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CORN WET MILLING: SEPARATION CHEMISTRY AND TECHNOLOGY

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I. INTRODUCTION

A. BASIC PROCESS AND PRODUCTS

The typical corn kernel (*Zea mays* L) contains approximately 70 to 73% starch, 9 to 10% protein, 4 to 5% fat, 1 to 2% ash, 2% sugars, and 9 to 10%

crude fiber. The purpose of corn wet milling is to separate the kernel into its constituent chemical components. Wet milling processing begins with steeping whole kernel corn in an aqueous solution of sulfur dioxide and lactic acid (produced by microorganisms) at 50°C for 24 to 48 hours. The corn is then coarsely ground and the lipid-containing germ and fibrous hull portions are separated. After the remaining components are more finely ground, the starch and protein are separated using hydrocyclones, essentially continuous centrifuges; corn starch is slightly more dense than corn protein. Germ is further processed into oil and the protein and fiber components are usually blended and used as animal feeds. The wet starch is either dried, chemically modified to change its functional properties, converted into intermediate-sized glucose polymers, or fully depolymerized into sugars. Starch is also often used as a raw ingredient for adjacent processing facilities that produce ethanol or other alcohols and other industrial chemicals. The wet milling process is depicted in Fig. 1.

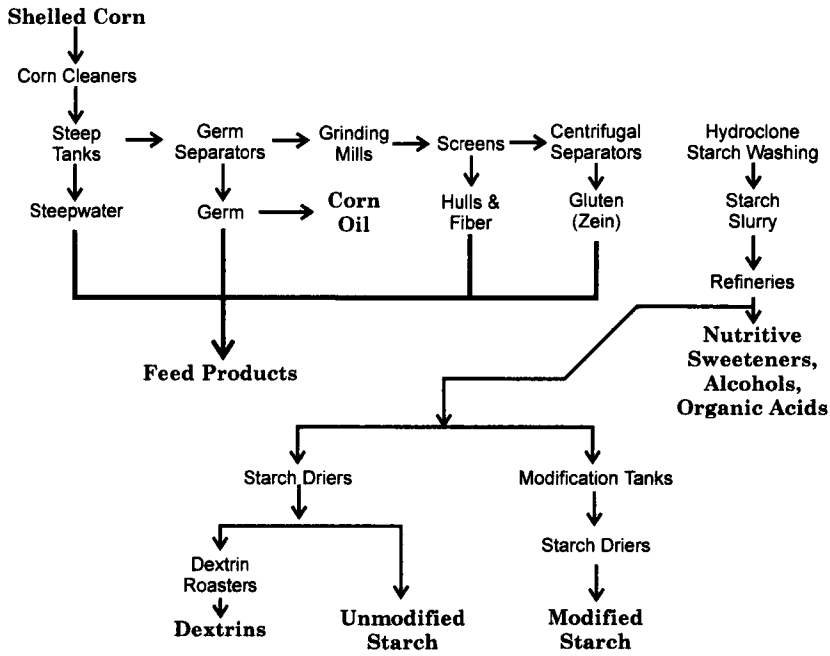


FIG. 1. Wet milling process flow. Based on Anonymous (1994). Used with permission. Artwork modified by David S. Jackson.

B. INDUSTRY SCALE

Approximately 7000 to 9000 million bushels of corn are produced yearly in the United States; 20% is used for domestic food and industrial purposes (including wet milling) and 60% for feed. The remainder is exported or stored. Wet milling is a capital- and energy-intensive process: A typical small plant costs approximately $100 million to build and bring on-line and processes more than 50,000 bushels of corn daily. The wet milling industry purchases approximately $5 billion (1992 US$) of corn, goods, and services each year (Anonymous, 1993).

II. CORN: STRUCTURE AND TYPES USED

Zea mays L . (corn) has been the major source of refined starch in the United States and most Western countries since the mid-1800s (Watson, 1984). Corn is a relatively cheap commodity ($2.00 to $2.50 per Winchester bushel) and found in good supply. High-ash-content wheat flour is the second largest starch source, but its production is small in comparison to corn. Sorghum was once wet milled for starch, but because corn has a higher milling efficiency, sorghum is no longer being wet milled in the United States. A thorough knowledge of the basic structure of the corn kernel is essential to understanding and ultimately improving the wet milling process.

Corn, which is better known as maize outside the United States, is a member of the grass family Gramineae. Domesticated cultivars are subspecies of *Z. mays.* Corn is a member of the cereal grains, which produce dry, one-seeded fruits. Several varieties of corn have been bred for specific uses. Types are currently classified as dent, popcorn, flint, floury, and sweet corn (Watson, 1987). Other mutant varieties include opaque, amylomaize, waxy, and dull waxy. Yellow dent, initially bred for animal feed, is most common and milled in highest quantities by the wet milling industry. Yellow dent is of low cost, is widely available, has a high starch content, and contains large amounts of yellow pigments. Yellow pigments, which concentrate into the gluten fraction during milling, are valued by the poultry industry (Watson, 1984). Waxy, dull waxy, high amylose, and other mutant types are milled for the specialty starches that they contain. White corn is commonly used for specialty food uses, such as alkaline processing. Flint-type corns are most commonly grown in Europe and Turkey.

Corn has an atypical structure compared with other fruits of the Gramineae family. The corn kernel (Fig. 2) is a caryopsis that is usually shelled

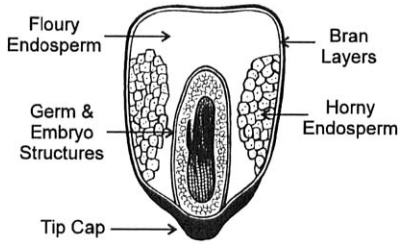


FIG. 2. A corn kernel section. Based on Anonymous (1994). Used with permission. Artwork modified by Kristi A. Snell.

from the female inflorescence known as the ear (cob). The major structural components of the caryopsis are the germ, endosperm, pericarp, and tip cap. The composition of each corn type varies. Bebic (1982) compared yellow dent, flint, waxy, and opaque-2 varieties. In comparison to the other corn types, opaque-2 hybrids contained higher levels of albumen (water soluble) and globulin (NaCl soluble) proteins at the expense of prolamin (ethanol soluble) protein content. The waxy mutant had the largest percentage of pericarp, whereas the dent hybrids contained the most starch. Opaque-2 mutant, bred for higher lysine and tryptophan content, was less dense and had the least amount of pericarp. Breeding programs have used modifier genes to increase opaque-2 corn's endosperm density by increasing g-zein protein composition two to five times (now termed *quality protein maize*) (Wallace *et al.*, 1990). Commercially viable high-oil corn, used largely for animal feed, has also become available.

The seed fruit is protectively covered by several layers of dead, cellulosic tube cells termed the pericarp (Wolf *et al.*, 1952). The pericarp is the true fruit coat. It is collectively composed of all layers exterior of the seed coat. The outermost layer of the pericarp, the epidermis, is covered by a waxy cutin layer that retards moisture absorption into the caryopsis. The mesocarp cross cell layer contains pits and open areas and provides capillary interconnections between all cells and facilitates water absorption (Watson, 1987). The pericarp extends to the base of the kernel and connects to the tip cap. Inside the tip cap are spongy, star-shaped cells that form an open structure that is continuous with the cross-cell layers of the pericarp (Wolf *et al.*, 1952). This structure is responsible for liquid uptake from the tip cap to pericarp's open cellular layers in intact kernels (Cox *et al.*, 1944). The pericarp and tip cap account for approximately 5 and 0.8% of the dry kernel weight, respectively.

