*Kirk-Othmer Encyclopedia of Chemical Technology.*


# STARCH

Starch [9005-25-8], $(C_6H_{10}O_5)_n$, the main reserve food of plants, constitutes two-thirds of the carbohydrate caloric intake of most humans but only 47% of the carbohydrate caloric intake by Americans, who also get about 52% of their carbohydrate calories from sugar. Commercial starches are obtained from seeds, particularly corn, waxy corn, high amylose corn, wheat, and rice, and from tubers or roots particularly potato, sweet potato, and tapioca (cassava). Their principal use is in foods; the major nonfood uses are in sizing of paper and textiles, and as adhesives (qv).

Egyptian papyrus bonded with a starchy adhesive has been dated to 3500–4000 BC. Pliny the Elder (23–74 AD) described Egyptian use of wheat starch modified by boiling in vinegar to produce a smooth surface for papyrus documents.

Enzyme technology, especially immobilized-enzyme technology, has allowed production of sweeteners (qv) from corn starch, ie, corn syrup or high fructose corn syrup (HFCS), and often also provides sources of chemical feedstocks to replace petroleum. Enzymes, notably $\alpha$-amylase, glucoamylase, and glucose isomerase, catalyze specific polysaccharide-degrading reactions to produce various glucose syrups. Immobilized enzyme technology has significant advantages because of the recoverability of the enzymes and their re-use in a continuous system, rather than in batch systems. Starch conversion technology, especially conversion to glucose and fructose-containing syrups, has been reviewed (1) (see Enzyme applications; Syrups).

The quasi-crystalline structure of natural starch granules causes them to be insoluble in water at normal room temperature and gives them relative resistance to carbohydrases other than $\alpha$-amylase and glucoamylase unless the granules become swollen. Three-dimensional arrangements of crystalline and amorphous zones in starch granules have been suggested (2).

## 1. Physical Properties

Starch granules in plants vary in diameter from 1–150 $\mu$m (3). Among commercial starches, rice starch (3–9 $\mu$m) has among the smallest granules and potato starch (15–100 $\mu$m), the largest (4). Corn starch granules are 5–26 $\mu$m with an average diameter of 15 $\mu$m. Amaranth starch granules are 1–3 $\mu$m in diameter. Microscopic examination of corn starch granules reveals a distinct growth point known as the hilum (3), ie, the nucleus from which granule growth begins. Polarized light microscopy reveals a birefringence which, along with x-ray diffraction, is evidence of granule semicrystallinity. Between crossed Nicol prisms of the microscope, a black maltese cross (cross of isoclines) is observed centered on the hilum. Cereal starches give an A-type x-ray pattern, tuber starches a B-type pattern, and a few starches give an intermediate, C-type diffraction pattern (5). From x-ray fiber diffraction patterns it has been determined that the starch molecule(s) fiber axis is perpendicular to the visible growth rings in the granule (6). The fiber period in starch is generally around 1.06 nm and a model has been proposed (7, 8) for both A and B x-ray patterns in which the starch molecules are left-handed parallel double-helices in hexagonal packing. Diffraction patterns may also be used to provide estimates of the relative amount of crystalline and amorphous phases, ie, x-ray crystallinity. Other methods of instrumental

analysis have been applied to the solid-state structure of starch including optical and electron microscopy, small-angle light scattering, thermal analysis (differential scanning calorimetry, dsc), and $^{13}$C-nmr spectroscopy (9). Cross-polarization/magic angle spinning experiments allow distinction between double-helical arrangements in starch and amorphous single chains. Such information is crucial in understanding the ultrastructure of raw starch granules.

Undamaged starch granules are insoluble in cold water but imbibe water reversibly accompanied by a slight swelling. With continued uptake of water at ambient temperature granule diameter increases 9.1% for corn and 22.7% for waxy corn (10). In hot water a larger irreversible swelling occurs producing gelatinization, which takes place over a discrete temperature range that depends on starch type.

| Starch | Range, °C |
|---|---|
| potato | 59–68 |
| tapioca | 58.5–70 |
| corn | 62–72 |
| waxy corn | 63–72 |
| wheat | 58–64 |

At a specific temperature during heating (lower limit of gelatinization temperature), the kinetic energy of the molecules is sufficient to overcome intermolecular hydrogen bonding in the interior of the starch granule. The amorphous regions of the granule are initially solvated and the granule swells rapidly, eventually to many times its original size. During swelling, some of the linear amylose molecules leach out of the granule into the enveloping solution. When a cooked starch paste containing a mixture of linear amylose molecules, swollen granules, and granule fragments is cooled, the dispersion thickens, and if sufficiently concentrated may form a gel. This property of forming thick pastes or gels is the basis of most starch uses. The effect of thermal treatment on starch depends strongly on whether it occurs in excess water, limited water, under pressure, or in extrusion cooking. In excess water it appears that starch swelling is a two-stage process consisting of initial granule swelling followed by granule dissolution; both steps are irreversible (11). In limited water, thermal responses have been interpreted as being due to starch crystallite melting (12, 13). In extrusion cooking, granules are physically torn apart, allowing more rapid penetration of water into the granule (14). Starch fragmentation (dextrinization) appears to be the predominant reaction during extrusion, in contrast to normal gelatinization (15). It has been reported that during extrusion the average molecular weight of amylose decreases by a factor of 1.5 and the average molecular weight of amylopectin decreases by a factor of 15 (16). Effects of starch structure on starch rheological properties during gelatinization or extrusion have been well reviewed (17).

The starch gelatinization temperature range begins with the onset of granule swelling and ends at the point where nearly 100% of the granules are gelatinized. The designated range over which gelatinization occurs depends on the method of measurement. The most sensitive microscopic method follows the loss of birefringence of a starch–water mixture on a Kofler hot stage (18). Chemical additives affect the gelatinization temperature range in a predictable way that may be important in specific industrial applications. Chemicals such as sodium sulfate, sucrose, and D-glucose inhibit gelatinization and increase the gelatinization temperature range, probably by competing for available water. Other chemicals, such as sodium nitrate, sodium hydroxide, and urea, lower the gelatinization temperature range, possibly by disrupting the granular intermolecular hydrogen bonds.

Physical properties of starch can be altered by mechanical treatments. If granular integrity is disrupted, as by grinding dry starch, the starch gelatinizes more easily, perhaps even in cold water. Damaged granules are quite reactive to chemicals and enzymes. Underivatized gelatinized granules are fragile. Even agitation of a cooked paste ruptures a majority of the swollen granules. As a result, a cooled paste loses viscosity and gelling ability. Physical properties of starches may also be altered by chemical modification of the starch. Acid

treatment, oxidation, cross-linking, and esterification are some of the chemical means used to modify peak viscosity, hot cooked paste stability, gelation, and freeze–thaw stability (19).

The concept and use of food polymer science in describing the behavior of starch during and after thermal treatment has been developed (20, 21). In this theory a fringed micelle model is used in describing starch as being composed of microcrystalline regions covalently cross-linked by flexible chain segments. In such a quasi-crystalline system the important thermal transitions are a glass-transition, $T_g$, for the amorphous component, and a phase-transition (crystalline melting temperature), $T_m$, for the micellar component. Using this model and theory, the antiplasticizing effect of sugars on starch gelatinization as well as gelation and retrogradation (staling) mechanisms have been explained (21). This theory and supporting experimental data (largely dsc) have been applied in investigating structure–function relationships of cookie and cracker ingredients (22). Use of dsc as a diagnostic tool in the investigation of cookie dough as well as in the analysis of staling in such low moisture baked goods has been described (22).

Specific optical rotation values, $[\alpha]_D$, for starch pastes range from 180 to 220° (5), but for pure amylose and amylopectin fractions $[\alpha]_D$ is 200°. The structure of amylose has been established by use of x-ray diffraction and infrared spectroscopy (23). The latter analysis shows that the proposed structure (23) is consistent with the proposed ground-state conformation of the monomer D-glucopyranosyl units. Intramolecular bonding in amylose has also been investigated with nuclear magnetic resonance (nmr) spectroscopy (24).

