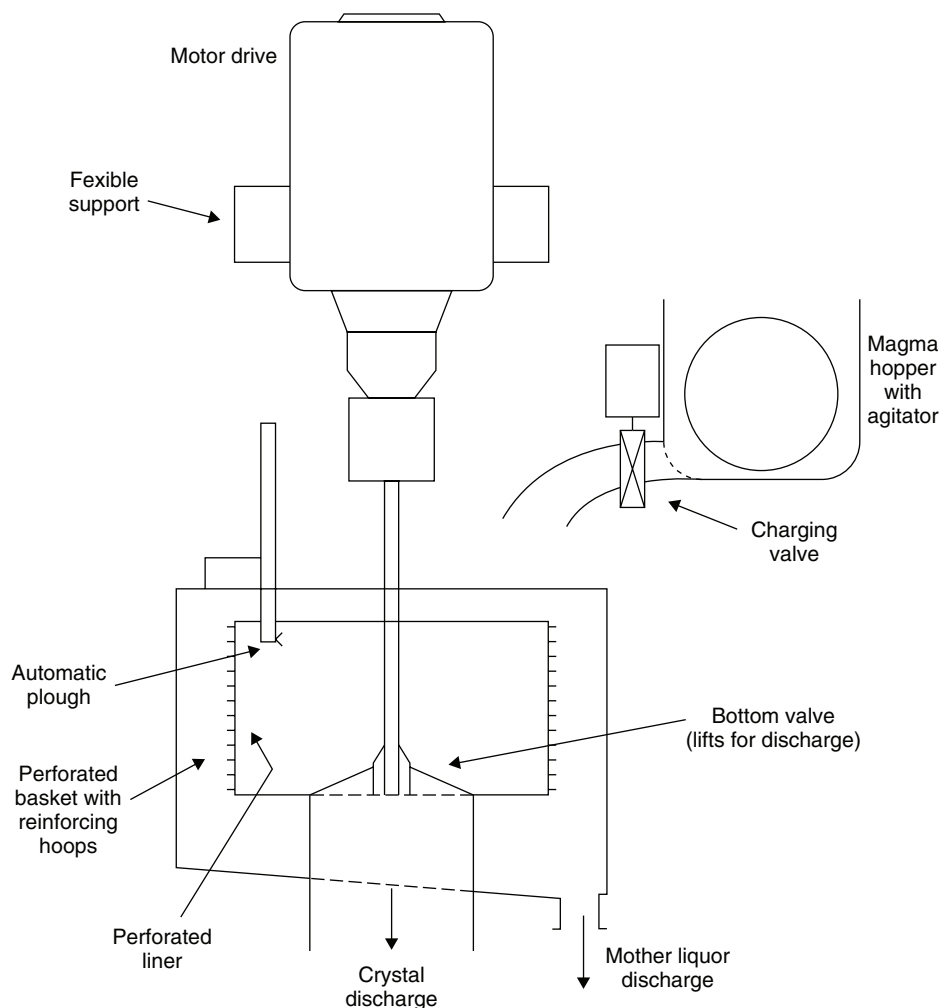


Figure 21.15 Basket centrifuge.<sup>47</sup>

## 6. Oligosaccharide Syrups

Beginning in the 1990s, oligosaccharide sweeteners produced from sucrose, soy flour or corn starch gained increasing attention. Malto-oligosaccharides and isomalto-oligosaccharides from starch contain 1,6 and/or 1,4 linkages. Glucose/corn syrups may be described as a concentrated solution of glucose and varying amounts of a mixture of malto-oligosaccharides, including isomalto-oligosaccharides. In the production of oligosaccharide syrups, oligosaccharides are emphasized (over glucose/dextrose) through the use of certain enzymes, a transglucosidase in particular<sup>49</sup> (see Chapter 7).

Starting with a feedstock of 65–70% maltose, made by one of the methods previously described, the liquor is passed through an adsorption separation column. This results in a product with a maltose level of approximately 98% which may be crystallized, leaving a predominately maltotriose fraction which is purified as a syrup.

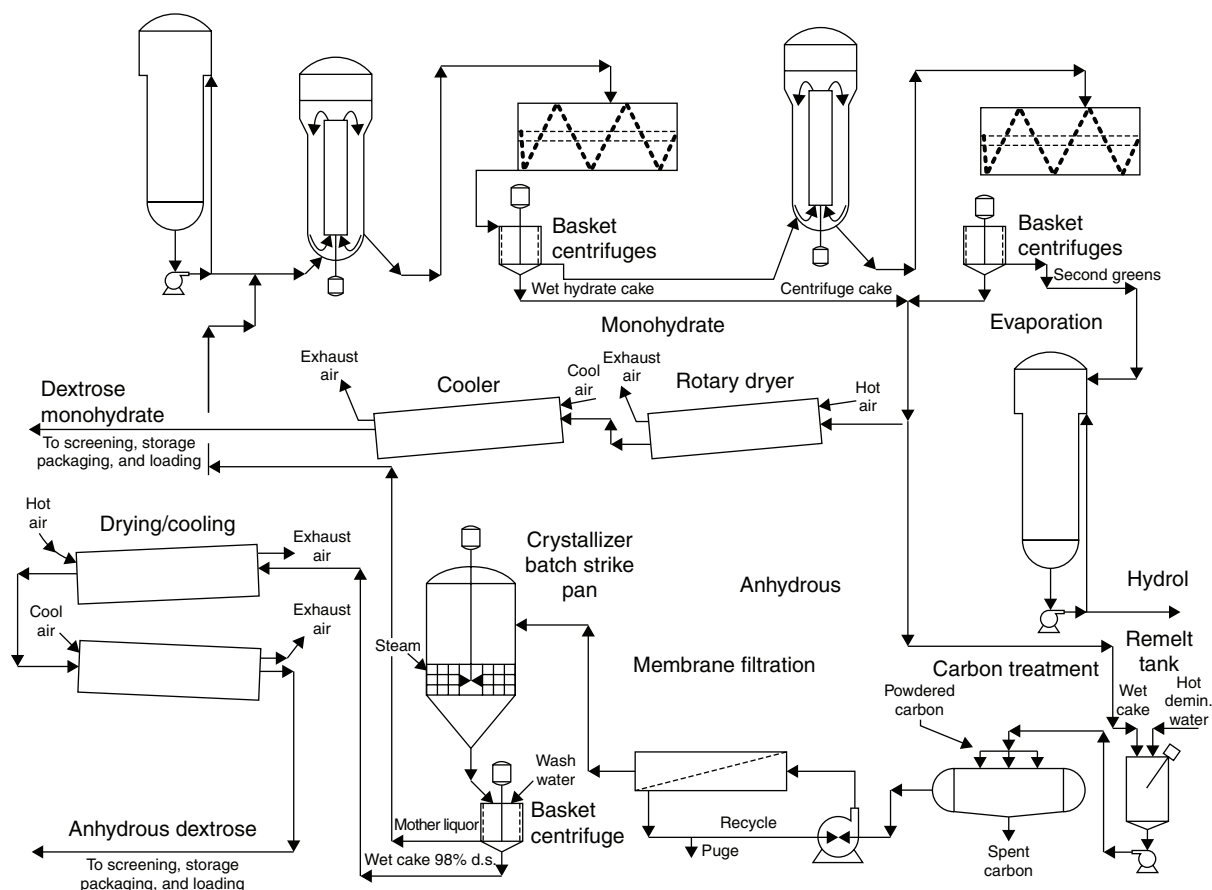


Figure 21.16 Typical anhydrous dextrose and dextrose monohydrate process.<sup>48</sup>