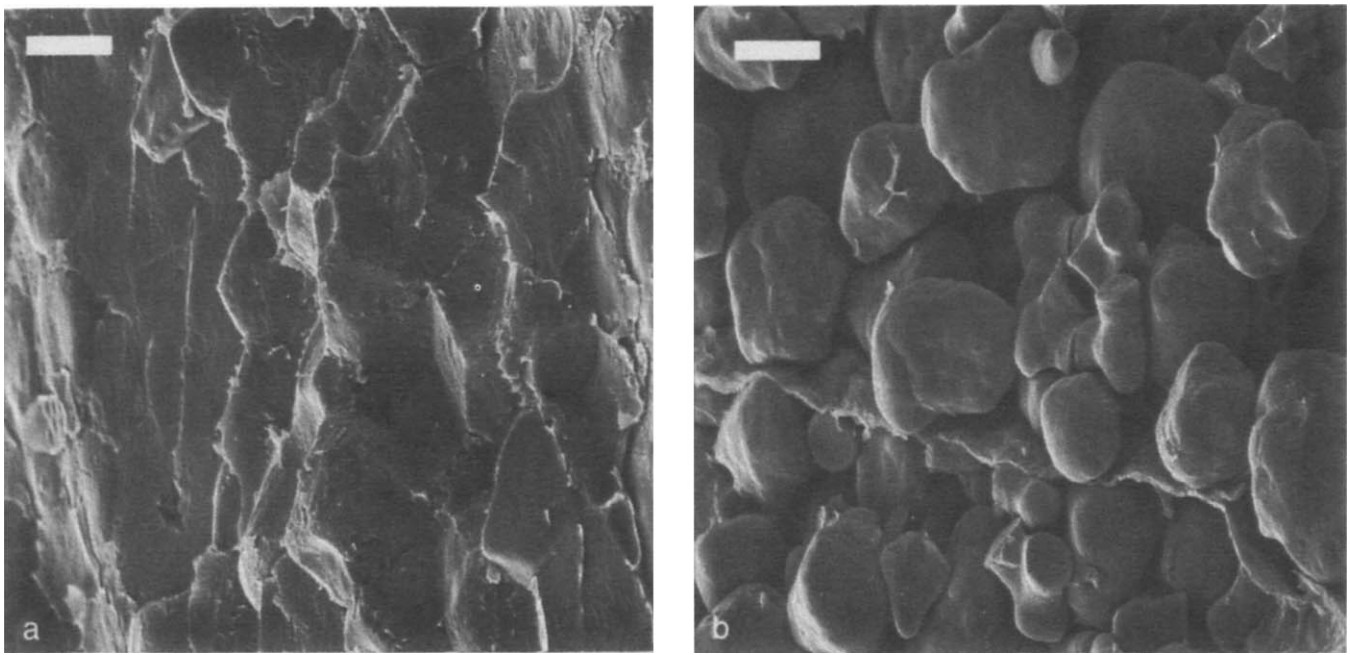
The outermost layer of the endosperm is enveloped by thick, tough structural cells. A thin, hyaline, and almost invisible membrane, termed

the seed coat, girdles the outermost structure of the true seed (Wolf *et al.*, 1952). It adheres tightly to the outer surface of the aleurone layer and is thought to impart semipermeable properties to the endosperm. The outer layer of the endosperm is a single layer of cells called the aleurone. These cells, granular in appearance, contain protein but little or no starch. The aleurone accounts for approximately 3% of the kernel weight (Watson, 1984). This section of the kernel is collected in the fiber fraction during wet milling.

The endosperm constitutes approximately 82 to 84% of the dry weight of the kernel and contains 86 to 89% of the starch (Watson, 1984). Starch granules of normal dent corn contain approximately 75% amylopectin and 25% amylose. Amylose-to-amylopectin ratios, and hence starches' functional properties, have been genetically manipulated to form many unique hybirds (such as dull waxy mutants). The endosperm tissue also contains 74% of the kernel's protein and 16% of the kernel's lipid. Most of the endosperm's lipid is bound to cell contents and only 18% is found as triacylglycerides (Watson, 1987).

The endosperm is composed of elongate cells packed with starch granules of 5 to 30 μm embedded in a continuous protein matrix (Watson, 1987). These cells are large with thin walls of cellulosic material (Wolf *et al.*, 1952). The intergranular starch–protein matrix is deposited and contained within the large cellular structures. The binding and structural integrity between the protein and starch make corn kernels quite hard. Kernel fracturing occurs through the starch granules, resulting in a large number of visible broken granules, instead of severing the strongly bound protein matrix (Hoseney, 1986). Duvick (1961) observed by light microscopy that "a transparent glue (clear viscous cytoplasm)" surrounded the starch granules and protein bodies within cells of mature endosperm. The encompassing protein matrix is composed of an amorphous protein material (Christianson *et al.*, 1969). The fact that water alone will not allow a good separation of protein and starch during wet milling suggests that the protein composition is quite different in corn than it is in wheat (Hoseney, 1986). The bonds holding the matrix proteins together can be loosened by treatments with alkali, reducing agents such as mercaptoethanol (ME), or sulfites used in the wet milling process (Wall and Paulis, 1978).

Protein bodies contained within the matrix were first described by Duvick (1961), who concluded that they were the sites of zein deposition. Zein is an alcohol extractable protein, a prolamin. It is a major component of protein bodies within the kernel. In its native state, it displays high-molecular-mass aggregates (Watson, 1987). Although zein's amino acid composition has a low sulfhydryl content, zein bodies can be peptidized by ME, dithiothreitol, or other reducing agents (Watson, 1987). The appar-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ent sizes, as shown by sodium dodecyl sulfate–polyacrylamide electrophoresis (SDS–PAGE), suggest that the aggregates are dimers, trimers, and sometimes even larger sets. Because of the amino acid composition of zein, isoelectric points cannot be reliably assigned (Watson, 1987).

Unlike other cereals, the corn kernel endosperm can contain both translucent (vitreous, hard, horny) and opaque (floury) areas within each kernel (Figs. 2, 3). Dent hybrids are usually the result of crossing very vitreous, flint varieties with soft, floury varieties and have an average ratio of about 1 : 2 floury : horny regions (Wolf *et al.,* 1952). The ratio varies greatly among corn types and can be correlated to protein content and composition (Wolf *et al.,* 1952; Paiva *et al.,* 1991). Furthermore, individual kernels from the same field, or even ear, differ significantly in the vitreous-to-floury ratio (Paulsen *et al.,* 1983; Watson, 1987). The translucent or horny section of the endosperm is tightly compacted and contains polygon-shaped starch granules. The dense horny endosperm results in good dry milling characteristics, but requires long steeping periods for efficient protein–starch separation during wet milling (Watson, 1984). The floury or opaque region develops during drying as the endosperm shrinks. The shrinking tears and separates cells, forming voids or air pockets. This region is characterized by larger cells, large round starch granules, and a relatively thin protein matrix (Wolf *et al.,* 1952). The porous texture of the floury region allows for easy recovery of starch (Watson, 1984).

The germ is the embryo or reproducing section of the kernel and is alive and respirating in a typical, healthy kernel. The germ is composed of a plumule, a radicle, and a scutellum. The scutellum functions as a nutritive organ for the plumule and makes up 10 to 12% of the kernel dry weight. The major part of the scutellum is composed of thick-walled isodiametric cells densely packed with cytoplasm. Oil is contained within these cells as droplets (Jacks *et al.,* 1967). The scutellum's cells contain 84% of the kernel's lipids; nearly all are free triacylglycerides (Tan and Morrison, 1979). The scutellum's surface, adjacent to the endosperm, is covered by the secretory epithelium; it contains amylase enzymes that diffuse into the endosperm and digest starch during germination (Dure, 1963). The scutellar epithelium adheres to the endosperm by an insoluble substance composed of pentoglycans and proteins (Seckinger *et al.,* 1960). This bond, which resists chemical or physical means of separating the germ and endosperm, is responsible

FIG. 3. Scanning electron micrographs of corn kernel endosperm scraped from a typical corn hybrid. (a) Hard (horny, vitreous) endosperm "enrobing" starch granules. (b) Soft (floury) endosperm with individual starch granules clearly visible among some protein material. Bar = 10 μm.

for the prolonged steeping period requirements necessary for its efficient separation (Watson, 1984). The germ contains 22% of the kernel protein, 82% of the ash, and 65% of the sugar (Watson, 1984).