## 2. Chemical Properties

Most normal starches contain two distinct types of D-glucopyranose polymers. Amylose is an essentially linear polymer of $\alpha$-D-glucopyranosyl units linked $(1\longrightarrow 4)$ as shown in Figure 1. Although amylose molecules are generally thought of as being linear chains of $\alpha$-D-glucopyranosyl units, most amylose preparations contain amylose molecules with two to five branches. These long branches allow the molecules to possess nearly the same properties as truly linear molecules. Starch gives a characteristic blue color when stained with iodine, due to insertion of iodine into an amylose helical structure to form a complex with iodine on the inside of the helix. Amylopectin [9037-22-3] also forms a complex, but its color is purple to reddish brown, depending on the source of the amylopectin (25). In the presence of amylose this color reaction is usually obscured by the amylose–iodine blue. The characteristic blue color of the iodine–amylose complex has been employed both as a qualitative and quantitative test for starch. Amylose [9005-82-7] may be isolated by complete aqueous gelatinization and dispersion of starch and mixing the hot starch solution with an organic complexing agent such as 1-butanol (26) in water. On cooling, the amylose–butanol complex crystallizes and is removed by centrifugation. Recrystallization of the amylose–1-butanol complex and subsequent removal of the 1-butanol produces a pure amylose. Fractionation of amylose and amylopectin has been reported employing gel filtration chromatography and elution with aqueous sodium chloride (27). However, some starches contain only highly branched molecules. These are termed waxy starches because of the vitreous sheen of waxy corn grains when cut. Alternatively, some mutant seed varieties produce starches having up to 85% linear molecules (high amylose starch), although most starches have about 25% linear and 75% branched molecules. Starches high in amylose are subject to significant intermolecular association, leading to what is known as resistant starch (28–30). Resistant starch is that fraction not extracted from dietary fiber unless the sample is treated with dimethyl sulfoxide or alkali; the starch is resistant owing to retrogradation of the amylose. However, other types of resistant starch occur, such as the physically segregated starch in some beans, the ungelatinized B-type starch granules from potatoes or green bananas, and chemically modified starch (30). Resistant, retrograded, high amylose starches find some use as fat replacers in a variety of food types. Amylopectin is a highly branched polymer of $\alpha$-D-glucopyranosyl units containing $1\longrightarrow 4$ links with $1\longrightarrow 6$ branch points (Fig. 2). When starch is fully converted to the methyl ether and its fractions are hydrolyzed (31), 4.67% tetra-*O*-methyl-D-glucopyranose is obtained from the amylopectin and 0.32% from the amylose. These particular methyl ethers can only come

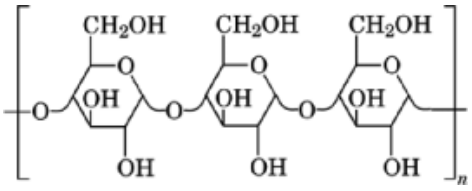

**Fig. 1.** Structure of amylose.

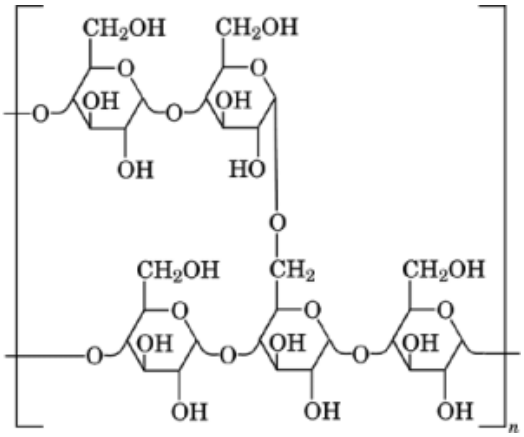

**Fig. 2.** Branch point structure in amylopectin.

from nonreducing end groups, and show that the average branch consists of ∼25 D-glucopyranosyl units in amylopectin and that amylose consists of ∼350 D-glucopyranosyl monomers per chain.

Knowledge of the fine structure of starch molecules has benefitted from the use of starch-degrading enzymes such as $\alpha$-amylase, isopullulanase, neopullulanase, $\beta$-amylase, glucoamylase, cyclomaltodextrin glucanotransferase, and phosphorylase. Debranching enzymes that catalyze hydrolysis of (1⟶6-$\alpha$-D-glucosidic linkages, such as isoamylase, pullulanase, ($R$)-enzyme (limit dextrinase), and amylo-1,6-glucosidase 4-$\alpha$-D-glucanotransferase, have also found much application in starch structural studies. Separation of amylose and amylopectin, and products from enzymatic hydrolysis, by size exclusion chromatography (sec) is critical for determination of molecular weight distribution. High performance anion-exchange chromatography has also been employed in the examination of homoglucan oligomers from starch hydrolysis. The specific analytical structural features of amylose, amylopectin, and the starch granule itself have been reviewed (32, 33).

When dispersed in solution, amylose behaves as a random coil or double helix. On cooling a dispersion, molecules associate via hydrogen bonding to form an insoluble precipitate. This mechanism of reassociation, called retrogradation, is significant in many food systems. In baked goods such as bread it is believed that most amylose is retrograded by the time the bread has cooled to room temperature and any subsequent changes in texture, typically referred to a staling, are as a result of reassociation of the longer outer chains of the wheat amylopectin (34). Because of its retrogradation, corn starch is not used in starch-thickened frozen cream pies or gravies because of its changed physical properties on cooling and freezing. Such retrograded products from regular corn starch have an unacceptable spongy texture and appearance. Amylopectin and its simple modifications do not as easily retrograde and are usable in food systems requiring freeze–thaw stability. Waxy varieties of corn, barley, and rice starch which contain no amylose are the thickeners of choice for starch-thickened frozen foods.

Starch not only varies in polymer structure but also in molecular weight distribution. Several techniques have been used to determine the molecular weight of starch molecules, including end-group analysis for amylose, osmotic pressure determination, and light-scattering methods. Low angle laser light scattering (aqueous size exclusion chromatography) is useful in the investigation of molecular weight distribution and the degree of branching in starch (35). Osmotic pressure measurements provide a weight range of 10,000–60,000 for amylose (36). The degree of polymerization (DP) of amylose usually falls in the range of 200–20,000 DP, although there are some exceptions (33). Using anaerobic techniques to prevent oxidative degradation, measurements suggest that amylose has a molecular weight range of $(1.6 - 7.0) \times 10^5$ (37). Amylose extracted from starch with dimethyl sulfoxide has a molecular weight of $1.9 \times 10^6$ daltons, measured by light-scattering techniques. Amylopectin, a much larger molecule, has a molecular weight range of $4 - 5 \times 10^8$ (38). Measurements based on light scattering indicate that large amylopectin molecules ($250 \times 10^6$ daltons) are present in Easter lily starch (39), and in potato starch have a molecular weight of $36 \times 10^6$ (40). Molecular weight distributions in starch and methods used to measure them have been reviewed (33).

Starch hydrolysis is accomplished in industry by using acid, enzymes, or both sequentially. Commercially, starch usually is hydrolyzed with thermoduric $\alpha$-amylase or glucoamylase at elevated temperatures to produce commercial D-glucose. Partial hydrolysis with acids produces molecular fragments called dextrins and low molecular weight sugar-like fragments (41). On acid hydrolysis, D-glucose is produced in amounts that increase throughout the reaction (42). Acid treatment of starch causes random cleavage of $\alpha - 1 \longrightarrow 4$ and $\alpha - 1 \longrightarrow 6$ linkages. Other products are oligosaccharides and acid breakdown products of D-glucose such as 5-hydroxymethylfurfural and levulinic acid. Oligosaccharides are produced by incomplete hydrolysis of starch and by reversion, that is, by acid-catalyzed recombination of two or more D-glucose monomers to produce numerous oligosaccharides.

$\alpha$-Amylase hydrolyzes starch mainly to a mixture of D-glucose and maltose, and limits dextrins derived from the amylopectin. $\alpha$-Amylase randomly cleaves $\alpha$-$(1 \longrightarrow 4)$ glucosidic bonds. The $\alpha(1 \longrightarrow 6)$ bonds of amylopectin are resistant to $\alpha$-amylase so when a branch point is encountered, hydrolysis ceases and the molecular remnant is an $\alpha$-amylase limit dextrin. $\alpha$-Amylase is a common enzyme present in human and animal digestive tracts and in plants and microorganisms. Plant and animal enzymes are involved in starch conversion *in vitro*, but the principal enzymes in commercial starch digestion are microbial in origin. Such enzymes are employed in distilling, brewing, baking, and textile and paper manufacture.

$\beta$-Amylase occurs in many plants, such as barley, wheat, rye, soy beans, and potatoes, where it is generally accompanied by some $\alpha$-amylase. $\beta$-Amylase initiates hydrolysis at the nonreducing end of an amylose or amylopectin chain, and removes maltose units successively until the reducing end of the molecule is encountered in amylose or a branch is met in amylopectin. $\beta$-Amylase is used commercially in the preparation of maltose syrups. After $\beta$-amylase hydrolysis of amylopectin there remains a $\beta$-amylase limit dextrin. $\beta$-Amylase has been used as a probe of the fine structure of amylopectin (43–46).