Maltotriose syrups may also be prepared by the use of maltotriose-forming amylases combined with pullanase or isoamylase enzymes (see Chapter 7). In one such process, waxy maize starch is treated with alpha-amylase, followed by pullulanase. The syrup resulting from this procedure contains 60–85% low molecular weight oligosaccharides.<sup>50</sup> Maltose syrups may also be treated with transglucosidases from *Aspergillus* sp. to produce high isomalto-oligosaccharide levels. Typical profiles of some commercial syrups are given in Table 21.5.<sup>51</sup>

### III. Composition and Properties of Sweeteners from Starch

#### 1. Carbohydrate Profiles

Early work by Hoover<sup>52</sup> provides a framework for determining how physical properties would change on the basis of the degree of conversion of the sweetener being considered (Table 21.6). At that time, most syrups were divided into loose classifications

**Table 21.5** Saccharide compositions of several syrups<sup>51</sup>

	DE:	High maltotetraose syrup		Acid-conversion syrup	Enzyme-conversion syrup
		Type I	Type II		
Glucose		30.8	36.2	32.6	47.0
		1.0	2.0	10.3	3.0
Maltose		7.8	8.5	8.3	53.5
Maltotriose		10.2	11.0	8.4	15.8
Maltotetraose		50.5	72.0	8.1	3.2
Maltopentaose		2.5	1.0	6.9	2.0
Others (>DP5)		28.0	5.5	58.0	22.5

**Table 21.6** Relationship between degree of conversion and functional property

Property or functionality that increases with an increasing degree of conversion	Property or functionality that decreases with an increasing degree of conversion
Browning	Bodying
Fermentability	Cohesiveness
Flavor enhancement	Foam stabilization
Flavor transfer	Prevention of sucrose crystallization
Freezing point depression	Prevention of coarse ice crystal formation during freezing
Hygroscopicity	Viscosity
Osmotic pressure	
Sweetness	

based on DE as a measure of the relative degree of conversion. As already mentioned, subsequent advances in enzyme technology and the proliferation of syrups based on the carbohydrate profile diminished the importance of DE in describing the nature of a syrup. Rapid and inexpensive methods of analysis, such as liquid chromatography, have allowed producers to focus on the carbohydrates present in sweeteners and how they impact the physical properties of the syrup.

Physical properties of a syrup depend heavily on its carbohydrate profile. The carbohydrate profile, in turn, is determined by the type of conversion and the nature of the enzyme treatment (previously discussed). Table 21.2 gives typical DE and carbohydrate profiles of syrups in common production today. Because enzyme treatments can provide sweeteners with different carbohydrate profiles but the same DE value, it is usual to refer to a product using more than one descriptor, e.g. a 43 DE, high-maltose syrup. This issue becomes particularly important when addressing functional differences and applications of starch-derived sweeteners.

## 2. Solids

In addition to DE values and carbohydrate profiles, syrups are usually identified by their solids level. The traditional means of expressing the solids of a glucose/syrup is the Baume number. Extensive work comparing the Baume number to refractive index

**Table 21.7** Refractive index-dry substance tables for typical glucose syrups<sup>58</sup>

Syrup	% DS	RI 20°C	RI 45°C	Be Comm 140°/60°F +1	Sp. G. AIR/AIR 100°/60°F	Total lbs/ gal, 100°F	Dry sub lbs/ gal, 100°F
28 DE	78.00	1.4943	1.4892	42.00	1.4064	11.73	9.15
36 DE	80.40	1.4993	1.4941	43.02	1.4202	11.84	9.52
34 HM	80.60	1.4988	1.4936	42.99	1.4197	11.84	9.54
43 HM	80.90	1.4988	1.4937	43.01	1.4199	11.84	9.58
43 DE	80.70	1.4988	1.4936	43.02	1.4201	11.84	9.55
43 DE IX	80.80	1.4990	1.4938	43.00	1.4198	11.84	9.56
53 DE	83.50	1.5044	1.4992	44.13	1.4354	11.97	9.99
63 DE	82.00	1.4982	1.4931	43.02	1.4201	11.84	9.71
63 DE IX	84.00	1.5064	1.4985	44.01	1.4337	11.95	10.04
66 DE	84.30	1.5044	1.4993	44.09	1.4347	11.96	10.04
95DE	71.00	1.4644	1.4595	36.39	1.3348	11.13	7.90
HFCS 42	71.00	1.4643	1.4589	NA	1.3372	11.15	7.92
HFCS 55	77.00	1.4789	1.4728	NA	1.3809	11.51	8.98
Liquid fructose	77.00	1.4780	1.4715	N/A	1.3763	11.47	8.84

**Table 21.8** Refractometer corrections for HFS 55, 0.05% ash (dry basis)<sup>59</sup>

Dry substance, % by weight	Refractive index, 20°C	Brix (1936)	Refractometer correction	Brix (1966)	Refractometer correction
10.00	1.34771	9.92	0.08	9.93	0.07
20.00	1.36352	19.81	0.19	19.82	0.18
30.00	1.38054	29.69	0.31	29.68	0.32
40.00	1.39881	39.53	0.47	39.48	0.52
50.00	1.41841	49.24	0.76	49.22	0.78
60.00	1.43944	58.93	1.07	58.92	1.08
70.00	1.46197	68.70	1.30	68.59	1.41
77.00	1.47870	75.52	1.48	75.35	1.65
80.00	1.48611	78.43	1.57	78.24	1.76

has produced easily-used tables to convert the various measures of solids measurement.<sup>53-56</sup> Unlike glucose syrups the solids content of high-fructose syrups is stated as the dry substance.<sup>57</sup> Table 21.7 shows the comparison of dry solids to degrees Baume for several typical sweeteners.<sup>58</sup>