Watson (1987) described the important structural components of the kernel as pectic substances, hemicelluloses, and cellulose. Sandstead *et al.* (1978) found that corn bran was composed of 70% hemicellulose, 23% cellulose, and 0.1% lignin on a dry weight basis. No detailed structural analysis of maize kernel cell wall polysaccharides has been reported, but a general description can be based on our present understanding of cell walls (Watson, 1987). Endosperm cell walls have only thick primary cell walls, whereas the cells of the pericarp and tip cap also have secondary cell walls. Cellulose, a linear homopolymer of 10,000 D-glucose units linked $\beta(1,4)$, is the basic structural unit of higher plant cell walls (Aspinall, 1982). Several matrix polysaccharides are associated with cellulose in both primary and secondary cell walls. Arabinoxylans, polymers with backbones of $\beta(1,4)$-linked D-xylose with (1,3)-linked L-arabinose branches, account for 90 to 95% of corn seed hemicellulose (Oomiya and Imazato, 1982). They are the major component of the primary cell walls of monocotyledonous and endosperm cells. Primary cell walls of monocotyledonous cells also contain arabinogalactans, xyloglucans, some pectic polysaccharides, and one or more arabinans.

The structural integrity of the kernel (caryopsis) has dictated the starch recovery (milling) process used. An understanding of kernel structure is of utmost importance for selecting methods of degrading the kernel structure and releasing free starch granules on milling.

III. STEEPING: PROCESS AND EQUIPMENT

A. CLEANING

Received shelled corn is first cleaned to remove broken kernels, chaff, pieces of cob, and other undesirable foreign matter. The presence of foreign matter may contaminate milled fractions or interfere with the free flow of steepwater within and between the steeps. Steeping of broken kernels releases starch in the steepwater, which gelatinizes and causes an undesirable viscosity during evaporation of the steepwater into steep liquor (May, 1987).

B. STEEPING

Steeping is the first critical processing step of wet milling. It is the aqueous soaking of whole corn kernels under controlled conditions of temperature,

time, sulfur dioxide concentration, and lactic acid concentration (Watson, 1984). Too much emphasis cannot be placed on the importance of steeping for ensuring a smooth milling operation and a maximum yield of prime-quality starch (Cox *et al.*, 1944). The chief purposes of the steeping process are to (1) to soften the corn kernel for milling, (2) to reduce or inhibit the activity of undesirable microorganisms, and (3) to assist in pure starch recovery (Bartling, 1940). Proper steeping at 48 to 50°C for 35 to 50 hours allows a milling recovery of 90% of the kernel's starch with a residual protein content of 0.40% or less (Watson, 1984). Altering or "rushing" the steeping process results in inferior yields and impure fractions.

Typical industrial steeping methods have changed little over the past 100 years. Commercial steeping systems are a battery of 6 to 20 (usually 10–12) conical-bottomed tanks of 50- to 330-metric tons (t) (2000–13,000 bu) capacity connected in series by a system of piping and pumps (Blanchard, 1992). Older systems moved steepwater from steep to steep in batches. In newer systems, steepwater is continuously circulated countercurrent to the age of the steeping corn. Fresh steepwater, to which 0.10 to 0.20% sulfur dioxide has been added, is continuously applied to the steep tank containing the longest (oldest) steeping corn. Sulfur dioxide is obtained in liquid form or from burning of elemental sulfur on site (Blanchard, 1992). Water for steeping is usually recycled from other processing areas of the plant, typically starch washwater, to conserve water. Approximately 1.2 to 1.4 m^3 of water is used to steep each metric ton (8–9 gal/bu) of corn (May, 1987). The steepwater is circulated through the battery by continuously drawing from an orifice in the bottom of each steep containing older corn and adding to the top side of the next steep in the battery series containing slightly fresher corn. As a steep containing the oldest, fully steeped corn is drained and removed from the battery series for milling, a new tank (steep) of fresh corn is added in the series from the opposing end, and each tank in the series shifts in a countercurrent direction relative to the flowing steepwater.

The chemical concentration of the steepwater continuously changes as it circulates from older to newer corn. Carbohydrates and denatured sulfoproteins leach from the kernels and increase in concentration within the steepwater as it circulates. Sulfur dioxide concentration exponentially diminishes from the initial concentration of 0.10 to 0.20% to approximately 0.02% (Wagoner, 1948). As the sulfur dioxide concentration diminishes, *Lactobacillus* species ferment leached reducing sugars into lactic acid from about midway in the battery series to the newest corn (Oomiya and Imazato, 1982). These strains of *Lactobacillus,* which closely resemble *Lactobacillus bulgaricus,* have a higher tolerance of acids, sulfur dioxide, and elevated temperature than the putrefactive microorganisms that would otherwise predominate in aqueous corn steeps (Liggett and Koffler, 1948). The steep-

ing conditions provide a selective medium for colonization by *Lactobacillus.* The biota found in each plant may differ based on natural selection or adaption to the steephouse environment. In older steeps, the pH is balanced between the acidic sulfur dioxide and buffering compounds leached from the corn. The combined weak acidity of the lactic acid and buffering action of leached solubles maintain a pH of 3.8 to 4.1 as sulfur dioxide is removed by the corn kernels. The desired pH is regulated in the steephouse by balancing the number of steeps in the system, concentration of sulfur dioxide, steepwater flow, and timing of corn addition and removal for grinding (Watson, 1984).

The steepwater that has passed through the steep battery is diverted to an evaporator. Approximately 0.7 to 0.8 m^3/t (4.5–5.5 gal/bu) is drawn off as light steepwater containing about 6% solids at 4° Baumé (Blanchard, 1992). An evaporator concentrates the collected inorganic matter, phytin, proteins, and carbohydrates to a 50% solids by-product usually termed steep liquor. The condensate has a pH of about 3 (Blanchard, 1992).

C. STEEPWATER ABSORPTION

New corn generally contains 13 to 15% moisture, but high-moisture corn, usually available during and shortly after the harvest season, generally has better milling properties (Wagoner, 1948). The initial moisture content of corn influences its end-use properties (Dorsey-Redding *et al.,* 1990). Moisture within equilibrated kernels is not uniformly distributed (Song *et al.,* 1992).

Cleaned grain entering the steeping battery is first immersed in light steepwater containing water, lactic acid, leached solubles, and a very low concentration of sulfur dioxide (Roushdi *et al.,* 1979). Because the pericarp is impregnated with waxes and lipids, the outer surfaces of the kernel are semipermeable to water and solutes (Wolf *et al.,* 1952). The pericarp has a permeability of 1.8×10^{-7} g cm/cm^2 atm s at 50° under Fick's diffusion model (Tolaba *et al.,* 1990); thus, the outer surfaces of the kernel are not a major route for absorption of steepwater. Steepwater, however, does enter the kernel's tip cap, penetrating the open structure of the spongy cells interconnecting the tip cap to the pericarp, and flows through the loose, open cross-cell and tubular layers between the pericarp and seed coat. The flux of steepwater is from the basal end of the kernel to the crown. The large intercellular spaces in the cross-cell layers form a major moisture transfer route from the tip cap to the endosperm (Watson, 1984). Therefore, the tip cap is the major route for steepwater uptake into the kernel. Song *et al.* (1992) showed, by magnetic resonance imaging, that the glandular layer of the scutellum (the tissue between the germ and floury

endosperm) is a path for moisture transfer to central areas of the kernel, such as the floury endosperm. This moisture penetration route has less resistance than moisture transfer through the pericarp and vitreous endosperm to the floury endosperm. Because of density, structural, and compositional differences within the kernel, moisture transfer through the kernel is not uniform with respect to time. Moisture penetrates the floury endosperm and other open structures more easily than the vitreous (horny) endosperm. Moisture diffuses through the endosperm and germ about eight times faster than the pericarp (Tolaba *et al.,* 1990). The kernels absorb approximately 0.5 m^3/t (3.5 gal/bu) and reach a maximum moisture content of approximately 45% in the first 8 to 10 hours of steeping (May, 1987).