Cyclomaltodextrin glucanotransferase (CGTase) produces commercially important cyclomaltodextrins from starch by a cyclization reaction. $\alpha$-Cyclodextrins (six D-glucopyranosyl units in a ring) are produced by *Bacillus macerans*, *Klebsiella pneumoniae*, and *B. stearothermophilus*; $\beta$-cyclodextrins (seven-membered rings) by *B. megaterium*, *B. circulans*, *B. ohbensis*, and alkalophilic *Bacillus*; and $\gamma$-cyclodextrins (eight-membered rings) by *Bacillus* sp. AL6 and *B. subtilis* No. 313 (47). CGTase also catalyzes transfer of D-glucosyl residues, using starch as the donor, to the C-4 position of D-glucose, D-xylose, and various other deoxy and methylated glucoses to produce oligosaccharides.

Glucoamylase degrades both amylose and amylopectin, yielding D-glucose as the only product. Thus, the enzyme splits both $1 \longrightarrow 4{-}\alpha{-}\text{D}{-}$ and $1 \longrightarrow 6{-}\alpha{-}\text{D}{-}$-glucosidic bonds, although the $1 \longrightarrow 4$ bonds are hydrolyzed more rapidly. Glucoamylase removes single D-glucose units from the nonreducing end(s) of the molecule. Glucoamylases are produced by some species of fungi in the *Aspergillus* and *Rhizopus* genus, and also by specific yeasts and bacteria.

Depolymerization of starch in alkaline solution proceeds more slowly than in acid and produces isosaccharinic acid derivatives rather than D-glucose as a major product. The mechanism involves a $\beta$-elimination-type reaction (48).

Oxidation of starch hydroxyl groups by hypochlorite gives aldehydes, ketones, or carboxylic acids. Periodic acid treatment results in opening the sugar ring with formation of aldehyde groups at C2 and C3 positions. Starch is oxidized with other reagents including nitrogen dioxide, chlorine, permanganate, dichromate, and ozone to produce various aldehydes, ketones, and carboxylic acids and derivatives.

Etherification and esterification of hydroxyl groups produce derivatives, some of which are produced commercially. Derivatives may also be obtained by graft polymerization wherein free radicals, initiated on the starch backbone by ceric ion or irradiation, react with monomers such as vinyl or acrylyl derivatives. A number of such copolymers have been prepared and evaluated in extrusion processing (49). A starch–acrylonitrile graft copolymer has been patented (50) which rapidly absorbs many hundred times its weight in water and has potential applications in disposable diapers and medical supplies.

Starch derivatives are also used to encapsulate pesticides (qv) in a cross-linked starch–xanthate to improve safety in handling and reduce water leaching losses (51, 52). Little or no pesticide is lost during drying. The encapsulated formulations have excellent shelf life when dry, but when placed in water or soil the pesticide is readily released.

## 3. Manufacture

### 3.1. Wet-Milling of Corn Starch

Milling of corn, *Zea mays*, provides a quality starch, used in food and nonfood applications. Other grains are milled for starch, but corn is the principal source because of its steady price. Corn wet-milling processes are fully automated to provide well-separated grain components (53). At least eight new plants have been constructed in the United States since the 1970s. Corn may be dry-milled using screening and air classified for separation of particle size, but this process incompletely separates oil, protein, starch, and hull (54).

To understand the milling process, it is necessary to examine the structure of the corn kernel (Fig. 3) (55). Principal parts of the kernel are the tip cap (0.8%), pericarp or hull (5%), germ or embryo (11%), and the endosperm (82%). The tip cap and pericarp are separated in the fiber fraction in wet-milling, or in the bran fraction in dry-milling. The germ is comprised mainly of protein and lipids, whereas the endosperm consists of starch granules embedded in a proteinaceous cellular matrix. The principal U.S. corn crop, dent corn, has two distinct regions of endosperm, floury and horny. Floury endosperm at the grain center has loosely packed starch in less dense proteinaceous cells, whereas horny endosperm at the grain periphery contains densely packed starch granules in a region of high protein content. Starch granules in the more dense horny endosperm are polygonal as opposed to the more round granules in the floury endosperm. Most dent corn has a ratio of floury to horny endosperm of about 1:2. Horny endosperm requires thorough steeping to soften the protein matrix and ensure maximum starch recovery. The germ next to the endosperm is the scutellum, a repository for enzymes required for hydrolyzing the endosperm during embryonic development during germination to produce a new corn plant. Because the scutellar epithelium is strongly bound to the endosperm, long steeping times are required for separation. The average composition of corn grain on a dry basis is 71.3% starch, 9.91% protein, and 4.45% fat (56, 57). Normal water content is 10–15%.

A flow chart for a typical corn-milling operation is shown in Figure 4. Corn is first cleaned by screening to remove cob, sand, and other foreign material, followed by aspiration to remove lighter dust and chaff. The grain is then transferred with water containing $\sim$0.1% sulfur dioxide at pH 3–4 to large vats (steeps) which softens the kernels for milling. The steeping process requires careful control of countercurrent water flow at 48–52°C. Corn is introduced into the steeps at a moisture content of 15% and attains a final moisture content

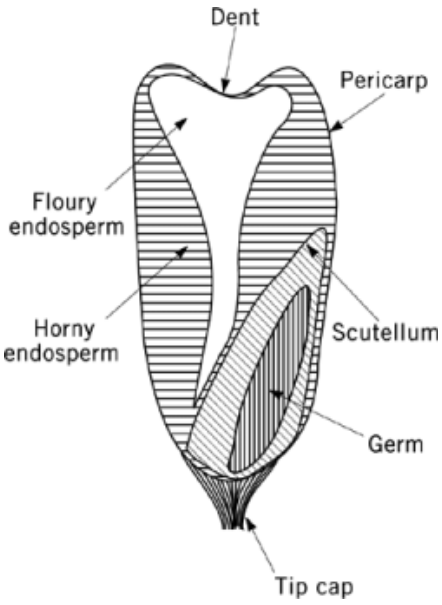


**Fig. 3.** Schematic cross-sectional view of a corn kernel.

of 45% at the end of 30–40 h. Water absorption is accelerated by sulfur dioxide (58) in the steep water and results in a 55–65% increase in kernel volume (59–61).

Sulfur dioxide was initially added to corn steep water to prevent the growth of degradative microorganisms, but it is now known to be indispensable in maximizing starch recovery. It acts on the nitrogen-containing components of corn which include 10% albumin and nonprotein nitrogen, 10% globulin, 38% zein, and 42% glutelin (62). Sulfur dioxide softens and then disperses the glutelin matrix (61), allowing maximum starch release and recovery, especially from the horny endosperm. Although sulfur dioxide inhibits the growth of microorganisms, after several hours its concentration decreases and lactic acid bacteria resembling *Lactobacillus bulgaricus* begins to grow. Because of toxicity problems with sulfur dioxide it has largely been replaced with sodium bisulfite.

Steeped corn is coarsely ground in an attrition mill to free the germ. The mill gap during this step must be adjusted to maximize the amount of germ freed but with a minimum of breakage of the germ, which would cause oil loss and present problems in later purification steps. Germ is removed from the aqueous slurry in a hydroclone (cyclone separator) (Fig. 5), where suspended components are separated by density (63, 64), the endosperm and fiber exiting in the hydroclone underflow and the germ from the center. The germ fraction is then screened, washed to remove residual starch, dewatered to 50–55% water content, and processed to produce corn oil.

The cyclone underflow is re-milled to complete the release of starch granules. Some starch factories use a Bauer mill, a combination attrition–impact mill (65); others favor the Entoleter mill, an impact mill only (66). After the second milling, the suspension contains starch, gluten, and fiber. Fiber is removed by flowing the slurry over fixed concave washing screens. It is retained on the screen while starch and gluten pass through. Collected fiber is slurried and rescreened to remove any residual starch and protein. This fiber is later combined with the grain's gluten to a content of 21% for animal feed use.