When the solids content of glucose syrups is measured by refractometers calibrated in degrees Brix, some correction must be applied to obtain the true solids level. Brix measurements are commonly used in the sucrose industry and refer to the percentage of sucrose in solution. The Brix tables were modified in 1936, 1966 and 1974, resulting in minor changes as shown in Table 21.8.<sup>59</sup> These corrections have been incorporated into high-fructose syrup tables commonly used in the beverage industry (Table 21.9).<sup>60</sup>

### 3. Viscosity

Glucose syrups exhibit the viscosity characteristics of Newtonian fluids. The coefficient of viscosity is constant and is measured in poises (dyne-seconds/cm<sup>2</sup>), which is

**Table 21.9** Relationship of refractive index to Brix for high-fructose syrups<sup>60</sup>

42% High-fructose syrup									
Solids, %	Refractive Index		Ref. Brix (20°C)		Density (vac) 20°C	Sp. Grav (air) 20°C	Lbs/US gal. (20°C)		Hydr. Brix 20°C
	20°C	45°C	1936	1966			Total	Solids	
70.500	1.463	1.458	9.270	69.170	1.344	1.347	11.211	7.903	69.540
70.600	1.464	1.458	9.370	69.270	1.345	1.348	11.216	7.918	69.630
70.700	1.464	1.458	9.460	69.370	1.346	1.348	11.221	7.933	69.730
70.800	1.464	1.459	9.560	69.460	1.346	1.349	11.226	7.948	69.830
70.900	1.464	1.459	9.660	69.560	1.347	1.350	11.231	7.963	69.920
71.000	1.465	1.459	9.760	69.660	1.347	1.350	11.236	7.977	70.020
71.100	1.465	1.459	9.860	69.750	1.348	1.351	11.241	7.992	70.120
71.200	1.465	1.460	9.950	69.850	1.349	1.351	11.246	8.007	70.210
71.300	1.465	1.460	0.050	69.950	1.349	1.352	11.251	8.022	70.310
71.400	1.466	1.460	0.150	70.040	1.350	1.353	11.256	8.037	70.410
71.500	1.466	1.460	0.250	70.140	1.350	1.353	11.261	8.052	70.500

55% High-fructose syrup									
Solids, %	Refractive Index		Ref. Brix (20°C)		Density (vac) 20°C	Sp. grav (air) 20°C	Labs/US gal. (20°C)		Hydr. Brix 20°C
	20°C	45°C	1936	1966			Total	Solids	
76.5	1.477	1.472	75.000	74.830	1.382	1.385	11.522	8.814	75.380
76.6	1.478	1.472	75.090	74.930	1.382	1.385	11.527	8.829	75.480
76.7	1.478	1.472	75.190	75.020	1.383	1.386	11.532	8.845	75.580
76.8	1.478	1.472	75.290	75.120	1.384	1.386	11.537	8.861	75.670
76.9	1.478	1.473	75.390	75.220	1.384	1.387	11.543	8.876	75.770
77.0	1.479	1.473	75.480	75.310	1.385	1.388	11.548	8.892	75.870
77.1	1.479	1.473	75.580	75.410	1.385	1.388	11.553	8.907	75.960
77.2	1.479	1.473	75.680	75.510	1.386	1.389	11.558	8.923	76.060
77.3	1.479	1.473	75.770	75.600	1.387	1.390	11.564	8.939	76.160
77.4	1.480	1.474	75.870	75.700	1.387	1.390	11.569	8.954	76.250
77.5	1.480	1.474	75.970	75.800	1.388	1.391	11.574	8.970	76.350

the force per unit area necessary to maintain unit difference in velocity between two parallel layers of fluids that are one unit distance apart. The poise is the absolute viscosity of the solution. Viscosity in starch-derived sweeteners is due primarily to the solids level and the percentage of higher saccharides present. As might be expected, at the same solids level, sweeteners with relatively long chains of branched molecules have higher viscosity than sweeteners with high concentrations of monosaccharides, an effect compounded by the presence of weak hydrogen bonds.

The viscosity of syrups is usually reported in either centipoises (mPa s) or SSU (Saybolt Seconds Universal) units. SSU units are related to centipoises by the following equation:<sup>61</sup>

$$\text{SSU} = \frac{\text{centipoises} \times 4.55}{\text{specific gravity}}$$



**Table 21.10** Viscosity (centipoises) of syrups of different DS and temperatures<sup>62</sup>

DS	Temperature °F	Dextrose equivalent			
		35.4	42.9	53.7	75.4
85	60				457 000
	80	7 080 000	1 410 000	537 000	83 200
	100	1 000 000	227 000	85 200	17 000
	120	188 000	50 100	20 000	4 270
	140	44 900	13 000	6 310	1 660
	160	13 000	5 190	2 290	589
	180	4 420	1 760	944	275
80	60		266 000	89 100	24 000
	80	126 000	59 600	17 800	4 570
	100	29 900	15 000	5 010	1 550
	120	8 910	4 840	1 800	603
	140	3 350	1 860	785	282
	160	1 410	851	367	141
	180	687	386	196	75.9
75	60	39 800	18 200	7 590	6 030
	80	10 000	5 390	2 140	741
	100	3 020	1 880	807	331
	120	1 260	817	372	159
	140	620	389	191	83.2
	160	325	197	103	47.9
	180	180	110	62.0	28.8

**Table 21.11** Color designations of glucose syrups<sup>63</sup>

Optical density	Visual color
0.025	Water white
0.035	Very light straw
0.050	Light straw
0.075	Straw to very light yellow
0.100	Medium light yellow
0.125	Light yellow
0.150	Medium yellow
0.200	Yellow

Typical values for the viscosity of a number of syrups produced by acid conversion measured at various temperatures and solids levels are given in Table 21.10.<sup>62</sup>

