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Paul E. Ramstad

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Although other books on the chemistry and technology of corn have been published, none is recent. Much new knowledge is contained in this book. Authorities in many fields have contributed chapters or have reviewed manuscripts. Among them are agronomists, geneticists, entomologists, mycologists, food scientists, chemists, engineers, and economists who hold responsible positions in universities, government, and industry. Anyone interested in any aspect of corn research and development, marketing, utilization, etc., should find this volume useful. The editors, as representatives of The American Association of Cereal Chemists, are grateful to each of the authors and reviewers. We also wish to thank the AACC staff for their advice, help, and technical editing. We also owe thanks and appreciation to the Agricultural Research and Development Center, The Ohio State University, Wooster, Ohio, for use of facilities and to secretaries Georgia Miller and Gwen Alaura, photographer Ken Chamberlain, and draftsman, Newell Hartrum.

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CONTENTS

CHAPTER 11

CORN DRY MILLING: PROCESSES, PRODUCTS, AND APPLICATIONS

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I. INTRODUCTION

A. History of Corn Dry Milling

The history of corn milling follows very closely the history of corn development, which most experts agree originated in North America; corn was probably not introduced into Europe until after Columbus discovered the New World. This history goes back several thousand years, as recorded by several investigators. Mangelsdorf and co-workers (1964) reported the discovery of 7,000-year-old plant remains, which they identified as a wild progenitor of modern corn. Over 20,000 specimens of corn, about half intact cobs, have been found in several caves in both the Tehuacan valley of Mexico and the southwestern United States. These corn samples have been dated between 4,000 and 6,500 years old (*Mangelsdorf et al, 1967; Mangelsdorf, 1974*).

In addition to fossil corn, artifacts used with corn have been found. Belt (1928) observed that the ancient Indians of Nicaragua buried the stones they had used for grinding corn along with their dead. Undoubtedly, these stones were considered indispensable for the person's future life. They were essentially the first rudimentary means of milling corn.

For a look at the key developments of early corn dry milling, one can examine the implements used in pioneer America. Initially, the early settlers adopted the use of the Indian metate, which was only a slight improvement over the early grinding stones. With this device, the corn was ground between a hand-held stone and a concave bedstone.

One step up from the metate was the hominy block. Early directions for making this device were quite simple, as recorded by Hardeman (1981):

> Near the cabin cut off a hardwood tree three or four feet above the ground and hollow out the top. *From a springy limb of another tree extending over the stump,* tie a pestle or block of wood by a strong line.

The hominy block was operated by repeatedly plunging the wood pestle into the hollow stump until the corn had been sufficiently crushed into meal.

The hominy block was eventually replaced by a single-family, stone device called a quern (pronounced kwern). This was a small, burred-stone grinding apparatus, apparently invented in ancient Rome. It was operated by pouring corn through the cone-shaped axle hole at the top. An off-set handle was used to rotate the capstone on the stationary "netherstone," and the cornmeal worked out between the stones and fell into a tub surrounding the quern.

The principle of this type of revolving stone mill was applied on a much larger scale as early as 1620 (Hardeman, 1981). It expanded to become the local grist mill, which was eventually used to process both corn and wheat. Energy to operate the mill was supplied by livestock, occasionally by humans and by water. By the mid-1800s, most of the mills in the United States were operated by water, although steam-driven mills were used in some sections of the country.

A number of grist mills are still used to grind corn today, particularly in the southern states (Larsen, 1959). As in pioneer America, the mills are relatively small, and finished product distribution is limited to a small geographic area. These milling systems have gradually given way to the more sophisticated tempering-degerming systems, which were introduced in the early 1900s.

B. Present Milling Capacity in the United States

According to Brekke (1970a), as of 1965 there were 152 dry corn mills in the United States with a daily capacity of 50 cwt (2.27 t) or more. By 1969 this number had dropped to 115. More recent statistics (Anonymous, 1984b) suggests that the decline in dry mills has tapered off, with 88 mills still operating in 1984. Of this total, 66 are smaller mills located in the southern states and California (two), with most of the remaining mills (20) in the Midwest.

TABLE I
Principal Corn Dry-Milling Companies: Plant Locations and Estimated Mill Capacities[a]

Company	Mill Location	Estimated Daily Capacity (1,000 bu)[b]
Archer Daniels Midland	Lincoln, NE (Gooch Mills)	15
Evans Milling Co.	Indianapolis, IN	30
Illinois Cereal Mills Inc.	Paris, IL	65
Krause Milling Co.	Milwaukee, WI	55
Lauhoff Grain Co.	Danville, IL	70[c]
	Crete, NE (Crete Mills)	50
Lincoln Grain, Inc.	Atchison, KS	45[d]
Martha White Foods[e]	Nashville, TN	25
Midstate Mills, Inc.	Newton, NC	15
The Quaker Oats Co.	Cedar Rapids, IA	20
	Chattanooga, TN	15
	St. Joseph, MO	10
J. R. Short Milling Co.	Kankakee, IL	30
Total		445

[a] With the exception of two companies, the figures are based on unpublished data.
[b] Divide figures in this column by 2.205 to convert to metric tons.
[c] Anonymous (1978).
[d] Anonymous (1984a).
[e] Headquarters in Nashville, TN, with five separate mills: three in Tennessee, one in Georgia, and one in West Virginia.