Kernels swell appreciably on steepwater absorption. Aqueous absorption causes a volume expansion of 55 to 65% (Anderson, 1963). The kernels mainly have a linear hygroscopic expansion with a typical cubic expansion of 0.018 to 0.020 $m^3/m^3/\%$ moisture content for dent hybrids, with higher-density varieties exhibiting a larger coefficient of expansion (Muthukumarappan and Gunasekaran, 1990).

D. ROLE OF LACTIC ACID

Lactic acid, in conjunction with water, is considered the first major steeping chemical in which kernels are steeped. The resulting reduction in internal pH, along with high steeping temperatures, results in the death of respirating cells (Watson, 1984). Cell membranes become porous and allow leaching of solubles and absorption of sulfur dioxide.

Commercial wet millers cite three reasons for maintaining lactic acid fermentations within the steeping batteries: (1) separation of milled components (especially starch and gluten) is optimized, (2) the effectiveness of sulfur dioxide in preventing growth of undesirable microorganisms is most operative at pH 3.8 to 4.2, and (3) mineral scale deposition on water evaporation equipment is lessened at lower pH (Boundy *et al.,* 1967). Lactic acid also affects the form of the protein found in the steepwater. If lactic acid concentrations are not high enough in the steepwater sent to the evaporators, the proteins are in a form that can be heat-denatured; they coagulate readily to form a "liver paste" inside the evaporator tubes that readily collects and is difficult to remove (Blanchard, 1992).

The importance and role of lactic acid in protein dispersion and starch release are disputed among scientists and those in the wet milling industry. Cox *et al.* (1944) reported that the protein disintegration effect of steeping kernels in 0.1% lactic acid alone was approximately equivalent to that brought about by water alone, and kernel softening action was roughly equal to that found after a 0.1% sulfur dioxide steep. Steeping with 0.2 or

1.0% lactic acid produced protein disintegration approximately equivalent to a 0.1% sulfur dioxide steep and a softening action equivalent to 0.2% sulfur dioxide. Steep solution containing both lactic acid and sulfur dioxide softened and disintegrated the kernel to a similar extent as with higher sulfur dioxide concentrations. Watson (1967) stated that lactic acid aided in softening the corn, but Watson and Sanders (1961), in work on 10-mm-thick sections of endosperm, concluded that neither lactic acid, nor any other acids, had an effect on starch release below pH 9.0. Roushdi *et al.* (1979) reported that high lactic acid production resulted in lower yields and quality of starch than steeping with only high levels of sulfur dioxide. Eckoff and Tso (1991a) reported increased starch yield and reduced sulfur dioxide requirements with lactic acid addition to steeps. If the pH of a solution is not low enough to cause formation of sulfur dioxide ionic species, the gaseous molecule complexes with glucose and other carbonyl compounds in proportion to their concentration, thus becoming unavailable (Pointing and Johnson, 1945; Gehman and Osman, 1954). Lactic acid's pH-lowering effect may enhance the effectiveness of sulfur dioxide while steeping under low concentrations. Recent response surface work in our laboratory has shown that levels of lactic acid play a pivotal role in softening kernel structure, and influence the absorption rate of sulfur dioxide (Shandera *et al.,* 1995).

E. ROLE OF SULFUR DIOXIDE

Sulfur dioxide was initially added as an antimicrobial agent to control putrefactive organisms, but it was found indispensable for obtaining optimum starch yields and purity. Because of the solubility and bonding properties of the endosperm proteins, water alone will not disrupt starch granules from the adhering protein matrix (Cox *et al.,* 1944). Although steeping kernels reach their maximum moisture content in the first 8 to 10 hours, the time required for maximum starch yields is at least 40 to 50 hours (Watson *et al.,* 1951).

As a steep shifts in position within the battery, its sulfur dioxide concentration increases. Because kernels reach their maximum moisture content before immersion in steepwater with high sulfur dioxide concentrations, high concentrations of sulfur dioxide are not directly transported into the kernel by steepwater, as with lactic acid. Fan *et al.* (1965) found that the uptake of sulfurous acid during steeping of corn could be modeled using Fick's second law equation with a diffusivity of 10^7 cm^2 s^{-1}. The pericarp is a diffusive barrier, even to the gaseous sulfur dioxide (Eckoff and Okos, 1990). Sulfur dioxide primarily enters the tip cap at the basal end of a sound kernel and travels through the cross and tube cells of the pericarp surrounding and into the endosperm. The absorption route is similar to

that of steepwater. Sulfur dioxide also diffuses through the germ into the endosperm. Adsorption of gaseous sulfur dioxide within yellow dent kernels increases with decreasing temperature. Eckoff and Okos (1990) found 250% greater adsorption at 3°C than at 25°C [760 mm Hg with 30% (w.b.) kernel moisture] The adsorption of sulfur dioxide was independent of vapor pressure and kernel moisture content (above 20%). The similarity of activation energy for sulfur dioxide transfer in the kernel to that found in water by Chang and Rochelle (1981) suggests that moisture is an important factor in ionic transfer of sulfur dioxide through the kernel.

Increasing steepwater sulfur dioxide concentrations excessively may not increase absorption. Nierle (1972) estimated that only 5.7% of the sulfur dioxide used in steeping is absorbed by the corn. Of this, 45% is absorbed by the endosperm protein, 2% in the starch, and 40% in the germ. Only 12% of the absorbed sulfur dioxide reacts with the matrix protein. Eckoff and Okos (1990) showed that the germ holds three times more, and the bran holds 50% more, sulfur dioxide per unit weight than the endosperm when kernels are gassed with sulfur dioxide. Unbound sulfur dioxide is driven off during milling and processing of the steep kernels.

F. KERNEL DEGRADATION

The effects of steeping agents (50°C, 24-hour steep) on corn kernel structure were first comprehensively observed using microscopy by Cox and co-workers (1944). Modern scanning electron microscopy can also be used to aid in our understanding of kernel degradation during wet milling (Fig. 4). Water is an essential steeping chemical, in that it hydrates the kernel components and acts as a transportation medium for both lactic acid and sulfur dioxide. When steeping with sulfur dioxide, the endosperm's protein matrix gradually swells, becomes globular, and finally disperses over time. The degree of protein degradation (peptidization) was shown to be directly related to starch yield and ease of milling. Starch purity is usually proportional to sulfur dioxide concentration. Cox *et al.* (1944) found that protein dispersion increased with increasing sulfur dioxide concentration to 0.4%. Lactic, acetic, and hydrochloric acids were tested as steeping agent replacements for sulfur dioxide. Although lactic acid produced some softening action, other acids had little effect. Sulfur dioxide's mode of action was concluded to be other than acidic.

Wagoner (1948) noted that cross cuts of kernels steeped in commercial countercurrent batteries for 12 hours had an intact protein matrix, starch was still held tenaciously, and cellulose cell walls were very firm. Only slight changes were noted in cross sections of steeping kernels until after 24 hours, when the sulfite content of the steepwater began to rise rapidly. Thereafter,