#### 4. Browning Reaction and Color

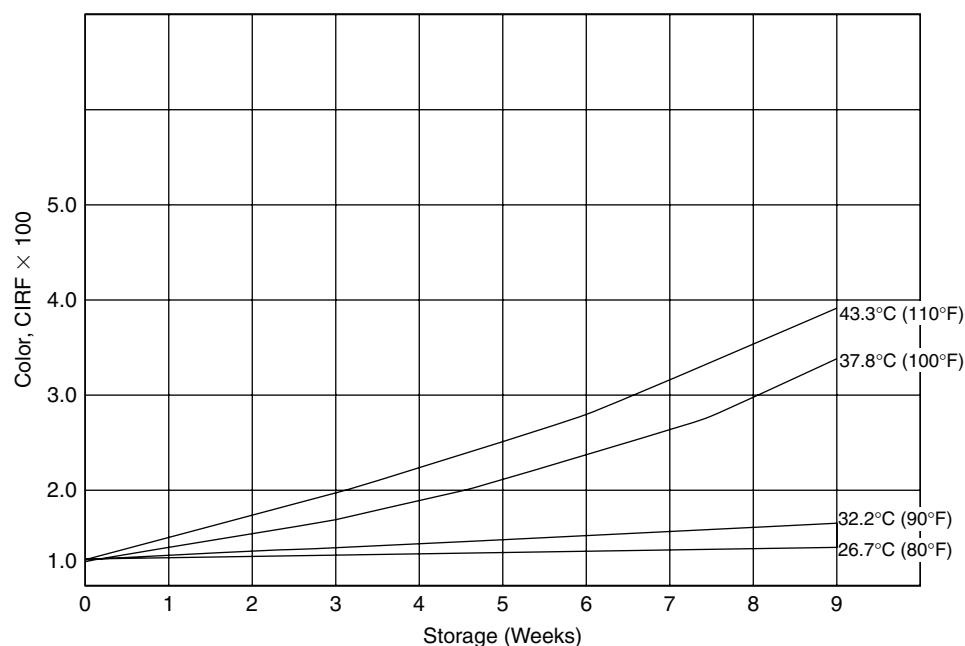
The color of starch-derived sweeteners is often referred to as ‘water white,’ but it is more meaningful to express color of syrup in terms of absorbance (optical density, Table 21.11).<sup>63</sup> Typically, the color of commercial corn sweeteners, particularly high-fructose and dextrose syrups, is expressed in absorbance measured against a reference standard of water at 450 nm and 600 nm, as shown in Figure 21.17.<sup>64</sup>

Several reactions can cause color development in starch-derived sweeteners. Because they contain reducing sugars, they will react with proteins and amino acids

$$\text{Color} = \frac{(A_{450} - A_{600})}{N} \times 100$$

Where N is the path length in centimeters

**Figure 21.17** Equation for calculating color of syrups.<sup>64</sup>



**Figure 21.18** Color stability of a high-fructose syrup containing 42% fructose, 50% glucose and 8% other saccharides (71% solids).<sup>67</sup>

via the non-enzymic browning reaction between sugars and primary or secondary amines (Malliard reaction) to form what are referred to as 'color bodies.'<sup>65,66</sup> Color development that occurs in the absence of nitrogenous compounds with the application of heat or acids is the result of caramelization. Excessive heating of starch-derived sweeteners will result in partial caramelization and development of undesirable flavors. The degree and rapidity of color development will be in direct proportion to the amount of reducing sugars present. This is used to advantage in certain food applications, such as in baking. The rate of color development may be retarded by demineralization of the sweetener. Selection of a sweetener with a lesser amount of monosaccharides will also slow color development. Figure 21.18 shows the rate of color development of a 42% high-fructose syrup under different conditions of storage.<sup>67</sup>

## 5. Fermentability

Starch-derived sweeteners provide a highly fermentable substrate for many industrial applications. The ability of yeast to ferment starch-derived syrups is directly

**Table 21.12** Fermentable extract values of corn syrups compared with dextrose<sup>68</sup>

Glucose syrup or dextrose	Fermentable extract, % db <sup>a</sup>
36 DE	24.8
42 DE	41.5
54 DE	53.4
62 DE	70.0
64 DE	76.1
68 DE	79.0
HFCS	95.0
Dextrose	100.0

<sup>a</sup>db = dry basis

**Table 21.13** Theoretical versus actual fermentability<sup>69</sup>

Adjunct	Weight %				Fermentability	
	DP <sub>1</sub>	DP <sub>2</sub>	DP <sub>3</sub>	DP <sub>4+</sub>	Calc.	Det.
Dextrose	99.8	0.2	0.0	0.0	100.0	99.8
Maltose syrup	7.1	58.8	19.7	14.4	85.6	85.5
High-conversion syrup	32.7	28.8	14.3	24.2	75.8	72.8
Acid syrup	18.8	15.3	14.7	51.2	48.8	47.1
Maltodextrin	0.9	3.2	2.8	93.1	6.9	11.4

proportional to the monosaccharide and disaccharide content of the sweetener. Table 21.12 gives the fermentable extract value for a number of sweeteners.<sup>68</sup> The fermentable extract of a sweetener is generally calculated as the sum of the DP<sub>1</sub>, DP<sub>2</sub> and DP<sub>3</sub> components, although there may be some slight variation between theoretical and actual results, as shown in Table 21.13.<sup>69</sup> The fermentation pathway is different for glucose and fructose, and high levels of glucose have been shown to impair the mechanism for maltose and maltotriose utilization.<sup>70</sup>

## 6. Foam Stabilization and Gel Strength

In whipped and aerated products, low DE sweeteners have the ability to stabilize foam structures, because of the relatively high polysaccharide level and hydrogen bonding that enhances the effectiveness of the albumin or gelatin. The concentration and type of sweetener affects the gel–sol transition process, in part by regulating water availability.<sup>71</sup> Syrups may be used to achieve the high soluble solids concentrations (>55%) required to effect gelation of high methoxyl pectin (HM pectin) solutions used to make jams, jellies and preserves. When glucose syrups are used, the gels may be firmer than when high-fructose syrups are used.<sup>72</sup>

**Table 21.14** Estimating the freezing point depression of various sweeteners<sup>73</sup>

Sweetener	Sucrose equivalence value (SE) <sup>a</sup>	Freezing point equivalence factor <sup>a</sup>
Sucrose	100	1.00
Lactose	100	1.00
Maltose	100	1.00
Dextrose	180	0.55
Fructose	180	0.55
90%	187	0.53
55%	185	0.54
42%	180	0.55
Glucose syrups		
62 DE	114	0.58
52 DE	95	1.05
42 DE	79	1.27
36 DE	72	1.39
32 DE	63	1.59
28 DE	58	1.67
Dextrin (C18-C40)	67	1.47

<sup>a</sup>The sucrose equivalence value is based on the molecular weight of sugar. The freezing point equivalence factor for freezing point depression of a sweetener is based on the molecular weight relative to that of sucrose. The percentage of sweetener is multiplied by the appropriate freezing point equivalence factor to give the freezing point depression

## 7. Freezing Point Depression

The freezing point of solutions containing sweeteners can be calculated based on their concentration in that solution and their average molecular weight. For a given condition, the effect on the freezing point is inversely proportional to the average molecular weight of the sweetener. Lower conversion syrups in solution will not depress the freezing point as much as higher conversion syrups. The relative effect of various sweeteners on the freezing point of a solution compared to sucrose has been reported by Arbuckle<sup>73</sup> and is shown in Table 21.14 and Figure 21.19. The relative degrees to which these sweeteners affect the freezing point also depends on the solids level.<sup>74</sup> Sweeteners also act in a manner similar to stabilizers, determining the time and degree of ice crystal formation by controlling the migration of free water.<sup>75</sup>