Indications are that only 17 of the dry-milling plants account for most of the corn processed by the industry. A list of the principal milling companies is shown in Table I. Of the 17 mills, at least 12 are fairly large operations having daily capacities of between 10,000 and 70,000 bu (250–1,750 t) and utilizing tempering-degerming processes. Ten of the mills are located in the Midwest, and five are relatively small plants in the South.

The total of 445,000 bu (11.1×10^3 t) of corn per day (from Table I) corresponds to an annual volume of about 111 million bushels (2.77×10^6 t). This represents 92% of the corn processed by the whole industry for the 1977/1978 crop year (Anonymous, 1982) and indicates that most of the corn processed by dry millers in this country today is processed by the larger-capacity, tempering-degerming systems.

II. TEMPERING-DEGERMING SYSTEMS

A. Process with the Beall Degerminator

The Beall degerminator, introduced in 1906 (Larsen, 1959), set the stage for the development and production of refined dry-milled corn products. Although other types of degerminating equipment have been introduced since 1906, the Beall machine has remained the mainstay for most U.S. companies employing tempering-degerming systems. It has allowed the dry-milling industry to move from numerous small, locally operated grist mills with limited capacity and distribution to larger, more efficient plants processing 20,000–70,000 bu (500–1,750 t) per day with nationwide distribution. It has also allowed for the production of higher-quality, low-oil, essentially germ- and bran-free endosperm-based products with greatly extended shelf life and product stability.

Probably the major reference work cited by most of the recent authors in the field is that of Stiver (1955). This work describes the processes and equipment used by the corn dry millers in very detailed fashion, as do the more recent reviews by Brekke (1970a) and Anderson and Watson (1982). Their excellent discussions, flow charts, etc., are not reproduced here. However, the key aspects of the process are briefly reviewed to provide the reader sufficient background to the subsequent sections of this chapter.

As shown in the flow chart in Fig. 1, shelled, whole U.S. No. 2 yellow corn is received and placed in storage in standard corn silos. Today most of the corn is delivered by truck or railcar directly to the corn mills from country elevators or individual farms. Most corn mills have one to two weeks of storage capacity, which could amount to well over one million bushels (25×10^3 t), depending on the size of the mill.

The corn is first dry cleaned, which includes passage under a magnet (positioned over a belt conveyor) to remove tramp metal, aspiration to remove fines and pieces of cob, and screening to separate whole corn from broken corn. The desire is to have only whole kernels entering the corn mill. After wet cleaning to remove surface dirt, dust, rodent excreta, etc., the corn is adjusted to about

20% moisture and placed in a tempering bin. Optimum tempering moisture and times have been reported by Brekke and co-workers (Brekke et al, 1961, 1963; Brekke and Weinecke, 1964; Brekke, 1966, 1967, 1968, 1970a, 1970b; Brekke and Kwolek, 1969).

The product is then processed in the Beall degerminator, in which the whole moist corn is essentially treated by an abrading action to strip the bran or pericarp and germ away from the endosperm while leaving the endosperm intact. The most efficient way to operate the degerminator has been reported by Brekke et al (1961, 1963), Brekke and Weinecke (1964), and Weinecke et al (1963). This is obviously an ideal picture of what the corn miller would like to have happen. In fact, some of the bran and germ remain attached to the endosperm and must be removed in subsequent aspiration and milling processes. Also, some of the endosperm remains associated with the bran and germ fractions, all of which are separated by subsequent use of aspirators and gravity tables.

Let us assume that most of the endosperm is separated from bran and germ. The Beall is set up so that the large pieces of endosperm, known as "tail hominy," proceed through the end of the degerminator. This fraction is dried, cooled, and sifted, and part of it is isolated as large flaking grits. (The conditions for obtaining maximum yield of flaking grits have been reported by Brekke [1966, 1967] and Brekke and Kwolek [1969]). The remainder is sent to the roller mills for reduction into smaller fractions, such as coarse, medium, or fine grits; meals; or flours. The bran and germ fractions (together) pass through a screen on the underside of the degerminator and become the "thru stock" stream. This stream is dried, cooled, aspirated to remove the bran, and processed on gravity tables to separate germ and endosperm.