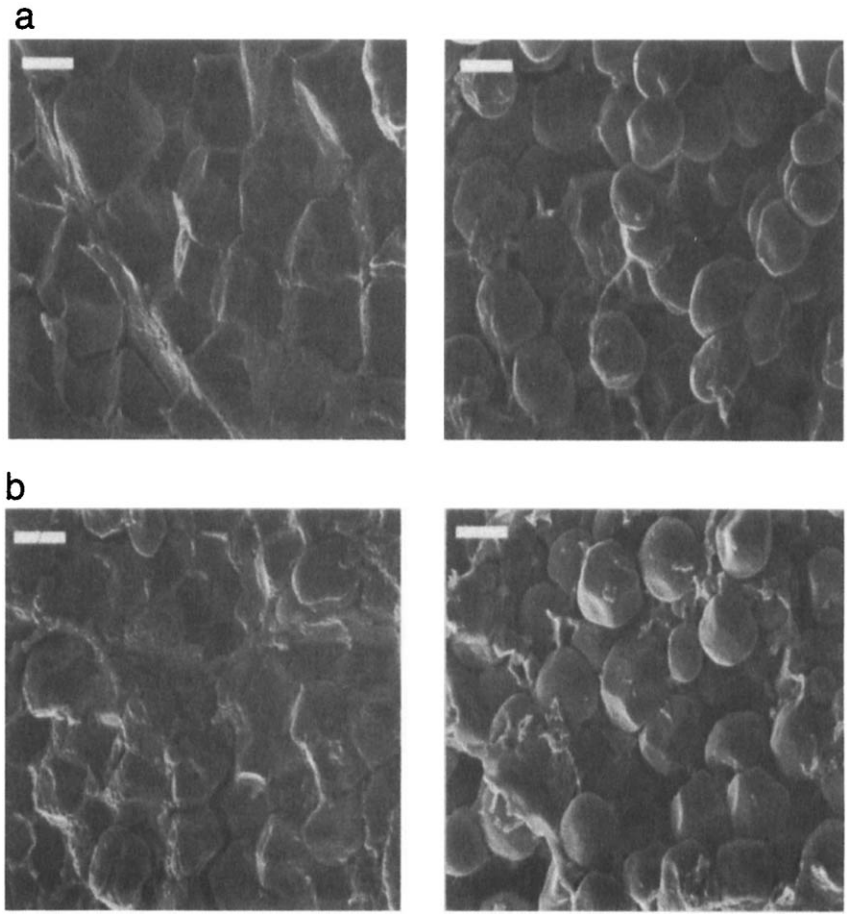

FIG. 4. Scanning electron micrographs of corn kernels steeped in water or 1% lactic acid and 0.15% sulfur dioxide. As steeping time increased, the lactic acid–sulfur dioxide steep solution was able to disrupt the hard endosperm so that individual starch granules are clearly visible. Small holes are visible in the hard endosperm starch granules of the water-treated samples; these represent broken granules, which are more fragile than the protein matrix. (Also compare with Fig. 3.) Bar = 10 μm. Hard endosperm section is on the left, and soft endosperm section is on the right. (a) Steeped in water 3 hours. (b) Steeped in lactic acid–sulfur dioxide 3 hours. (c) Steeped in water 53 hours. (d) Steeped in lactic acid–sulfur dioxide 53 hours.

protein matrix degradation continued as the ions migrated throughout the interior of the kernel. After approximately 50 hours, a well-steeped kernel showed no protein matrix structure, but had intact cellulose walls and free starch granules. Most of the protein network was dispersed into the steep solution, and the remainder was folded back around the cellulose walls.

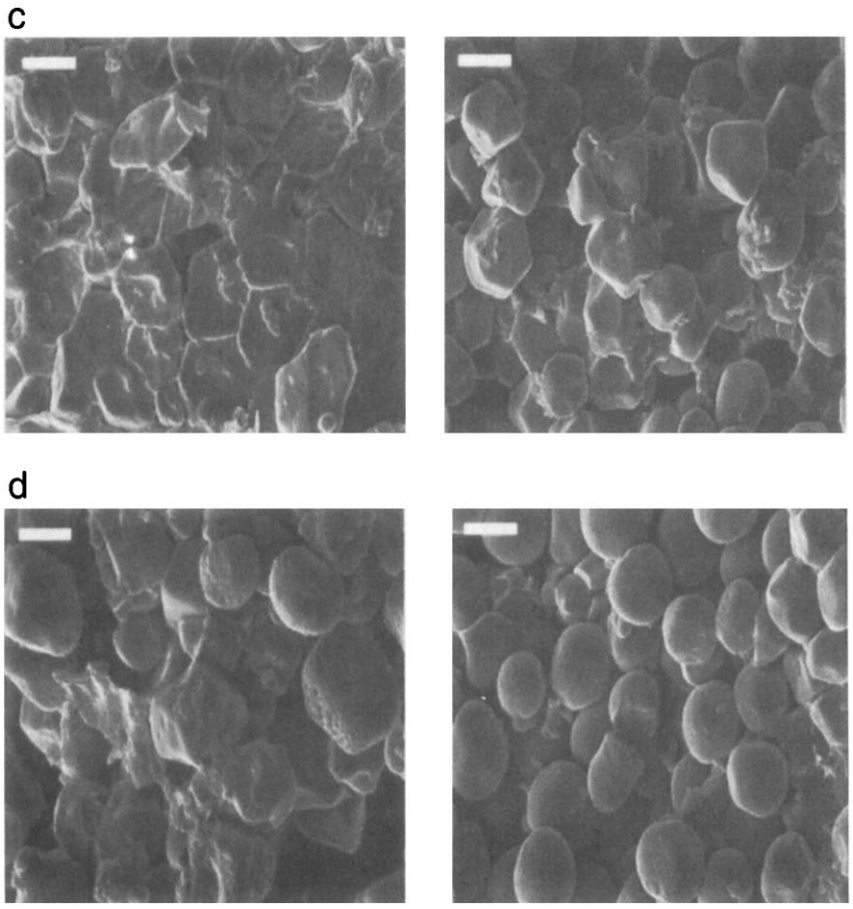

FIG. 4 (*Continued*).

Watson and Sanders (1961) studied sulfur dioxide effects on matrix protein under conditions where diffusion of sulfur dioxide was not limiting. Sections of horny (vitreous) endosperm, 10 mm thick, were steeped under high, constant bisulfite concentrations. Loss of starch granules from the protein matrix, on gentle agitation, was 50 to 70% complete in 1 hour and complete in 4 hours at 52°C in 0.2% bisulfite solution. The rate and extent of starch release from the matrix increased with bisulfite concentration (0.05–0.2%) and with increasing steeping temperature (52–60°C). Further experiments showed that at pH levels below 9, the pH of the medium did not have a significant effect on starch release.

Sulfuric ionic species are responsible for degrading the intercellular structure of kernels. Sulfurous acid does not exist as a distinct chemical species.

In water, sulfite anion, bisulfite anion, and sulfur dioxide (as a dissolved gas) exist in equilibrium as a sequence of acids and bases based on sulfurous acid, H_2SO_3 (King *et al.*, 1981). The sulfuric species present in aqueous solution relates to the pK_a of the species and the pH of the solution. The steeping kernel's internal pH of 3.6 to 4.0, reported by Wahl (1970), favors the bisulfite anion. Swan (1957) demonstrated that sulfite or bisulfite ions react with the sulfhydryl groups of cystine in wool protein, reducing the disulfide linkage between tertiary structures. The result is a protein fraction (P′) having one cysteine (–SH) and a second protein (P″) on which a *S*-sulfo derivative of the cysteine moiety has been formed:

$$\underset{\text{(native protein)}}{\text{P′S–SP″}} + \text{HSO}_3^- = \underset{\text{(reduced)}}{\text{P′SH}} + \underset{\text{(sulfoprotein)}}{\text{P″SSO}_3^-} \qquad (1)$$

Boundy *et al.* (1967) confirmed this reaction (1) within the intercellular protein matrixes of corn. Soluble *S*-sulfoproteins are produced and thus prevent reformation of disulfide bonds and structure. Proteins become either peptidized and soluble, thus leaching into the steepwater, or are denatured and folded back against the cell walls. Although other alkaline reducing agents give similar results, none are of commercial importance.

Separation of protein and starch is not always complete. Goossens *et al.* (1988) described grits (inseparables) as dense particles from the horny endosperm. Their structure consists of a three-dimensional honeycomb-like protein matrix filled with small starch granules. Many of the grits are enclosed by the fibrous cell wall. Grits result when steeping and milling fail to recover available starch, thus resulting in yield losses. The glutenin portion of the protein matrix can only be completely dissolved with a combination of reducing agents and hydrogen bond breaking chemicals (NaOH, urea, detergent) (Watson, 1984); thus, typical steeping and milling procedures may not completely degrade kernel structure.

G. ROLE OF TEMPERATURE

Steeping is generally done at 48° to 52°C to control microbial growth (Watson, 1984). Steeping temperatures above 55°C are unfavorable for endemic lactobacilli (May, 1987). Maintaining steeping temperatures of 45° to 55°C favors lactic acid production (Watson, 1967). Putrefaction and production of butyric acid and alcohols by other microorganisms occur during steeping at temperatures less than 45°C (May, 1987).