The resultant starch–gluten suspension, known as mill starch, is concentrated by centrifugation. The low density of gluten, compared to starch, permits easy separation. As a result, protein content is reduced to 1–2%. The starch suspension from the centrifugal separator is diluted and subjected to 8–14 stages of hydroclone

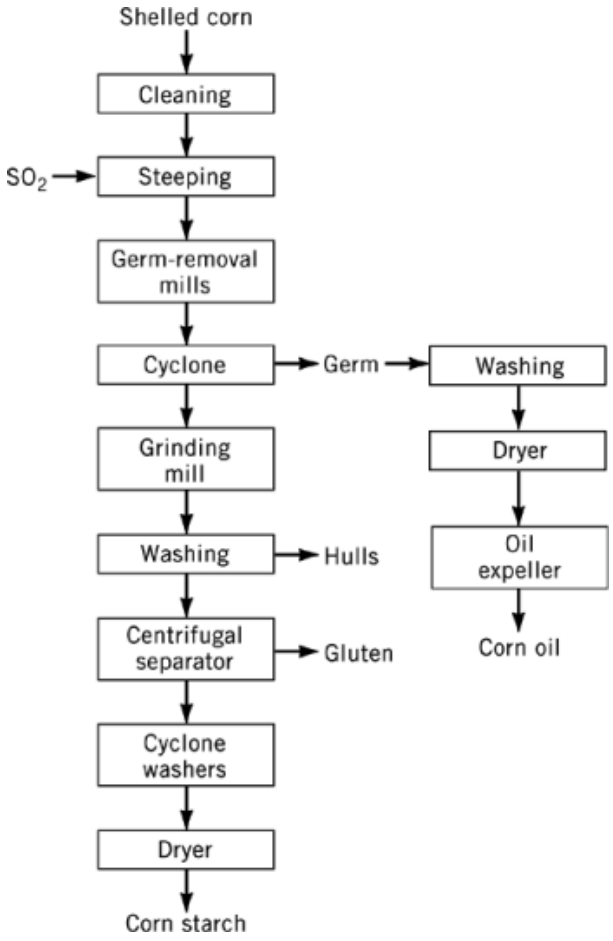


**Fig. 4.** Typical corn-milling operation.

washing (67, 68). Concentrated starch underflow from these processes is again diluted and passed through a final battery of hydroclones to wash the starch and remove most of the remaining protein.

This starch suspension may be dried and marketed as unmodified corn starch, modified by any of a number of chemical or physical means, gelatinized and dried, or hydrolyzed to produce corn syrup. During processing of corn, wet-milling uses about 0.2 $m^3$ $H_2O$/100 kg corn (20 gal/100 lb) with the water removed before marketing. Starch is usually dewatered by centrifugation, followed by injection into a column of hot air (200–260°C). Starch granules dry rapidly and are collected in cyclones (69, 70). Large amounts of energy used in drying starch makes the wet-milling industry the second most energy-intensive food industry in the United States (71). The main product of milling is unmodified corn starch, a white powder with a pale yellow tint. Unless the corn used is a white variety, absolute whiteness requires chemical bleaching. The final product usually has a moisture content of about 11% and may contain 1% protein, ash, lipids, and fiber (18, 72–76).

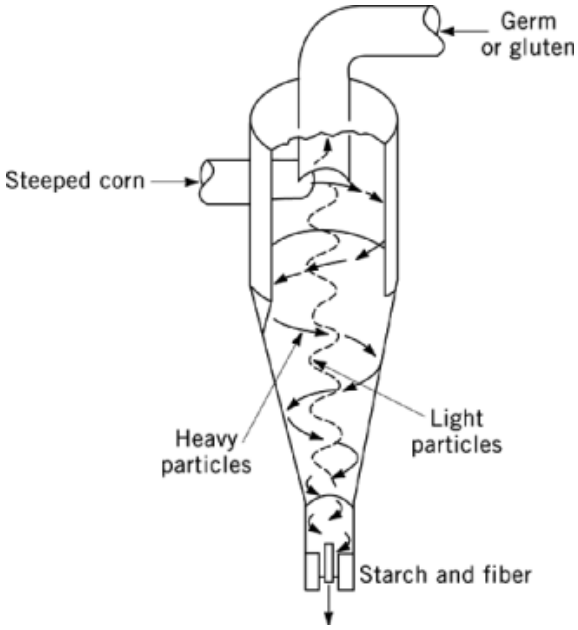


**Fig. 5.** A cyclone separator.

### 3.2. Chemical Modification

Production and use of acid-modified starch have been reviewed (77). Treating starch with acid under non-gelatinizing conditions was explored in the late nineteenth century (78) and many acid modifications were patented (79). Acidic treatment below the gelatinization temperatures initially attacks amorphous regions of the granule but leaves the crystalline regions relatively unaffected (5, 80, 81). In corn starch modification, amylopectin is more extensively depolymerized than amylose. Properties of acid-treated starches, as compared to the unmodified starches, include decreased hot paste viscosity (82–84), decreased intrinsic viscosity (85, 86), lower gel strength (84), and higher gelatinization temperature range (83, 87). However, mild acid treatment of starch produces what is known as thin-boiling starch which has excellent cooled gel strength. In fact, this product is used in starch gum candy (eg, orange slices) manufacture. Similar acid-modified starches are also employed in textiles, gypsum board, and paper and paperboard manufacture (88).

In industrial production of acid-modified starches, a 40% slurry of normal corn starch or waxy maize starch is acidified with hydrochloric or sulfuric acid at 25–55°C. Reaction time is controlled by measuring loss of viscosity and may vary from 6 to 24 hs. For product reproducibility, it is necessary to strictly control the type of starch, its concentration, the type of acid and its concentration, the temperature, and time of reaction. Viscosity is plotted versus time, and when the desired amount of thinning is attained the mixture is neutralized with soda ash or dilute sodium hydroxide. The acid-modified starch is then filtered and dried. If the starch is washed with a nonaqueous solvent (89), gelling time is reduced, but such drying is seldom used. Acid treatment may be used in conjunction with preparation of starch ethers (90), cationic starches, or cross-linked starches. Acid treatment of 34 different rice starches has been reported (91), as well as acidic hydrolysis of wheat and corn starches followed by hydroxypropylation for the purpose of preparing thin-boiling and nongelling adhesives (92).

Starch oxidation was investigated as early as 1829 by Liebig. The objective, as with other modifications, was to obtain a modified granular starch. The oxidant commonly employed is sodium hypochlorite, prepared

from chlorine and aqueous sodium hydroxide. This reaction is exothermic and external cooling must be provided during preparation of the oxidant.

$$2\,NaOH + Cl_2 \longrightarrow NaOCl + H_2O + NaCl$$

To produce oxidized starch, a slurry of starch granules is treated with alkaline hypochlorite for an appropriate period, neutralized, washed to remove the inorganic salts, and finally dried to a moisture content of 10–12%. Temperature, an important process variable, is usually in the range of 21–38°C. Structure of the unmodified starch influences the type and extent of oxidation reactions (93, 94). As with acid hydrolysis, most oxidation occurs primarily in the loosely organized, amorphous region of the starch granule (93–95). Chemical changes (93, 94) include formation of carboxyl and carbonyl groups and breaking of some D-glucosyl linkages. The changes result in a decrease in polymer molecular weight. Oxidized starches are bleached white by the hypochlorite. As they are anionic, they can strongly absorb cationic pigments such as methylene blue. Oxidation results in lower gelatinization temperatures, decreased hot-paste viscosity, and lower paste setback (96).

Corn and rice starches have been oxidized and subsequently cyanoethylated (97). As molecular size decreases due to degradation during oxidation, the degree of cyanoethylation increases. The derivatized starch shows pseudoplastic flow in water dispersion; at higher levels of cyanoethylation the flow is thixotropic. Corn and rice starches have been oxidized and subsequently carboxymethylated (98). Such derivatives are superior in the production of textile sizes. Potato starch has been oxidized with neutral aqueous bromine and fully chemically (99) and physically (100) characterized. Amylose is more sensitive to bromine oxidation than amylopectin and oxidation causes a decrease in both gelatinization temperature range and gelatinization enthalpy.

Sodium chlorite oxidation of corn and rice starches is recommended for the production of textile sizes (101) and oxidized starch is recommended as a hardening agent in the immobilization of microbial cells within gelatin (102).

Changes in starch due to heat treatment were investigated in the 1930s (103, 104). Later work on dextrinization showed that the products of dry heat treatment, the pyrodextrins, were soluble in cold water and did not retrograde (105). In dextrinization, starch is thermally degraded with production of low molecular weight dextrins, some of which recombine to form a more highly branched structure. Incipient pyrolysis eliminates water from a few D-glucopyranosyl groups, producing C–C double bonds and internal carbohydrate anhydrides such as anhydroglucose.