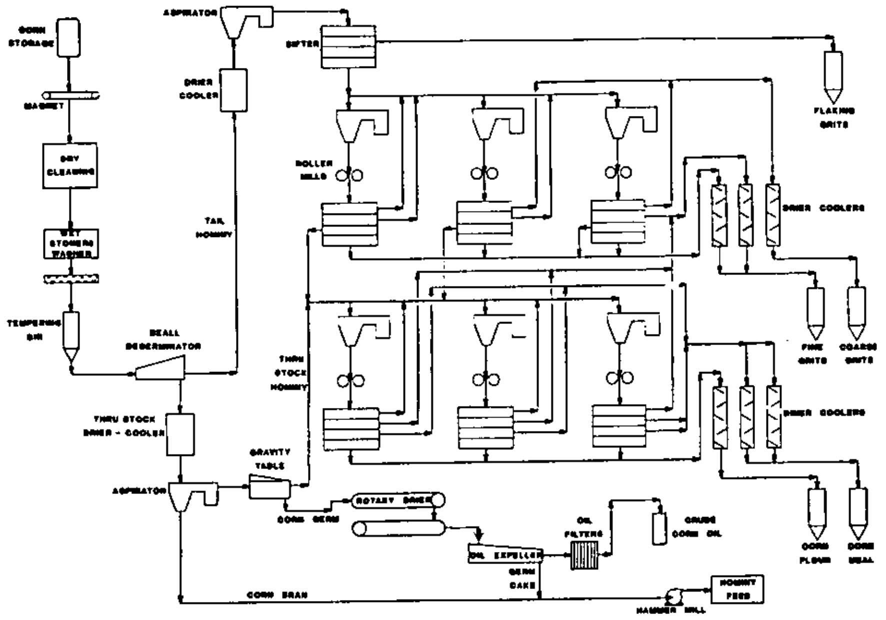

Fig. 1. Production flow chart for a typical corn tempering-degerming system.

The germ can then be expelled or hexane-extracted to remove the oil, and the spent germ or germ cake becomes one of the by-product streams. (Some of the corn dry millers do not further process the germ but sell it to other companies that do). The fines separated from the thru stock endosperm are usually high in oil, fine fiber, and tip caps; they become one of the by-product streams known as "standard meal." The bran, germ cake, standard meal, and broken corn (isolated from whole corn before entering the corn mill) are combined, dried, and ground up together to become the main by-product of the corn dry millers, which is known as "hominy feed." Since none of the dry millers refine corn oil, the crude oil obtained from either expelling or extraction is sold to one of several oil refiners in the United States. The main portion of the endosperm isolated from the thru stock is processed in the same way as the tail hominy fraction to produce prime grits, meals, and flours.

As indicated by Stiver (1955) and others, after the degerminator, the roller mills and sifters are the core of the corn milling system. The larger pieces of corn endosperm are sent to a series of roller mills, where they pass between sets of corrugated rolls; the corrugations vary in size, depending on the level of particle size reduction required. The ground endosperm stream proceeds to the sifters, which can separate the mixture into as many as 16 different fractions.

The larger-sized particles can be sent to another set of rolls for further reduction, or combined with other streams of similar particle size, aspirated, dried, cooled, and sent to a finished product bin. Similarly, the medium-sized and small-sized particles may be further milled and sifted and streams of similar size combined to give finished corn grits, meals, and flours of uniform composition.

In several of the major corn dry-milling plants, corn grits and/or flours are further processed in acid modification systems, in extrusion-cookers, or the like, to provide a wider variety of modified corn products for both food and nonfood use. These specialty products are discussed in more detail in several subsequent sections of this chapter.

B. Alternative Milling Systems

At least two alternative dry-milling systems can be employed to produce refined dry-milled corn products (Brekke, 1970a). They have been described as the Miag process, now more correctly the Buhler-Miag process (Wyss, 1974), and the Ocrim process. Both of these systems were developed in Europe and have been used to some extent throughout the world. Selected pieces of equipment from the two systems have also been incorporated into several corn mills in this country. Since the systems have been discussed in detail by Brekke (1970a), no further description is given here.

III. DRY-MILLED PRODUCTS—TYPES, VOLUMES, AND COMPOSITION

The primary products derived from the tempering-degerming process are corn grits, cornmeals, and corn flours. An infinite number of products are possible as the result of particle size reduction on the roller mills, from flaking grits as coarse as four- to six-mesh down to fine-grind corn flour with 95% passing through a 100-mesh sieve. However, most of the products can be classified into one of the six main groups shown in Table II.

At one time, brewer's grits, in particular, included numerous products covering the particle size range from 10–12 mesh grits to cornmeal. In the brewing process, the size of the particulate material remaining after cooking and enzymatic hydrolysis of the corn adjunct has a definite impact on the manner in which the hydrolyzed starch liquor, known as "wort," filters. The nature of this residual, high-protein material appears to be unique to the particular type of brewing equipment and process employed. Otherwise, essentially no differences in composition are found between coarse, regular, and fine grits.