## 8. Boiling Point Elevation

As in the case of freezing point depression, boiling point elevation depends on the carbohydrate profile. In general, the boiling point is increased as the level of conversion increases. Table 21.15 shows the relationship of boiling point to solids content for various sweeteners.<sup>76</sup>

## 9. Gelatinization Temperature

This relationship is important to aspects of baking where sweetener concentration and replacement can impact the gelatinization temperatures of starch granules. Substitution of fructose for sucrose lowers the gelatinization temperature (Figure 21.20).<sup>77</sup>

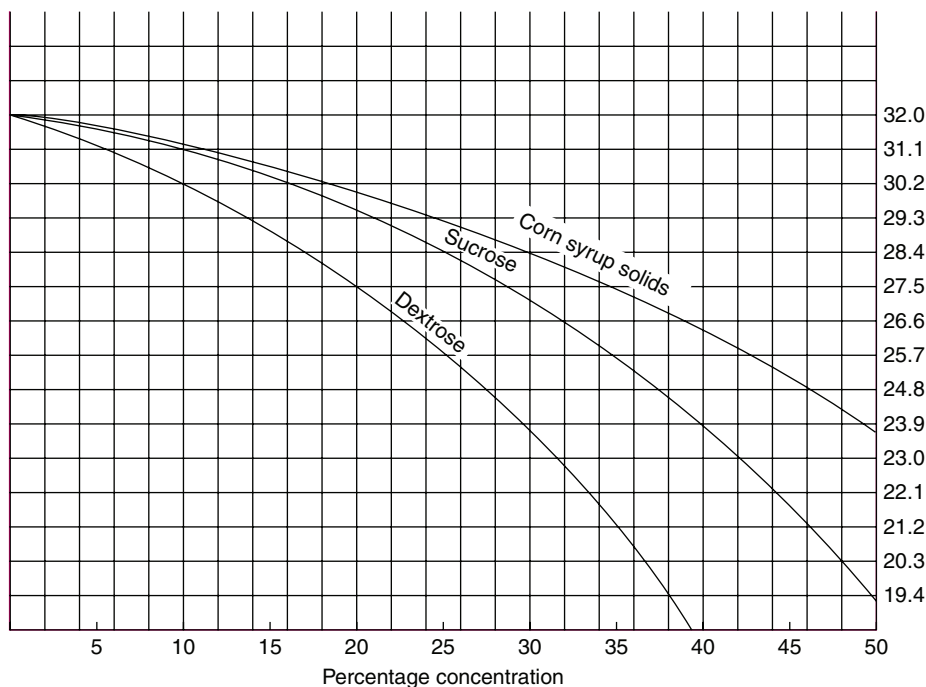


Figure 21.19 Freezing point relationships of solutions of dextrose, sucrose and syrup solids.<sup>73</sup>

**Table 21.15 Boiling point elevation of glucose syrups (760mm Hg)<sup>76</sup>**

Syrup DE	% dry substance					
	20	40	60	70	80	85
30	0.39	1.18	3.55	6.3	11.1	15.1
42	0.56	1.60	4.81	8.3	14.3	19.2
55	0.76	2.09	5.98	10.1	16.9	22.3
65	0.91	2.51	6.86	11.3	18.5	23.8
80	1.17	3.16	8.15	12.9	20.3	25.3
95	1.38	3.62	8.95	13.9	21.1	26.1

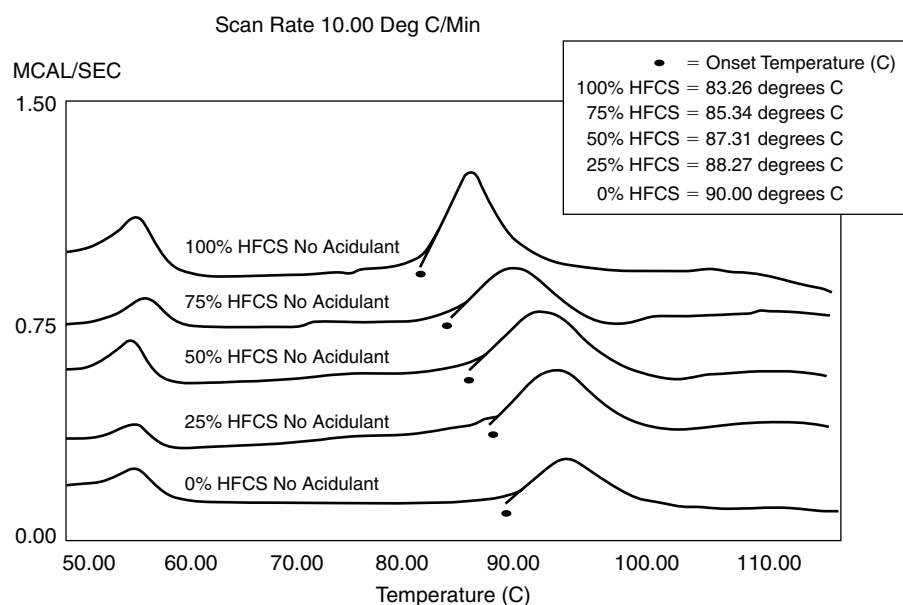
In addition to lowering the water activity and forming sugar bridges between starch chains restricting flexibility, there is also an antiplasticizing effect of saccharide solutions relative to water.<sup>78</sup>

### 10. Humectancy and Hygroscopicity

A hygroscopic material absorbs moisture from its surrounding atmosphere, while a humectant material is one that resists changes in relative moisture content. The gain or loss of moisture in a corn syrup is dependent on the relative humidity of the atmosphere surrounding the syrup. Moisture absorption values for several sweeteners are shown in Table 21.16.<sup>79</sup>

## 11. Crystallization

Starch-derived syrups are able to crystallize, depending on the type of carbohydrates present, the solids level and the temperature. This property can be used to advantage, as in the manufacture of hard candy, or can be one to be avoided, as in the case of



**Figure 21.20** Effect of increasing amounts of high-fructose syrups on the gelatinization temperature of starch in a cake batter.<sup>77</sup>