Higher steeping temperatures should increase steeping efficiency. Chemical reaction rates generally increase with temperature. Diffusion of moisture is generally enhanced by the temperature of the fluid medium and has an exponential relationship with the inverse of the fluid temperature (Steffe

and Singh, 1980; Walton *et al.*, 1988). Adsorption of water vapor into kernels increases with absolute temperature in an Arrhenius-type relationship (Muthukumarappan and Gunasekaran, 1990). Cox *et al.* (1944) reported that higher steeping temperatures (38–55°C) increased endosperm protein peptidization and dispersion. Temperature does not influence volumetric expansion of the kernel on moisture uptake (Muthukumarappan and Gunasekaran, 1990).

H. BIOCHEMICAL EFFECTS

Steeping effects are both chemical and enzymatic. The added sulfur dioxide and microorganisms producing lactic acid are considered the main effectors of the process. Other research, however, has pointed out the additional importance of catabolic enzymes present in the kernel and those produced during fermentation by *Lactobacillus* sp. Only about 10% of the nitrogen in corn is in the form of nonprotein nitrogen and, therefore, accounts for only about 25% of the soluble nitrogen obtained during steeping. Only enzymatic degradation of dissolved protein can account for the fact that 85% of the nitrogen in incubated steepwater is dialyzable nonprotein nitrogen (Watson, 1984). Although lactic acid bacteria generally do not show much proteolytic activity, the species found in the steeps do contribute to significant protein degradation (Watson *et al.*, 1955). The bacteria populate the soft tissue region of the tip cap, and they may have a proteolytic effect on the matrix protein. Wall and Paulis (1978) have disputed the microbial-proteolytic hypothesis and have, instead, attributed this proteolytic effect to the kernel's indigenous proteases. Their theory was based on comparing normal- and high-temperature dried corn steeped in the presence of lactobacilli. Poor starch and protein separation differences were attributed to heat denaturation of catabolic enzymes within the kernel. Eckoff *et al.* (1991b) have attributed poor starch and protein separation to morphological changes of proteins in the heat-damaged kernel. Franzke and Wahl (1970) suggested that at least some biochemical degradation of kernel structure during steeping was due to hydrolyzing enzymes (i.e., amylases, proteases). Proteolytic activity during steeping is generally due to the activation of endogenous enzymes by sulfur dioxide, and these proteases improve the release of corn starch (Wahl, 1970).

IV. MILLING AND FINAL PROCESSING

After steeping, the softened grain is degerminated in two stages by coarse grinding in an attrition mill (Blanchard, 1992). The degerminating mill has

two counterrotating disks with intermeshing fingers that tear apart, rather than crush, the kernel. The disks are adjusted for freeing the maximum amount of intact germs. Germs are swollen and rubbery due to steeping. Hydroclones are used to separate the germs, which are less dense and contain most of the oil, from the rest of the kernel constituents, which are in a starch slurry of 7° to 8° Baumé (Watson, 1984). Loose starch and gluten are removed from germs by washing with 1.2 to 1.3 m^3 of water per metric ton of corn on 50° wedge-wire screens (May, 1987). After washing, the germs are dewatered and further processed to extract corn oil. The operation is optimized to recover a germ fraction containing 45 to 50% oil (May, 1987).

The remaining material consists of a starch slurry, gluten, fiber, and kernel fragments (Blanchard, 1992). On screening the slurry, the overs, containing mostly fiber (pericarp) and chunks of horny endosperm, are reground in fine-grinding mills to liberate most of the remaining starch and gluten. The second grind mills may be either of the impact type known as Entoleter mill or of the combined attrition and impact type such as the Bauer mill (Watson, 1984). The fiber is separated by pumping the slurry with considerable force on 120° wedge-wire screens, then washed, dewatered, and dried.

Gluten is separated from the remaining starch slurry, soluble impurities, and high-protein substances in high-speed nozzle centrifuges. Separation results from density differences between gluten (1.06 specific gravity) and starch (1.6 specific gravity) (May, 1987). Older systems separated starch and gluten by settling in large-diameter tanks. The gluten is thickened to 12% solids in centrifuges, dewatered to 42% solids by vacuum filtration, and dried to 88% solids for sale as a protein concentrate.

The remaining starch slurry still contains 3 to 5% protein and must be further purified. The desired final protein concentration is less than 0.4%, with about 0.01% free protein (May, 1987). The slurry is washed of the remaining gluten with fresh water in a countercurrent fashion using multiple stages of centrifuges. The starch is then dewatered, dried, and/or modified in further processing steps. The removed protein consists primarily consists of starch–protein complexes, termed middlings, which are recycled back to the primary separation step.

V. LABORATORY VERSUS COMMERCIAL MILLING

Most researchers have conducted laboratory steeping using batch methods. Steepwater, to which all chemicals are initially added, is held at the desired temperature in a single tank, with or without recirculation (Cox *et al.,* 1944; Zipf, 1951; Watson *et al.,* 1955; Wahl, 1970; Roushdi *et al.,* 1979;

Krochta *et al.*, 1981; Wehling *et al.*, 1993; Eckoff *et al.*, 1993). Wagoner (1948), Watson *et al.* (1951), and Steinke and Johnson (1991) have challenged the use of laboratory batch steeping methods because of the lower starch yields, timing of sulfur dioxide addition, and solubles exposure with respect to commercial countercurrent systems. Structural changes within the kernel, over time of steeping, differ between batch and countercurrent steeping systems (Steinke and Johnson, 1991). Watson *et al.* (1951) and Steinke and Johnson (1991) devised elaborate laboratory countercurrent steeping systems to mimic commercial systems. Nevertheless, high variation in the growth of lactobacilli, lactic acid fermentation, and the need for continuous operations have hindered the application of such systems to the laboratory bench top. Watson *et al.* (1955) and Watson and Sanders (1961) conducted wet milling research using batch steeping, not the developed countercurrent system. Weller *et al.* (1988) mimicked a countercurrent system by continuously pumping fresh steep solution through a set series of steeps, but only the last steep in the series was milled. This system was a simplified way of immersing new corn in light steepwater containing collected solubles and lactic acid; but microbial growth was still uncontrolled and large amounts of experimental materials were used to produce this effect. Laboratory batch steeping may be more sensitive and have less inherent variability with respect to comparison studies (Fox *et al.*, 1992). Although commercial systems are countercurrent, most university and industrial laboratory research is conducted using batch steeps.

Lactic acid use in laboratory steeping has also been inconsistent. Anderson (1963), Krochta *et al.* (1981), Neryng and Reilly (1984), and Steinke and Johnson (1991) used batch steeping methods without lactic acid addition. Eckhoff *et al.* (1993), Wehling *et al.* (1993), Ling and Jackson (1991), Weller *et al.* (1988), Wahl (1970), Franzke and Wahl (1970), and Watson *et al.* (1955) steeped with added lactic acid. The inconsistent use of lactic acid in laboratory steeping stems from confusion as to its function as a steeping agent.

During batch steeping, work in our laboratory has suggested that both lactic acid and sulfur dioxide play important roles in the degradation of kernels (Shandera *et al.*, 1995). Most notably, yields of starch are influenced by both lactic acid and sulfur dioxide concentrations (Fig. 5). It should, however, be noted that the impact of these chemicals during commercial steeping (especially regarding concentration effects) would be different; corn kernels are exposed to changing concentrations of lactic acid and sulfur dioxide during the commercial countercurrent steeping process.