In manufacture of pyrodextrins, dry starch is sprayed with dilute inorganic acid, usually hydrochloric, nitric, or acid salts, and re-dried to 1–5% water content. To produce a white dextrin, well-mixed acidified starch is hydrolyzed and heated to a final temperature of 110–150°C; at 135–160°C, a canary yellow dextrin is produced. When made with small amounts of acid, and a longer heating time to a temperature of 150–180°C, the product is known as a British gum. The rate of temperature increase and residual moisture content achieved during heating are crucial to proper conversion. The product must be cooled rapidly to prevent over-conversion. Acid may be neutralized at this point if desired. Chemical changes produced by acid–heat treatment lead to starches with lower water holding ability, lower dispersion viscosity, and greater hot water solubility compared to the original starch. Such preparations and their applications as adhesives have been thoroughly reviewed (106).

### 3.3. Hydroxylalkyl Starch Ethers

Starch hydroxyethyl ethers with a degree of substitution (DS) of 0.05–0.10 are produced in various ways, but usually their preparation begins at the end of the wet-milling process, utilizing a high solids–starch suspension. The ether modification of ungelatinized starch is filterable and can be produced economically in a pure form.

During corn wet-milling, a 40–50% solids–starch suspension is treated with a metal hydroxide and ethylene oxide at approximately 50°C to produce DS of 0.1 and the product is purified by filtration and washing.

### 3.4. Cationic Starches

The two general categories of commercial cationic starches are tertiary and quaternary aminoalkyl ethers. Tertiary aminoalkyl ethers are prepared by treating an alkaline starch dispersion with a tertiary amine containing a $\beta$-halogenated alkyl, 3-chloro-2-hydroxypropyl radical, or a 2,3-epoxypropyl group. Under these reaction conditions, starch ethers are formed that contain tertiary amine free bases. Treatment with acid easily produces the cationic form. Amines used in this reaction include 2-dimethylaminoethyl chloride, 2-diethylaminoethyl chloride, and *N*-(2,3-epoxypropyl) diethylamine. Commercial preparation of low DS derivatives employ reaction times of 6–12 h at 40–45°C for complete reaction. The final product is filtered, washed, and dried.

Quaternary ammonium alkyl ethers are prepared similarly: an alkaline starch is reacted with a quaternary ammonium salt containing a 3-chloro-2-hydroxypropyl or 2,3-epoxypropyl radical. Alternatively, such derivatives can be prepared by simple quaternization of tertiary aminoalkyl ethers by reaction with methyl iodide. Sulfonium (107) and phosphonium (108) starch salts have also been prepared and investigated. Further work has explained the synthesis of diethylaminoethyl starch (109) as well as the production of cationic starches from the reaction of alkaline starch with 3-chloro-2-hydroxypropylamine, 1,1,1-*N*-tris(3-chloro-2-hydroxypropyl)amine, and glycidyl trimethylammonium acetate (110). A dry cationization process for producing these materials, as opposed to the well known slurry process, has also been described (111).

### 3.5. Starch Phosphates

Starch phosphate monoesters may be prepared by heating a dry mixture of starch and acid salts of ortho-, pyro-, or tripolyphosphoric acid at 50–60°C for one hour. DS is generally low ($<0.15$), but higher DS derivatives can be prepared by increasing temperature, phosphate salt concentration, and reaction time. Phosphorylation of corn starch with sodium tripolyphosphate (STP) can be done in a Brabender single-screw extruder (112). Highest degree of substitution was obtained at an extruder temperature of 200°C, STP concentration of 1.4 g/100 mL of water, and a pH of 8.5. Highly phosphorylated, cross-linked potato starch is produced by heating starch in benzene or pyridine with phosphorus pentoxide (113). The DS of this material is approximately 1.0.

Starch in aqueous suspension may react to form diesters with phosphorus oxychloride, phosphorus pentachloride, and thiophosphoryl chloride (114). Cross-bonded starches can also be manufactured by reaction with trimetaphosphates (115), but these require more vigorous conditions than phosphorus oxychloride. Typically, a starch slurry and 2% trimetaphosphate salt react at pH 10–11 and 50°C for 1 h.

Low DS starch acetates are manufactured by treatment of native starch with acetic acid or acetic anhydride, either alone or in pyridine or aqueous alkaline solution. Dimethyl sulfoxide may be used as a cosolvent with acetic anhydride to make low DS starch acetates; ketene or vinyl acetate have also been employed. Commercially, acetic anhydride–aqueous alkali is employed at pH 7–11 and room temperature to give a DS of 0.5. High DS starch acetates are prepared by the methods previously detailed for low DS acetates, but with longer reaction time.

Of particular importance for modifications of starch are the enzyme degradation products such as glucose syrups, cyclodextrins, maltodextrins, and high fructose corn syrups (HFCS). Production of such hydrolysis products requires use of selected starch-degrading enzymes such as $\alpha$-amylase, $\beta$-amylase, and debranching enzymes. Conversion of D-glucose to D-fructose is mediated by glucose isomerase, mostly in its immobilized form in columns. Enzymic degradation of starch to syrups has been well reviewed (116–118), and enzymic isomerization, especially by immobilized glucose isomerase, has been fully described (119) (see Syrups).

## 4. New Starches

A factory for the first production of banana starch is under development by a United States corporation in Costa Rica. This large-granule starch has many properties of potato starch but also has other interesting and unique properties that are said to give it extensive usage in the food industry. In addition, it is expected to be low in cost because it is made from cull bananas, those that are cut from bunches because they are too small for marketing or those that have been injured during harvest. The total amount of cull bananas averages 25% of the crop.

Another likely commercial starch is that from amaranth seed, an expanding crop for food use, particularly its flour. Amaranth starch granules (1–3 micrometers dia) have potential for numerous food applications, one of which is as a fat replacer because of their small size and especially after minor surface hydrolysis with $\alpha$-amylase or glucoamylase to produce a fluffy surface (see Fat replacers).

## 5. Economic Aspects

Commercial starch is mainly corn starch, but smaller amounts of sorghum, wheat, and potato starch are also produced. In 1992, 1303 million bushels ($45.8 \times 10^6$ $m^3$) of corn were ground for starch and other products (120); 1 $m^3$ corn weighs $\sim$721 kg and yields 438 kg starch, 26 kg oil, and 142 kg combined gluten and hulls. In the United States in 1994–1995, 462 million bushels were used to produce high fructose corn syrup, 231 million bushels went to produce D-glucose, 533 million bushels were used for alcohol production, and 247 million bushels were converted to starch (121).

In 1991 U.S. starch production was ca $5 \times 10^6$ t. Of this figure $1.5 \times 10^4$ t were exported to Canada, $1.0 \times 10^4$ t went to the European Community (EC), and $7.5 \times 10^3$ t were sold to Pacific Rim countries. Additionally, Canada purchased another $4.8 \times 10^4$ t of variously modified starches (122). Total starch consumption in the EC was about $5.0 \times 10^6$ t in 1989 of which 42% ($2.1 \times 10^6$ t) were used by the chemical industry. The continuing development of high fructose corn syrup (HFCS) further stimulated the growth of the corn-refining industry. In 1979 HFCS was consumed at 6.8 kg per capita, accounting for about 12% of the total corn-sweetener market (123). By 1994 the amount consumed per capita had grown to 25.4 kg (124) and accounted for 54% of the corn sweetener market. The growth rate of corn-derived sweeteners has been phenomenal and is expected to continue to grow in the future. Growth potential for the corn wet-milling industry continues to be excellent because of predicted increases in HFCS production and demand for corn-derived alcohol. Ethanol production has utilized more than 5% of total U.S. corn production from 1990 to 1995.

## 6. Uses

### 6.1. Nonfood Uses

Native corn starch is principally used in nonfood applications in mining, adhesives, and paper industries. Pregelatinized starch is chemically unmodified, but it is physically modified. Pregelatinized starches are used to decrease water losses in oil-well drilling muds, in cold water-dispersable wallpaper pastes, and in papermaking as an internal fiber adhesive.

Modified starches may be acid-modified, oxidized, or heat-treated. Acid-modified (thin-boiling) starches are used mainly in textiles as warp sizes and fabric finishes. Here they increase yarn strength and abrasion resistance and improve weaving efficiency. Thin-boiling starches also have selected applications in paper and laundry starch preparations.