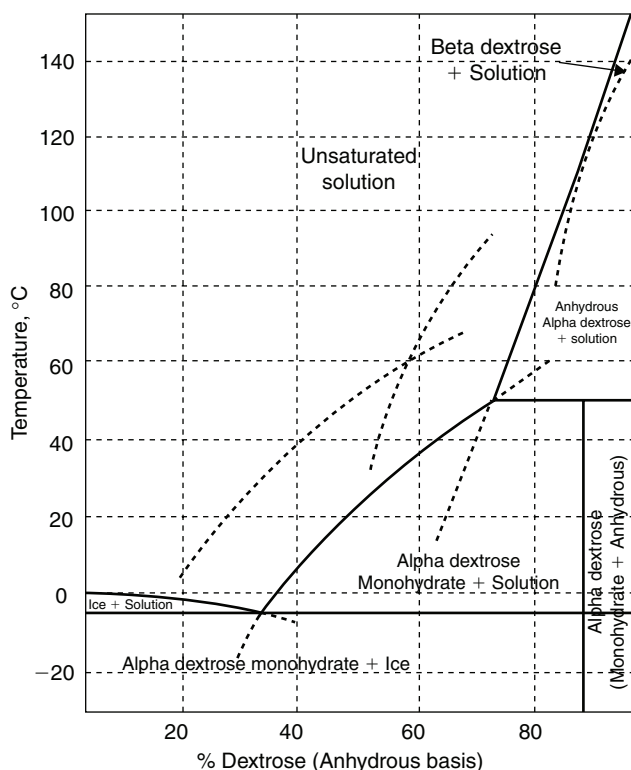
**Table 21.16** Moisture absorption by nutritive sweeteners<sup>79</sup>

Sugar	Relative humidity, %	Percent moisture absorption from 1 to 76 days (25°C)											
		1	3	7	11	17	20	26	30	40	50	60	76
Sucrose <sup>a</sup>	62.7	0.06	0.05	0.05	-	0.05	-	-	0.05	-	0.05	0.05	0.05
	81.8	0.05	0.05	0.05	-	0.05	-	-	0.05	-	0.05	0.05	0.05
	98.8	1.31	4.85	13.53	20.81	-	33.01	38.53	-	45.62	-	-	-
Dextrose <sup>b</sup>	62.7	0.04	0.04	0.04	-	0.38	-	-	0.43	-	0.79	1.07	1.74
	81.8	0.62	2.04	5.15	-	9.70	-	-	9.62	-	9.77	9.60	9.60
	98.8	4.68	8.61	15.02	20.78	-	28.43	33.95	-	42.82	-	-	-
Fructose <sup>c</sup>	62.7	0.65	1.41	2.61	-	7.09	-	-	13.01	-	18.35	21.85	21.40
	81.8	4.18	10.22	18.58	-	29.16	-	-	35.05	-	36.32	35.30	35.50
	98.8	11.09	18.43	30.74	37.61	-	45.95	49.41	-	54.99	-	59.14	-
Lactose	62.7	0.03	0.03	0.03	-	0.05	-	-	0.05	-	0.05	0.05	0.08
	81.8	0.07	0.07	0.07	-	0.07	-	-	0.11	-	0.11	0.11	0.07
	98.8	0.05	0.05	0.09	0.12	-	0.13	0.26	-	0.33	-	-	-

<sup>a</sup>Sucrose crystals liquefied after absorption of 16–18% moisture

<sup>b</sup>On reaching 15–18% moisture, crystals began to dissolve; when absorption reached 42%, the dextrose was completely liquefied

<sup>c</sup>All fructose crystals liquefied



**Figure 21.21** Phase diagram for aqueous solutions of dextrose/D-glucose.<sup>80</sup>

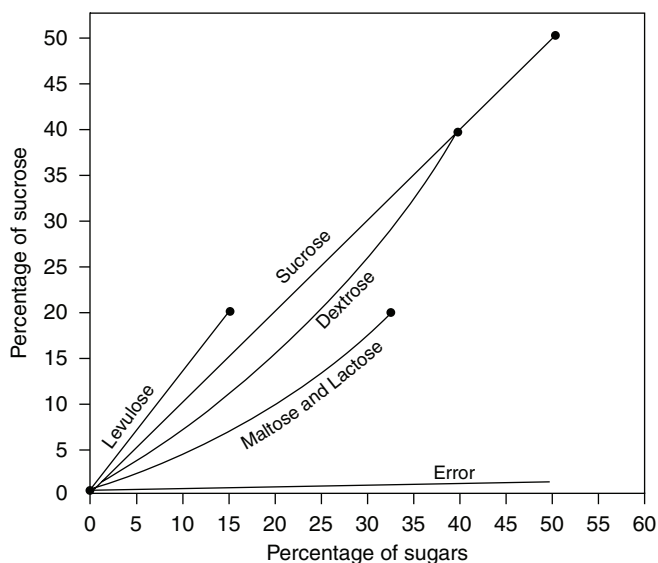
jam and jelly manufacture. In jelly manufacturing, one role of the syrup is to increase the solids level and the osmotic strength to the point that it is difficult for the system to support microbial growth, while maintaining a smooth, clear, non-crystallized structure. As previously discussed, the sweetener also binds most of the water present and induces gelation of the HM pectin solution. This process must be carefully controlled because too high a level of crystallizing sugars, such as dextrose, may induce crystallization on storage. The phase diagram for glucose is shown in Figure 21.21.<sup>74</sup>

## 12. Sweetness

Sweetness is an important and easily identifiable characteristic of glucose- and fructose-containing sweeteners. The sensation of sweetness has been extensively studied.<sup>80-82</sup> Shallenberger<sup>83</sup> defines sweetness as a primary taste. He furthermore asserts that no two substances can have the same taste. Thus, when compared to sucrose, no other sweetener will have the unique properties of sweetness onset, duration and intensity of sucrose. It is possible to compare the relative sweetness values of various sweeteners, as shown in Table 21.17,<sup>84</sup> but it must be kept in mind that these are relative values. There will be variations in onset, which is a function of the chirality of the sweetener,<sup>85</sup> variations in duration, which is a function of the molecular weight profile and is impacted by the viscosity, and changes in intensity, which is affected by

**Table 21.17** Relative sweetness values of various sweetener<sup>84</sup>

Type of sweetener	Sweetness relative to sucrose
30 DE acid-converted syrup	30–35
36 DE acid-converted syrup	35–40
42 DE acid-converted syrup	45–50
54 DE acid-converted syrup	50–55
62 DE acid-converted syrup	60–70
HFS (42% fructose)	100
HFS (55% fructose)	100–110
HFS (90% fructose)	120–160
Lactose	40
Dextrose	70–80
Fructose	150–170
Sucrose	100