Most authors have based, usually with slight modifications, their milling techniques on the previous work of Watson *et al.* (1951, 1955) and Anderson (1963). These methods degerminate the kernels with a modified Waring

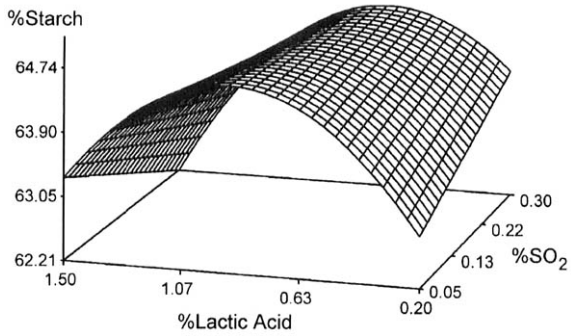

FIG. 5. Yield of starch obtained during batch laboratory corn wet milling with various concentrations of lactic acid and sulfur dioxide. The response surface model was significant at $P = 0.015$.

blender, fitted with a blunt blade and operated at a reduced speed to prevent germ damage. Germs are floated by adjusting specific density of the slurry and skimmed off. The slurry is either finely ground in a Quaker or similar crushing mill, or it is reground in the Waring blender operating at a high speed. Bran is recovered and washed on 55- to 48-μm mesh (No. 200–300 U.S.) standard testing sieves, nylon cloth, or linen cloth. Tabling has been the standard for separating starch and protein fractions. Steinke and Johnson (1991) separated starch by centrifugal techniques instead of tabling and identified an "inseparables" fraction consisting of small aggregates of starch and protein, which may be similar to the "grits" described by Goossens *et al.* (1988). Eckoff *et al.* (1993) investigated the accuracy and reproducibility of "traditional" laboratory wet milling techniques. Two critical control points were identified: (1) timing between the end of pumping the mill starch slurry during tabling to start of starch washing step, and (2) completeness of germ skimming and recovery. To increase precision between operators, they proposed controlling process water inputs and the lengths of individual process stages. The fiber fraction was separated using a mechanical vibrating screen, but hand mixing allowed more complete removal of starch and gluten from the fiber. Separating starch by tabling, in comparison to industrial techniques, was deemed to have the limitation of obtaining higher-quality starch in exchange for a lower starch yield and protein concentration in the gluten fraction. A gluten fraction was obtained by filtering the runoff from tabling the starch/protein slurry.

VI. RESEARCH TO IMPROVE WET MILLING

Various mechanical and chemical methods to reduce steeping time, and therefore input costs, have been explored. Superficially scratching the peri-

carp to increase water uptake in kernels had little effect in shortening steeping (Roushdi *et al.*, 1979). Krochta *et al.* (1981) reduced steeping energy input by reducing the corn-to-steepwater ratio or by degerminating kernels between two steeping periods. Neryng and Reilly (1984) increased the pH of their steep solution to 7 without affecting starch yields, but found difficulties in regulating microbial growth. They also found that preensiling high-moisture corn before milling increased starch yields, but resulted in decreased gluten recovery while increasing the protein content of steepwater solids. Meuser *et al.* (1985) proposed producing starch without sulfur dioxide using high pressure to disintegrate the morphological and structural components of the corn. Hassanean and Abdel-Wahed (1986) agitated steeping corn within and between steeps for faster moisture penetration and increased leaching of solubles, but current commercial steeping facilities would need to be modified, and energy requirements are higher. Eckhoff and Tso (1991a) found that pretreating corn with gaseous sulfur dioxide before steeping significantly increased starch yields when steeping for only 6, 12, and 24 hours. Mistry and Eckhoff (1992) proposed alkaline instead of sulfuric steeping of corn, but they found that starch obtained through alkaline isolation contained significantly more protein than traditional wet milling methods.

Over the past decade, several authors have studied the feasibility of using enzymes to enhance or replace current methods through direct addition of hydrolytic enzymes to steeping systems. Each has investigated a method based on knowledge of kernel structure, current steeping methods, and biochemical processes that take place.

Based on prior studies done on starch slurries and milling grits treated with various preparations of pepsin, papain, bromelain, and trypsin, Roushdi *et al.* (1979) increased the purity of starch by adding proteolytic enzymes to steeping corn. Because most proteases are effective only at pH 6 or higher, a significant shift in the sulfur dioxide species equilibrium from HSO_3^- to SO_3^{2-} could affect disulfide reducing capacities of kernel proteins by the steepwater (King *et al.*, 1981). The penetration of the high-molecular-weight enzymes into the endosperm was limited by the pericarp seed coat membrane. The limitations to this method are the large quantities of enzyme used and the need for lower steeping temperatures. Commercial protease usage on steeping grits from high-temperature dried corn was found to increase starch yield and purity (Eckhoff and Tso, 1991b). When steeping grits (endosperm chunks of corn), enzyme/substrate contact was not hindered.

Several investigators have explored enzymatic degradation of the corn's fibrous structure to aid steeping chemical penetration and separation of kernel constituents. Caransa *et al.* (1988) used cell wall-degrading enzymes during steeping to improve the separation of germ and starch from fiber

and gluten, to improve the quality of corn steep liquor by preventing the accumulation of phytic acid in corn steep liquor, and to shorten the steeping time. Ling and Jackson (1991) steeped corn with a commercial enzyme preparation of cellulase, β-glucanase, and arabinoxylanase activity, thus degrading the pericarp and cellular walls. Mean starch yields were increased only 1.2 percentage units, but starch yields were always higher, with shortened steeping times (24 hours) with enzyme usage. Within internal kernel layers, an inhibited enzyme–substrate contact between the starchy endosperm and the cellulosic pericarp layers was theorized to be a limiting factor. Steinke and Johnson (1991) steeped with a commercial enzyme preparation of cellulase, hemicellulase, β-glucanase, pectinase, and bromelain (0.25% v/v, each) using a laboratory countercurrent steeping system. Although levels of enzymes used would be uneconomical, corn milled more easily, even with only a 24-hour steeping period. Degradation of pericarp and cell walls allowed a clean separation of layers from the endosperm aleurone layer and underlying starchy cells on milling. Ironically, water diffusion into the kernel did not increase with enzymatic degradation of cellular components. The protease degrades starch–protein complexes, thus increasing starch purity and decreasing the amount of inseparables obtained.

Enzyme use in commercial steeping is limited due to mobility restrictions within the kernel, high steeping temperatures, sulfur dioxide, low pH, and relatively high cost. Possible negative, residual enzymatic action on final products and processes must also be considered.

VII. END PRODUCTS

A. PRODUCTS DERIVED FROM STARCH

Although starch, fiber, germ, and bran are the primary components from corn wet milling, the commercial refining process further converts all of these components into more readily marketable forms. Starch polymers (amylose and amylopectin) are, by far, the most readily convertible components because they are composed of glucose monomers.

1. Native Starches

After starch is washed, it can be dried to obtain common unmodified corn starch or prepared for modification into dextrins. Native starches can consist of "regular" corn starches that have granules containing 25% amylose polymers and 75% amylopectin polymers. Regular starches, when

cooked and cooled, produce firm, white opaque gels. High-amylose starches, commercially available from corn with either 50 or 70% amylose polymers (50 or 30% amylopectin polymers) can be cooked to produce very firm white to whitish yellow opaque gels. Cooked waxy starch gels, consisting of granules with nearly 100% amylopectin polymers, produce weaker, "slimy or stringy" gray-white translucent gels. Starches from corn with genetic modifications other than high amylose or waxy hybrids are also available. None, however, have approached the commercial success of waxy or high-amylose starches.

2. *Modified Starches*

Regular corn and its common high-amylose and waxy mutants provide a wide range of unique functionality for paper, food, and other industrial uses; their overall functionality and usefulness, however, can be extended by chemical and/or physical modifications. Modifications, typically to waxy or regular starches, include chemical crosslinking, chemical stabilization, bleaching, oxidizing, acid thinning, and ionic modification.

a. Crosslinking and Stabilization. Crosslinked starches are chemically treated to create stable gels after cooking. Chemical connections are established between adjacent starch polymers that result in less viscosity on cooking, because there is less granular swelling. In addition, however, there is also less viscosity breakdown during cooking and further processing (i.e., pumping), as the starch polymer structure is reinforced against shear-induced cleavage. Also, there is less subsequent retrogradation on cooling, as the reinforced chemical backbone prevents close polymer alignment. Waxy starch is often crosslinked; crosslinking eliminates the characteristic "slimy" gel texture, while retaining the less viscous translucent gel (compared with regular starch). Common crosslinking agents include sodium trimetaphosphate, phosphorus oxychloride, and mixed adipic–acetic anhydrite (Blanchard, 1992).