Oxidized starches, usually those prepared by hypochlorite oxidation, are used in paper coatings and adhesives (qv) to improved surface characteristics for printing or writing. Oxidized starches may also be employed as textile warp sizes and finishes, in manufacture of insulation and wallboard, and in laundry spray starch.

Starch pyrodextrins and British gums have the ability, in aqueous dispersion, to form films capable of bonding like or unlike materials. Thus, they have uses as adhesives for envelopes, postage stamps, and other products. These dextrins are used in glass-fiber sizing to protect the extruded fiber from abrasion, and as binders for metal core castings, water color paints, briquettes, and many other composite materials (qv).

Various organic chemicals, eg, ethanol, isopropyl alcohol, *n*-butanol, acetone, 2,3-butylene glycol, glycerol, fumaric acid, citric acid, and lactic acid, are derived from starch by fermentation (125). Other compounds derived from starch include D-glucose, sorbitol, methyl $\alpha$-D-glucopyranoside, and glycerol or glycol D-glucopyranosides.

### 6.2. Food Uses

Unmodified starch is used in foods that require thickening or gelling. Such foods include puddings, salad dressings, pie fillings, and candies. Pregelatinized starch is used in products where thickening is required but cooking must be avoided, such as instant pudding, pie fillings, and cake frostings.

Acid-modified starches are used in the manufacture of gum candies because they form hot concentrated pastes that form strong gels on cooling. Thermalized starches are used in foods to bind and carry flavors and colors. Sweetening agents (corn syrup, HFCS) are made from starch by enzymatic or acid treatment as previously noted.

## 7. Derivatives

Starches, as organic polyhydroxy compounds, undergo many reactions characteristic of alcohols, such as esterification and etherification. Because D-glucopyranosyl monomers contain, on average, three free hydroxyl groups, the degree of substitution (DS) may be a maximum of three. Commercial starch derivatives are generally very lightly derivatized ($\mathrm{DS} < 0.1$). Such modification produces distinct changes in colloidal properties and generally produces polymers with properties useful under a variety of conditions.

Hydroxyethyl group introduction at low DS results in distinct modification of physical properties. Among these are decreased gelatinization temperature range (126), increased granule swelling rate (127), and decreased ability of starch pastes to gel and retrograde.

Low DS hydroxyethyl starches are used as paper coatings and sizes to improve sheet strength and stiffness. They are also employed as paper-coating color adhesives, and to increase fiber bonding in paper products. Hydroxyethylstarches are also used as textile warp sizes. Hydroxyethylstarch [9005-27-0] has been investigated by hydrodynamic and magnetic spectroscopic methods (128) because of its increasing use as a plasma volume expander.

Hydroxypropyl and other hydroxylalkyl starches find uses as additives in salad dressings, pie fillings, and in other food thickening applications. Examination of hydroxypropylstarch [9049-76-7] by light microscopy/staining techniques (129) shows that the central granular region has a large proportion of the hydroxypropyl groups, possibly because of its low density. Fourier transform infrared spectroscopy (ftir) can be used to quantitate the degree of starch hydroxypropylation (130).

Cationic starches show decreased gelatinization temperature range and increased hot paste viscosity. Pastes remain clear and fluid even at room temperatures and show no tendency to retrograde. This stability is due to Coulombic repulsion between positively charged starch molecules in dispersion.

Quaternary ammonium starches, like tertiary ammonium derivatives, show lower gelatinization temperature ranges, increased paste clarity and viscosity, and reduced retrogradation. Quaternary ammonium starch

salts exhibit cold water swelling at a DS as low as 0.07. Cationic starches are used in paper manufacture principally for fiber and pigment retention. They also improve bursting strength and fold endurance, and have been employed as emulsifiers for water-repellent paper sizes. Because of their relatively high cost, cationic starches are not widely used in textile sizes, although they have been employed in ore refining as flocculating agents (qv).

Compared to native starches, monophosphate esters have a decreased gelatinization temperature range and swell in cold water at a DS of 0.07. Starch phosphates have increased paste viscosity and clarity and decreased retrogradation. Their properties are in many ways similar to those of potato starch, which naturally contains phosphate groups.

Starch monophosphates are quite useful in foods because of their superior freeze–thaw stability. As thickeners in frozen gravy and frozen cream pie preparations, they are preferred to other starches. A pregelatinized starch phosphate has been developed (131) which is dispersible in cold water, for use in instant dessert powders and icings and nonfood uses such as core binders for metal molds, in papermaking to improve fold strength and surface characteristics, as a textile size, in aluminum refining, and as a detergent builder.

In contrast to monophosphates, starch phosphate diesters contain cross-links between two or more starch chains. This covalent linkage in the granule produces a starch product which swells less but is more resistant to heat, agitation, and acid than natural starch.

Starch phosphate diesters show a significant increase in stability of the swollen granule. Depending on the degree of derivatization, the hot paste viscosity may be more or less than that of the parent starch. In contrast to starch phosphate monoesters, diester pastes do not produce increased clarity when in aqueous dispersion. Starches with high DS have exceptional stability to high temperatures, low pH, and mechanical agitation. If cross-linking is sufficient, swelling and gelatinization can be completely inhibited, even in boiling water.

Cross-linked starches are used as thickeners and stabilizers in baby foods, salad dressings, fruit pie filling, and cream-style corn. They are superior to native starches in their ability to keep food particles in suspension after cooking, greater resistance to gelling and retrogradation, freeze–thaw stability, and lack of syneresis. They are also used to produce high wet-strength paper (114), as ion exchangers, and as metal sequesterants to prevent oxidative rancidity in food-grade oils.

Starch acetates may have low or high DS. The industrial importance of low DS acetates results from their ability to stabilize aqueous polymer sols. Low DS acetates inhibit association of amylose polymers and reduce the association of the longer outer chains of amylopectin. These properties are important in food applications. Highly derivatized starches (DS 2–3) are useful because of their solubility in organic solvents and ability to form films and fibers.

Low DS starch acetates have reduced gelatinization temperature ranges and reduced tendency to retrograde after pasting and cooling. Gelling may be completely inhibited if the DS is sufficiently high. Low DS starch acetate polymers also form films which are useful in textile and paper manufacture.

Lightly derivatized starch acetates are employed in food because of the clarity of their gels and their stability. Applications include frozen fruit pies and gravies, baked goods, instant puddings, and pie fillings. Starch acetates are used in textiles as warp sizes and in paper to improve printability, surface strength, and solvent resistance.

In general, high DS starch acetates and amylopectin acetates give weak and brittle films and fibers. Amylose triacetate can be spun into strong fibers and cast into strong, clear films, although these have not yet been commercialized. It is soluble in organic solvents including acetic acid, pyridine, and chloroform. Films of such a high DS acetate, cast from chloroform solution, are pliable, lustrous, transparent, and colorless. These properties are useful in packaging materials (qv).

## BIBLIOGRAPHY

"Starch" in *ECT* 1st ed., Vol. 12, pp. 764–778, by R. W. Kerr, Corn Products Refining Co.; in *ECT* 2nd ed., Vol. 18, pp. 672–691, S. M. Parmerter, Corn Products Co.; in *ECT* 3rd ed., Vol. 21, pp. 492–507, R. L. Whistler and J. R. Daniel, Purdue University.