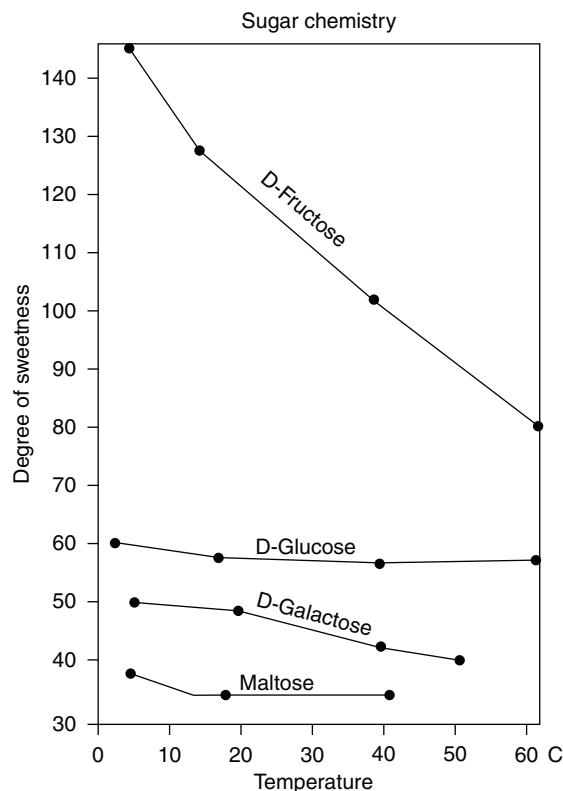
**Figure 21.22** Concentrations of sugars (on a percent dry solids basis) needed to give the same sweetness as sucrose solutions (levulose = fructose).<sup>85</sup>

the solids level and the particular isomers present (Figure 21.22).<sup>85</sup> Such variables are demonstrated by the performance of fructose in solution. The fructose molecule may exist in any of several forms. The exact concentration of any of these isomers depends on the temperature of the solution. At cold temperatures the sweetest form,  $\beta$ -D-fructopyranose, predominates, but at hot temperatures, fructofuranose forms predominate and the perceived sweetness lessens (Figure 21.23).<sup>86</sup>

### 13. Selection of Sweeteners

Selection of sweeteners for food applications is driven by cost, availability and consideration of the functional properties. In many cases, the desired properties may be





**Figure 21.23** Effect of temperature on the relative sweetness of sugar solutions.<sup>86</sup>

mutually exclusive in a given sweetener. This would be the case, for example, if a high degree of sweetness combined with a high viscosity were required in the sweetener. In such cases, blends of sweeteners or the use of other food ingredients would be required. Desirable physical properties of starch sweeteners as they apply to many food applications can be found in reference 87.

## IV. References

1. Kretchmer N. In: Kretchmer N, Hollenbeck CB, eds. *Sugars and Sweeteners*. Orlando, FL: CRC Press; 1991:8–9.
2. Kooi ER, Armbruster FC. In: Whistler RL, Paschall EF, eds. *Starch: Chemistry and Technology*. Vol. II. New York, NY: Academic Press; 1967:553–568.
3. Whistler RL. In: Whistler RL, BeMiller JN, Paschall EF, eds. *Starch Chemistry and Technology*. Orlando, FL: Academic Press; 1984:4–6.
4. Anon. *Nutritive Sweeteners From Corn*. Washington, DC: Corn Refiners Association; 1993:6.
5. Anon. *Corn Annual 2000*. Washington, DC: Corn Refiners Association; 2000:3.
6. Pancoast H, Junk WR. *Handbook of Sugars* 1980. Westport, CT: AVI Publishing; 1980 180.

7. Lloyd NE, Nelson WJ. In: Whistler RL, BeMiller JN, Paschall EF, eds. *Starch Chemistry and Technology*. Orlando, FL: Academic Press; 1984:611–660.
8. Anon. *Federal Register*. 1995 September 21;60(No. 183):48939.
9. Anon. *Census of Products, Grain Mill Products*. Washington, DC: U.S. Department of Commerce; 1992:20D-22.
10. Teague WM, Brumm PJ. In: Schenck FW, Hebeda RE, eds. *Starch Hydrolysis Products*. New York, NY: VCH Publishers; 1992:45–77.
11. MacAllister RV. *Adv. Carbohydr. Chem. Biochem.* 1979;36:15.
12. Katz F; *1995 Regulatory Seminar*. Washington, DC: Corn Refiners Association; 1995:78.
13. Alexander R. In: Schenck FW, Hebeda R, eds. *Starch Hydrolysis Products*. New York, NY: VCH Publishers; 1992:233–275.
14. Vance RV, Rock AO, Carr PW. US Patent 3 654 081. 1972.
15. Hebeda RE. In: Watson SA, Ramstad PE, eds. *Corn: Chemistry and Technology*. St. Paul, MN: American Association of Cereal Chemists; 1987:501–534.
16. Vuilleumeir SW. *The Outlook for Sweeteners*: Mckeany-Flavell Company; June 2000.
17. Blanchard PH. *Technology of Corn Wet Milling and Associated Processes*. Amsterdam, The Netherlands: Elsevier Science Publishers; 1992:232.
18. Scallett B, Ehrental I. US Patent 3 305 395. 1967.
19. BeMiller JN. In: Whistler RL, Paschall EF, eds. *Starch: Chemistry and Technology*. Vol. I. New York, NY: Academic Press; 1965:495–520.
20. BeMiller JN. *Advan. Carbohydr. Chem.* 1967;22:25.
21. Watson SA. In: Whistler RL, Paschall EF, eds. *Starch: Chemistry and Technology*. Vol. II. New York, NY: Academic Press; 1967:1–51.
22. Wright KN. In: Watson SA, Ramstad PE, eds. *Corn: Chemistry and Technology*. St. Paul, MN: American Association of Cereal Chemists; 1987:447–478.
23. Hassler JW. *Activated Carbon*. New York, NY: Chemical Publishing Company; 1963:115.
24. Conlee J. *Stärke*. 1971;23:366.
25. Schenck FW, Cotilion M. In: Schenck FW, Hebeda RE, eds. *Starch Hydrolysis Products*. New York, NY: VCH Publishing; 1992:531–554.
26. Rooney LW, Serna-Saldivar SO. In: Watson SA, Ramstad P, eds. *Corn: Chemistry and Technology*. St. Paul, MN: American Association of Cereal Chemists; 1987:399–429.
27. Komaki T. *Agri. Biol. Chem.* 1968;32:123.
28. Pazur JH, Kleppe K. *J. Biol. Chem.* 1962;237:1002.
29. Linko P. In: Kruger JE, Lineback D, Stauffer CF, eds. *Enzymes and their Role in Cereal Technology*. St. Paul, MN: American Association of Cereal Chemists; 1987:364.
30. Norman BE. *Starch/Stärke*. 1982;34:340.
31. Anon. *Nutritive Sweeteners from Corn*. Washington, DC: Corn Refiners Association; 1993:17.
32. Antrim RL, Colilla W, Schnyder BJ. *Appl. Biochem. Bioeng.* 1979;2:97.
33. Casey JP. *Research Management*. 1976;28.
34. Pedersen S. In: Tanaka A, Tosa T, Kobayashi T, eds. *Industrial Application of Immobilized Biocatalysts*. New York, NY: Marcel Dekker; 1993:185–207.