Stabilized starches are similar to crosslinked starches in that a chemical group is attached to the starch polymers. Typically, hydroxyl groups are processed to undergo esterification (with acetic anhydride, vinyl acetate, mixed acetic–adipic anhydride, monosodium orthophosphate, or succinic anhydride) or etherification (with propylene oxide or acrolein) (Blanchard, 1992). Unlike crosslinking, adjacent polymers are not physically linked. This results in starches that swell to high viscosities (as high as their native counterparts), but form less firm gels and resist retrogradation; the substituted group prevents close alignment of adjacent polymers.

b. Acid Modification. Acid-modified starches result when native starch is exposed to small amounts of acid (usually 0.5–0.25 *N* sulfuric acid) at temperatures 10° to 20°C below the starch gelatinization temperature. When compared with native starch, acid-modified starches do not attain as high a viscosity; consequently, more concentrated starch slurries can be prepared. Acid modification, however, creates polymer mixtures that appear to contain larger amounts of amylose (as amylose and as amylose-like polymers because of partial amylopectin depolymerization) (Jackson *et al.,* 1992, Zhang and Jackson, 1992). This polymer molecular size profile results in a starch that attains the same degree of gel firmness as its nonmodified native counterpart. Very firm gels can be created by cooking high concentrations of acid-modified starch; this starch is commonly used to manufacture jelly bean-type candies.

c. Other Modifications. Native starches can be further whitened and thermophilic spores destroyed by bleaching. Starch is treated with small amounts of hydrogen peroxide, peracetic acid, or sodium hypochlorite (Blanchard, 1992) to remove color-forming impurities and/or thermophiles. This results in starch that is ideally suited for canning and is used when starch is mixed with other bright-white ingredients (i.e., powdered sugar mixtures).

In a related process, starch oxidation is also a modification using sodium hypochlorite. Similar to acid modification, oxidizing results in partially depolymerized polymers. Oxidizing, however, also introduces carboxyl and carbonyl groups that inhibit amylose and amylose-type molecular reassociation after cooking (Blanchard, 1992). This results in a soft clear gel.

3. Products Using Fermentation or Enzymatic Technologies

Numerous products widely sold today, and a host of additional products destined to be made in the future, are based on technology designed to depolymerize starch into glucose or glucose oligomers.

a. Sweeteners and Maltodextrins. Corn sweeteners, depending on the desired end product, are produced using an acid, acid–enzyme, or entirely enzymatic process. Traditional corn sweeteners [with dextrose equivalents (DE)[1] approximately equal to 42] were manufactured as early as 1866; they typically were produced using hydrochloric acid (Hebeda, 1987). The acid depolymerizes the starch in an essentially random fashion. Because acid

[1] Dextrose is identical to glucose; the term is usually reserved for glucose obtained from starch. The extent of starch hydrolysis is measured according to a dextrose equivalent (DE) scale. DE is the reducing (group) content of a depolymerized starch expressed as dextrose (dry basis). Starch has a 0 DE value; pure glucose has a DE of 100.

can catalyze reactions other than depolymerization, this process is limited to syrups with 42 DE or less.

Forty-two-DE syrups can be produced using acid, or starch can be liquefied using α-amylase. Syrups of DE greater than 42 are prepared from 42-DE syrup using a mixture of α-amylase and glucoamylase enzymes. These syrups can be clarified and refined to produce high-glucose syrups or crystalline glucose.

High-glucose syrups can be further converted to products high in fructose. Although dependent on temperature, pH, and other factors, fructose is approximately 1.8 times as sweet as sucrose and 2.0 to 2.4 times as sweet as glucose. Usually, 42-DE corn syrups are treated with immobilized isomerase that converts some of the glucose into fructose. As a fructose–glucose equilibrium is established at approximately 51% fructose at 60°C, a good commercially viable product (with a reasonable isomerization reaction time) is produced with 42% fructose and 58% glucose (Hebeda, 1987; Blanchard, 1992). High-fructose corn syrups (HFCSs) are produced by chromatographically separating the fructose from a glucose–fructose mixture. The purified fructose can be crystallized or reblended to produce fructose syrups of various percentages. Commercially important HFCSs include 42% fructose, 55% fructose, and 90% fructose. Corn sweeteners are used in a wide array of food products because of their low cost, easy availability, and liquid (pumpable) state. In many sweetened products, such as soft drinks for example, HFCS has largely replaced sucrose as the nutritive sweetener of choice.

Maltodextrins are depolymerized starches with of less than 20 DE. They are produced similarly to corn syrups, but the enzymatic or acid depolymerization process is halted before the DE value reaches 20. Maltodextrins are essentially odor and taste free. Maltodextrins make excellent bulking agents and are used in puddings, soups, frozen desserts, and dry mixes (Hebeda, 1987).

b. Fuel Alcohol and Industrial Chemicals. Many wet milling plants not only have further refining capabilities to hydrolyze starch into sweeteners, they may also have (instead of or together with) facilities to produce alcohols or other industrial and food chemicals from glucose. Typically, these refineries rely on enzymes and yeast to convert starch into ethyl alcohol and carbon dioxide. A starch slurry from wet milling is converted to glucose using acid or enzymatic processes described earlier. The glucose syrup is then mixed with a small amount of steepwater (high in proteins and other nutrients required by yeast) and fermented by yeast. Microorganisms can also be used to convert glucose into a wide variety of other industrial chemicals, including many widely used organic acids.

B. NONSTARCH BY-PRODUCTS

In an effort to make the wet milling process as efficient and economical as possible, almost all of the by-products from corn wet milling are used. One of the most valuable by-products, on a weight basis, is the corn oil-containing germ fraction. After recovery during wet milling, the water in the germ is mechanically removed using a screw-type press and then dried in a steam dryer. In some cases, the dried germ is not extracted at a wet milling plant, but is shipped to a large facility specifically designed for oil production. The spent germ cake (germ after oil is extracted) is rich in relatively high-quality protein and makes an excellent feed for pigs and poultry. Its typical composition is 20% starch, 25% protein (N × 6.25), 1% fat, 10% crude fiber, and 25% pentosans (Anderson and Watson, 1982).

The gluten (protein) fraction can be processed separately or incorporated into other fractions for use as animal feed. This decision is based largely on the size of the plant and the economics associated with the animal feed market in the geographic region surrounding the production facility. If processed separately, gluten is mechanically dewatered and then dried using a rotary dryer. Gluten meals usually consist of 69% protein (N × 6.25), 19% starch, and 3% oil (Blanchard, 1992). In geographic regions where consumers prefer yellow-pigmented poultry, gluten meals make excellent poultry feeds because they are high in yellow pigments. The yellow xanthophyll pigments contribute to a bird's skin and egg yolk color.

The largest feed fraction obtained from wet milling is gluten feed. This fraction is a combination of corn fiber, spent germ cake (when available on site), and steepwater. Germ cake and/or gluten meal are added to obtain a total protein content of approximately 21% (10–12% moisture basis). Gluten feed is usually sold wet to nearby cattle feeders. The feed can also be dried, but dry feed is not as economically attractive to feeders who have other sources of grain and oilseed proteins available.

VIII. SUMMARY

Corn wet milling is a complicated, large-scale, and efficient industrial process designed to separate the chemical components from corn kernels. The success of wet milling, in terms of maximum yields, is largely dependent on the success of the steeping process. Improper steeping, or steeping of corn kernels that have unusual physical or chemical structures, results in lost product and lower profits. Steeping processes, however, are still based largely on an art that was developed more than 100 years ago. In the next 20 years, major seed corn producers expect that the market for corn with

unique starch characteristics and corn bred to produce speciality chemicals or have an altered composition will expand substantially. As the market increases for speciality corn, corn genetically bred with unique starch characteristics or corn with altered chemical composition, a thorough scientific understanding of steeping chemistry and the entire wet milling process will become increasingly important.

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