### Cited Publications


1. G. M. A. Van Beynum and J. A. Roels, eds., *Starch Conversion Technology*, Marcel Dekker, Inc., New York, 1985.
2. A. Imberty, A. Buleon, V. Tran, and S. Perez, *Starch* **43**, 375 (1991).
3. R. W. Kerr, in R. W. Kerr, ed., *Chemistry and Industry of Starch*, Academic Press, Inc., New York, 1950, 3–25.
4. O. B. Wurzburg, in T. E. Furia, ed., *Handbook of Food Additives*, Vol. **1**, The Chemical Rubber Co., Boca Raton, Fla., 1973.
5. D. French, in Ref. 3, 157–178.
6. D. French, in R. L. Whistler, J. N. BeMiller, and E. F. Paschall, eds., *Starch: Chemistry and Technology*, 2nd ed., Academic Press, Inc., New York, 1984, 183–247.
7. A. Imberty and Z. Perez, *Biopolymers* **27**, 1205 (1988).
8. A. Imberty, H. Chanzy, S. Perez, A. Buleon, and V. Tran, *J. Mol. Biol.* **201**, 365 (1988).
9. M. J. Gidley and S. M. Bociek, *J. Am. Chem. Soc.* **107**, 7040 (1985).
10. N. N. Hellman, T. F. Boesch, and E. H. Melvin, *J. Am. Chem. Soc.* **74**, 348 (1952).
11. G. Baumann, D. Hartenthaler, and K. Breslauer, *Center for Advanced Food Technology—Physical Forces Research Accomplishments*, January Report, Rutgers University, New Brunswick, N.J., 1988.
12. J. W. Donovan, *J. Food Agric.* **28**, 571 (1979).
13. J. W. Donovan, *Biopolymers*, **18**, 263 (1979).
14. B. C. Burros, L. A. Young, and P. A. Carroad, *J. Food Sci.* **52**, 1372 (1987).
15. M. H. Gomez and J. M. Aguilera, *J. Food Sci.* **49**, 40 (1984).
16. P. Colonna, J. L. Doublier, J. D. Melcion, F. deMonredon, and C. Mercier, *Cereal Chem.* **61**, 538 (1984).
17. J. L. Kokini, L.-S. Lai, and L. L. Chedid, *Food Technol.* **46**(6), 124 (1992).
18. T. J. Schoch and E. C. Maywald, in R. L. Whistler and E. F. Paschall, eds., *Starch: Chemistry and Technology*, Vol. **II**, Academic Press, Inc., New York, 1967, 637–647.
19. M. W. Rutenberg and D. Solarek, in Ref. 6, 311–388.
20. L. Slade and H. Levine, in A. M. Peason, T. R. Dutson, and A. Bailey, eds., *Advances in Meat Research*, Vol. **4**, AVI Publishing Co., Inc., New York, 1987, p. 251.
21. L. Slade and H. Levine, in R. P. Millane, J. N. BeMiller, and R. Chandrasekaran, eds., *Frontiers in Carbohydrate Research—1: Food Applications*, Elsevier Applied Science, New York, 1989, p. 215.
22. L. Slade and H. Levine, in H. Faridi, ed., *The Science of Cookie and Cracker Production*, Chapman and Hall, New York, 1994, p. 23.
23. B. Casu and M. Reggiana, *Stärke* **18**, 218 (1966).
24. M. St. Jacques, P. R. Sundararajan, J. K. Taylor, and R. H. Marchassault, *J. Am. Chem. Soc.* **98**, 4386 (1976).
25. D. Grebel, *Mikrokosomos* **57**, 111 (1968).
26. T. J. Schoch, *Cereal Chem.* **18**, 121 (1941).
27. J. F. Kennedy, Z. S. Rivera, L. L. Lloyd, and F. P. Warner, *Starch* **44**, 53 (1992).
28. H. N. Englyst, H. S. Wiggins, and J. H. Cummings, *Analyst*, **107**, 307 (1982).
29. H. N. Englyst, S. M. Kingman, and J. H. Cummings, *Eur. J. Clin. Nutr.* **46**, S33 (1992).
30. N.-G. Asp, *Am. J. Clin. Nutr.* **61** (suppl), 930S (1995).
31. W. Z. Hassid and R. M. McCready, *J. Am. Chem. Soc.* **65**, 1157 (1943).
32. W. R. Morrison and J. Karkalas, in P. E. Dey, ed., *Starch, Methods in Plant Biochemistry, Vol. 2, Carbohydrates*, Academic Press, Inc., New York, 1990, p. 324.
33. S. Hizukuri, in A.-C. Eliasson, ed., *Carbohydrates in Food*, Marcel Dekker, Inc., New York, 1996, p. 347.
34. K. Kulp and J. G. Ponte, *Crit. Rev. Food Sci. Nutr.* **15**, 1 (1981).
35. L.-P. Yu and J. E. Rollings, *J. Appl. Polym. Sci.* **33**, 1909 (1987).

36. K. H. Meyer, in H. F. Mark and A. V. Tobolsky, eds., *Physical Chemistry of High Polymeric Systems*, 2nd ed., Interscience Publishers, Inc., New York, 1950, p. 456.
37. C. T. Greenwood, *Stärke* **12**, 169 (1960).
38. W. Banks and C. T. Greenwood, *Starch and Its Components*, Edinburgh University Press, Scotland, 1975, p. 45.
39. B. H. Zimm and C. D. Thurmond, *J. Am. Chem. Soc.* **74**, 1111 (1952).
40. L. P. Witnauer, F. R. Senti, and M. D. Stern, *J. Polym. Sci.* **16**, 1 (1955).
41. G. S. C. Kirchoff, *Acad. Imp. Sci., St. Petersbourg, Mem.* **4**, 27 (1811).
42. T. deSaussere, *Bull. Pharm.* **6**, 499 (1814).
43. G. N. Bathgate and D. J. Manners, *Biochem. J.* **101**, 3C (1966).
44. E. Y. C. Lee, C. Mercier, and W. J. Whelan, *Arch. Biochem. Biophys.* **125**, 1028 (1968).
45. C. Mercier, *Stärke* **25**, 78 (1973).
46. J. J. Marshall and W. J. Whelan, *Arch. Biochem. Biophys.* **161**, 234 (1974).
47. S. Kitahata, *Handbook of Amylase and Related Enzymes: Their Sources, Isolation, Methods, Properties, and Applications*, Pergamon Press, Oxford, U.K., 1988, p. 154.
48. J. N. BeMiller, in R. L. Whistler and E. F. Paschall, eds., *Starch: Chemistry and Technology*, Vol. **I**, Academic Press, Inc., New York, 1965, p. 521.
49. E. B. Bagley, G. F. Fanta, R. C. Burr, W. M. Doane, and C. R. Russell, *Polym. Eng. Sci.* **17**, 311 (1977).
50. U.S. Pat. 3,935,099 (Apr. 3, 1974); U.S. Pats. 3,981,100, 3,985,616, and 3,997,484 (Sept. 8, 1975), M. O. Weaver, E. B. Bagley, G. F. Fanta, and W. M. Doane (to United States of America as represented by Secretary of Agriculture).
51. B. S. Shasha, W. M. Doane, and C. R. Russell, *J. Polym. Sci. Polym. Lett. Ed.* **14**, 417 (1976).
52. W. M. Doane, B. S. Shasha, and C. R. Russell, *Am. Chem. Soc. Symp. Ser.* **53**, 74 (1977).
53. S. A. Watson, in Ref. 18, 1–51.
54. O. L. Brekke, in G. E. Inglett, ed., *Corn: Culture, Processing, Products*, AVI Publishing Co., Westport, Conn., 1970, 262–291.
55. M. J. Wolf, C. L. Buzan, M. M. MacMasters, and C. E. Rist, *Cereal Chem.* **29**, 321 (1952).
56. G. Bianchi, P. Avato, and G. Mariani, *Cereal Chem.* **56**, 491 (1979).
57. G. C. Shove, in Ref. 52, 60–72.
58. L. T. Tan, H. C. Chen, J. A. Shellenberger, and D. S. Chung, *Cereal Chem.* **42**, 385 (1965).
59. L. T. Tan, P. S. Chu, and J. A. Shellenberger, *Biotechnol. Bioeng.* **4**, 311 (1962).
60. R. A. Anderson, *Cereal Chem.* **39**, 406 (1962).
61. M. J. Cox, M. M. MacMasters, and G. E. Hilbert, *Cereal Chem.* **21**, 447 (1964).
62. J. S. Wall, in Y. Pomeranz, ed., *Advances in Cereal Science and Technology*, Vol. **II**, American Association of Cereal Chemists, St. Paul, Minn., 1978, 135–219.
63. Brit. Pat. 701,613 (1953) (to Stamicarbon BV, Heerland, the Netherlands).
64. U.S. Pat. 2,913,122 (Nov. 17, 1959), F. P. L. Stavenger and D. E. Wuth (to Dorr-Oliver, Inc.).
65. U.S. Pat. 3,040,996 (June 26, 1962), M. E. Ginaven (to The Bauer Brothers Co.).
66. U.S. Pat. 3,029,169 (Apr. 10, 1962), D. W. Dowie and D. Martin (to Corn Products Co.).
67. U.S. Pat. 2,689,810 (Sept. 21, 1954), H. J. Vegter (to Stamicarbon NV).
68. U.S. Pat. 2,778,752 (Jan. 22, 1957), H. J. Vegter (to Stamicarbon NV).
69. F. Baunack, *Stärke* **15**, 299 (1963).
70. U.S. Pat. 4,021,927 (May 10, 1977), L. R. Idaszak (to CPC International, Inc.).
71. *Industrial Energy Study of Selected Food Industries for the Federal Energy Office*, Final Report, U.S. Dept. of Commerce, Washington, D.C., 1974.
72. R. L. Sims, *Sugar Azucar*, 50 (Mar. 1978).
73. *Corn Starch*, 3rd ed., Corn Industries Research Foundation, Washington, D.C., 1964.
74. W. R. Morrison, in Ref. 59, p. 221.
75. T. J. Schoch and E. C. Maywald, *Anal. Chem.* **28**, 382 (1956).
76. W. Bergthaller and G. Tegge, *Stärke* **24**, 348 (1972).
77. P. Shildneck and C. E. Smith, in Ref. 18, p. 217.
78. C. J. Litner, *J. Prakt. Chem.* **34**, 378 (1886).
79. U.S. Pat. 675,822 (Jan. 12, 1899), C. B. Duryea; U.S. Pat. 696,949 (May 24, 1901), C. B. Duryea.
80. K. H. Meyer and P. Bernfeld, *Helv. Chim. Acta* **23**, 890 (1940).