- 
35. Havewala Jr NB, Pitcher WH. In: Pye EK, Wingard LB, eds. *Enzyme Engineering*. Vol. 2. New York, NY: Plenum Press; 1974:315–328.
  36. MacAllister Jr RV. In: Pitcher WH, ed. Boca Raton, FL: CRC Press; 1980:82–112.
  37. Takasaki Y, Kosugi Y, Kanbayashi A. In: Penman D, ed. *Fermentation Advances*. New York, NY: Academic Press; 1969:561–589.
  38. Lloyd NE, Khaleeluddin K. *Cereal Chem*. 1976;53:270.
  39. Takasaki Y. *Agr. Biol. Chem*. 1967;31:309.
  40. Takasaki Y. *Agr. Biol. Chem*. 1971;35:1371.
  41. Shioda K. In: Schenck FW, Hebeda RE, eds. *Starch Hydrolysis Products*. New York, NY: VCH Publishers; 1992:565–566.
  42. Kusch T, Gosewinkel W, Stoeck G. US Patent 3 513 023. 1970.
  43. Hara K, Samoto M, Sawai M, Nakamura S. US Patent 3 704 168. 1972.
  44. Hanover LM, White JS. *Am. J. Clin. Nutr*. 1993;58(5, Suppl):7245.
  45. Hanover LM. In: Schenck FW, Hebeda RE, eds. *Starch Hydrolysis Products*. New York, NY: VCH Publishers; 1992:201–231.
  46. Dean GR, Gottfried JB. *Adv. Carbohydr. Chem*. 1950;5:127.
  47. Weber EJ. In: Watson SA, Ramstad PE, eds. *Corn: Chemistry and Technology*. St. Paul, MN: American Association of Cereal Chemists; 1987:311–349.
  48. Mulvihill PJ. In: Schenck FW, Hebeda RE, eds. *Starch Hydrolysis Products*. New York, NY: VCH Publishers; 1992:121–176 [Figure 5.5].
  49. Nakakuki T. Japan Patent JP 8916599 A2. 1989.
  50. Heady RE. US Patent 3 535 123. 1970.
  51. Okada M, Nakakuki Teruo. In: Schenck FW, Hebeda RE, eds. *Starch Hydrolysis Products*. New York, NY: VCH Publishers; 1992:335–367.
  52. Hoover WJ. In: Food Processing Catalogue, 1964–65 Edition. 1964.
  53. Wartman AM, Hagberg C, Eliason MA. *J. Chem. Eng. Data*. 1976;21:459.
  54. Kurtz F, Eliason MA. *J. Chem. Eng. Data*. 1979;24:44.
  55. Wartman AM, Bridges AJ, Eliason MA. *J. Chem. Eng. Data*. 1980;25:277.
  56. Wartman AM, Spawn TD, Eliason MA. *J. Agr. Food Chem*. 1984;32:971.
  57. Anon. *Quality Guidelines and Analytical Procedures*: International Society of Beverage Technologists; 1994:2.
  58. Anon. *Nutritive Sweeteners From Corn*. Washington, DC: Corn Refiners Association; 1993:30–31.
  59. Marov GJ. *Proceedings of the Society of Soft Drink Technologists*. 1982:91–98.
  60. Anon. *Quality Guidelines and Analytical Procedures*. NY: International Society of Beverage Technologists; 1994 [Table 1].
  61. Pancoast H, Junk WR. *Handbook of Sugars* 1980. Westport, CT: AVI Publishing; 1980:223.
  62. Erickson ER, Berntsen RA, Eliason MA. *J. Chem. Eng. Data*. 1966;11:485.
  63. Pancoast H, Junk WR. *Handbook of Sugars* 1980. Westport, CT: AVI Publishing; 1980:186.
  64. Anon. *Standard Analytical Methods*. 6th edn. Washington, DC: Corn Refiners Association; 1991 [Method E-16].
  65. Shallenberger RS, Birch GG. *Sugar Chemistry*. Westport, CT: AVI Publishing Company; 1975.

66. Waller GR, Feather MS. *The Maillard Reaction in Foods and Nutrition*. Washington, DC: American Chemical Society; 1983.
67. Pancoast H, Junk WR. *Handbook of Sugars* 1980. Westport, CT: AVI Publishing; 1980:246.
68. Pancoast H, Junk WR. *Handbook of Sugars* 1980. Westport, CT: AVI Publishing; 1980:181.
69. Hebeda RE, Styrlund CR. *Cereal Foods World*. 1986;31:685.
70. Phaweni M, O'Conner-Cox ESC, Pickerell ATW, Axcell BC. *J. Am. Soc. Brewing Chem.* 1993;51:10.
71. Keeney P. *Food Technol.* 1982;65.
72. da Silva JAL, Rao MA. *Food Technol.* 1995;49:70.
73. Arbuckle WS. *Ice Cream*. 4th edn. Westport, CT: AVI Publishing Company; 1986:74.
74. Critical Data Tables, Washington, DC: Corn Refiners Association; 1975.
75. Wittinger SA, Smith DE. *J. Food Sci.* 1986;51:1463.
76. Smith ER, Torgesen JL. *Phys. Chem. Sect. Rept. 5*. Washington, DC: National Bureau of Standards; 1950.
77. Johnson JM, Harris CH, Barbeau WE. *Cereal Chem.* 1989;66:155.
78. Kim CS, Walker CE. *Cereal Chem.* 1992;69:212.
79. Pancoast H, Junk WR. *Handbook of Sugars* 1980. Westport, CT: AVI Publishing; 1980:391.
80. Shallenberger RS, Birch GG. *Sugar Chemistry*. Westport, CT: AVI Publishing; 1975:180.
81. Birch GG, Green LF, Coulson CB, eds. *Sweetness and Sweeteners*. London, UK: Applied Science Publishers; 1971.
82. Shallenberger RS. *Advanced Sugar Chemistry*. Westport, CT: AVI Publishing; 1982.
83. Shallenberger RS. *Taste Chemistry*. London, UK: Blackie Academic&Professional; 1993.
84. Pancoast H, Junk WR. *Handbook of Sugars* 1980. Westport, CT: AVI Publishing; 1980:388.
85. Shallenberger RS, Birch GG. *Sugar Chemistry*. Westport, CT: AVI Publishing; 1975:154.
86. Shallenberger RS, Birch GG. *Sugar Chemistry*. Westport, CT: AVI Publishing; 1975:156.
87. Pancoast H, Junk WR. *Handbook of Sugars* 1980. Westport, CT: AVI Publishing; 1980:403.