81. W. C. Mussulman and J. A. Wagoner, *Cereal Chem.* **45**, 162 (1968).
82. G. V. Casar and E. E. Moore, *Ind. Eng. Chem.* **27**, (1935).
83. W. Gallay and A. C. Bell, *Can. J. Res. Sect. B* **14**, 381 (1936).
84. W. G. Bechtel, *J. Colloid Sci.* **5**, 260 (1950).
85. R. W. Kerr, in Ref. 3, p. 682.
86. S. Lansky, M. Kooi, and T. J. Schoch, *J. Am. Chem. Soc.* **71**, 4066 (1949).
87. H. W. Leach and T. J. Schoch, *Cereal Chem.* **39**, 318 (1962).
88. R. G. Rohner and R. E. Klem, in Ref. 6, 529–541.
89. U.S. Pat. 3,446,628 (May 27, 1969), T. J. Schoch, D. F. Stella, and H. J. Wolfmeyer (to Corn Products Co.).
90. E. T. Hjermstad, in Ref. 18, p. 425.
91. B. O. Juliano and C. M. Perez, *Starch* **42**, 49 (1990).
92. K. M. Chung and P. A. Seib, *Starch* **43**, 441 (1991).
93. J. Schmorak, D. Mejzler, and M. Lewin, *Stärke* **14**, 278 (1962).
94. J. Schmorak and M. Lewi, *J. Polymer Sci.* **A1**, 2601 (1963).
95. F. F. Farley and R. M. Hixon, *Ind. Eng. Chem.* **34**, 677 (1942).
96. T. J. Schoch, *Tappi* **35**, 4 (1952).
97. I. A. El-Thalouth, A. Ragheb, R. Refai, and A. Hebeish, *Starch* **42**, 18 (1990).
98. A. Hebeish, M. I. Khalil, and A. Hashem, *Starch* **42**, 185 (1990).
99. L. J. Torneport, B. A.-C. Salomonsson, and O. Theander, *Starch* **42**, 413 (1990).
100. P. Muhrbeck, A.-C. Eliasson, and A.-C. Salomonsson, *Starch* **42**, 418 (1990).
101. A. Hebeish, F. El-Sisy, S. A. Abdel-Hafiz, A. A. Abdel-Rahman, and M. H. El-Rafie, *Starch* **44**, 388 (1992).
102. E. De Alteriis, P. Parascandola, and V. Scardi, *Starch* **42**, 57 (1990).
103. J. R. Katz, *Rec. Trav. Chim.* **53**, 555 (1934).
104. J. R. Katz and A. Weidinger, *Z. Phys. Chem. Abt. A* **184**, 100 (1939).
105. B. Brimhall, *Ind. Eng. Chem.* **36**, 72 (1944).
106. H. M. Kennedy and A. C. Fisher, Jr., in Ref. 6, p. 593.
107. U.S. Pat. 2,989,520 (Apr. 22, 1959), M. W. Rutenberg and J. L. Volpe (to National Starch and Chemical Corp.).
108. U.S. Pat. 3,077,469 (June 28, 1961), A. Aszalos (to National Starch and Chemical Corp.).
109. E. A. El-Alfy, S. H. Samaha, and F. M. Tera, *Starch* **43**, 235 (1991).
110. M. I. Khalil, S. Farag, and A. Hashem, *Starch* **45**, 226 (1993).
111. G. Hellwig, D. Bischoff, and A. Rubo, *Starch* **44**, 69 (1992).
112. E. Salay and C. F. Ciacco, *Starch* **42**, 15 (1990).
113. K. Marusza and P. Tomasik, *Starch* **43**, 66 (1991).
114. U.S. Pat. 2,328,537 (Aug. 9, 1940), G. F. Felton and H. H. Schopmeyer (to American Maize Products Co.).
115. U.S. Pat. 2,938,901 (Nov. 23, 1956), (to Corn Products Co.).
116. N. E. Lloyd and W. J. Nelson, in Ref. 6, p. 611.
117. P. D. Fullbrook, in P. D. Fullbrook, *Glucose Syrups: Science and Technology*, Elsevier Applied Science Publishers, London, 1984, p. 65.
118. P. J. Reilly, in G. M. A. Van Beynum and J. A. Roels, eds., *Starch Conversion Technology*, Marcel Dekker, Inc., New York, 1985, p. 101.
119. R. van Tilburg, in Ref. 118, p. 175.
120. *Census of Manufactures*, U.S. Dept. of Commerce, Bureau of the Census, Washington, D.C., 1992.
121. *Feed Situation and Outlook Yearbook*, FDS-1995, U.S. Dept. of Agriculture, Washington, D.C., Nov. 1995.
122. J. R. Daniel, R. L. Whistler, A. C. J. Voragen, and W. Pilnik, in B. Elvers, S. Hawkins, and W. Russey, eds., *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Vol. **A25**, VCH, Weinheim, Germany, 1994, p. 21.
123. *Sugar and Sweetener Report*, SSR Vol. **4**, No. 12, U.S. Dept. of Agriculture, Washington, D.C., 1979.
124. *Sugar and Sweetener Situation and Outlook Yearbook*, SSSV20N4, U.S. Dept. of Agriculture, Economic Research Service, Washington, D.C., Dec. 1995.
125. G. E. Tong, *Chem. Eng. Prog.* **74**, 70 (1978).
126. T. J. Schoch and E. C. Maywald, *Anal. Chem.* **28**, 385 (1956).
127. A. Harsveldt, *Tappi* **45**, 85 (1962).
128. W.-M. Kulicke, D. Roessner, and W. Kull, *Starch* **45**, 445 (1993).

129. H. R. Kim, A.-M. Hermansson, and C. E. Eriksson, *Starch* **44**, 111 (1992).
130. B. Forrest, *Starch* **44**, 179 (1992).
131. U.S. Pat. 2,884,346 (Dec. 24, 1957), J. A. Korth (to Corn Products Co.).

#### General References

132. Refs. 3, 18, 48, and 122 are also general references.
133. W. Banks and C. T. Greenwood, *Starch and Its Components*, Edinburgh University Press, Edinburgh, Scotland, 1975.
134. C. T. Greenwood, *Adv. Carbohydr. Chem.* **22**, 483 (1967).
135. C. T. Greenwood and E. A. Milne, *Adv. Carbohydr. Chem.* **23**, 282 (1968).
136. R. V. MacAllister, *Adv. Carbohydr. Chem.* **36**, 15 (1979).
137. D. J. Manners, *Adv. Carbohydr. Chem.* **17**, 371 (1962).
138. J. J. Marshall, *Adv. Carbohydr. Chem.* **30**, 257 (1974).
139. J. A. Radley, ed., *Examination and Analysis of Starch and Starch Products*, Applied Science Publishers, Ltd., London, 1976.
140. J. A. Radley, ed., *Industrial Uses of Starch and Its Derivatives*, Applied Science Publishers, Ltd., London, 1976.
141. J. A. Radley, ed., *Starch Production Technology*, Applied Science Publishers, Ltd., London, 1976.
142. G. M. A. Von Beynum and J. A. Roels, eds., *Starch Conversion Technology*, Marcel Dekker, Inc., New York, 1985.
143. R. L. Whistler, J. N. BeMiller, and E. F. Paschall, eds., *Starch: Chemistry and Technology*, 2nd ed., Academic Press, Inc., New York, 1984.
144. R. L. Whistler, ed., *Methods in Carbohydrate Chemistry*, Vol. **4**, Academic Press, Inc., New York, 1964.
145. O. B. Wurzburg, ed., *Modified Starches: Properties & Uses*, CRC Press, Boca Raton, Fla., 1986.

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