This is also true of all products coming from the main portion of the corn endosperm, including flaking grits, coarse or fine brewer's grits, or corn cones—a very fine, uniform cornmeal. The composition of these materials is shown in Table III. Typically they contain 7–8% protein, less than 1% fat, ash, or fiber, and 77–79% starch (88–90%, dry basis).

The only material that varies somewhat in composition is corn flour, particularly that produced during normal roller milling of large grits to smaller

TABLE II

Typical Products of the Corn Tempering-Degerming System: Granulations and Product Volumes[a]

	Particle Size						
	From			To			
		Size			Size		
Product	Standard U.S. Mesh	in.	μm	Standard U.S. Mesh	in.	μm	Annual Volume[b] (million lb)
Flaking grits	−3.5	−0.223	−5,600	+6	+0.132	+3,350	750
Coarse grits	−10	−0.0787	−2,000	+15	+0.0512	+1,290	940
Regular grits	−15	−0.0512	−1,290	+30	+0.0234	+600	1,360
Cornmeal	−30	−0.0234	−600	+60	+0.0098	+250	190
Corn cones	−40	−0.0165	−425	+80	+0.0070	+180	190
Corn flour	−60	−0.0098	−250	+325	+0.0017	+45	330

[a] Data taken in part from Alexander (1973) and Brekke (1970a).
[b] Divide figures in this column by 2,205 to convert to million metric tons.

TABLE III

Typical Composition (%, as-is basis) of Dry-Milled Corn Products[a]

Component	Flaking Grits	Coarse or Fine Grits	Corn Cones	Corn Flour
Moisture	11.7	11.5	12.0	13.0
Protein	7.0	7.5	7.9	5.2
Fat	0.6	0.7	0.6	2.0
Crude fiber	0.2	0.2	0.3	0.5
Ash	0.2	0.3	0.3	0.4
Starch	78.3	78.0	77.4	76.4
Other polysaccharides	2.0	1.8	1.5	2.5

[a] Based on unpublished data.

grits. This fine fraction (−60 mesh) is usually referred to as "break flour." It contains less protein and somewhat more fat than the other prime products. Break flour is derived from the portion of the corn kernel known as the floury endosperm. Corn flour derived from the roller milling of grits, and coming mainly from the horny endosperm, is known as "reduction flour." It has the same composition as the starting corn grits.

IV. INDUSTRIAL APPLICATIONS

A. Current Market Volumes

The principal applications of the products of the corn dry-milling industry are shown in Table IV. These figures were estimated for the calendar year 1977. Most of the figures in Table IV have been corroborated with other published data for that year, as is discussed below.

The total product volume of 6.19 billion pounds (2.81×10^6 t) should be corrected to 6.05 billion pounds (2.74×10^6 t) to account for the noncorn ingredients in fortified corn products. This corrected figure compares fairly well to the 5.87 billion pounds (2.66×10^6 t) calculated from data for the daily plant capacities of the principal dry millers in Table I, using the following equation:

TABLE IV

Estimated 1977 Product Volumes of the Corn Dry-Milling Industry[a]

Application Areas		Quantity (million lb)[b]
Brewing, total		1,850
Food, general		
Breakfast cereals	800	
Mixes (pancake, cookie, muffin, etc.)	100	
Baking	50	
Snack foods	100	
Other foods (breadings, batters, baby foods, etc.)	75	
Total		1,125
Fortified foods (PL480), total		485[c]
Nonfood		
Gypsum board	100	
Building products (particleboard, fiberboard, plywood, etc.)	40	
Pharmaceuticals/fermentation	200	
Foundry binders	90	
Charcoal binders	75	
Other (paper, corrugating, oil well drilling fluids, etc.)	25	
Total		530
Animal feed,[d] total		2,200
Total		6,190

[a] Estimates based on unpublished data.
[b] Divide the figures in these columns by 2205 to convert to million metric tons.
[c] Corn products represent 65–70% of total shipments, or 315–340 million pounds.
[d] Data reported by Alexander (1973).

$$\begin{aligned}\text{Product volume} &= 445 \text{ million bu/day} \times 55 \text{ lb/bu} \times 250 \text{ days} \times 0.96\\ &\quad (\text{conversion factor}^{1})\\ &= 5.874 \text{ billion lb}\end{aligned}$$

It also compares quite well to a figure of 6.39 billion pounds (2.90×10^6 t), which was calculated using the value of 121 million bushels of corn processed in the 1977/1978 crop year, as reported in the 1982 *Commodity Year Book* (Anonymous, 1982).

The product with the largest volume was hominy feed, the chief by-product of the corn dry millers, which is sold for animal feed. The value of 2.2 billion pounds (1.0×10^6 t) was taken from published data (Alexander, 1973), which is in good agreement with the 2.285 billion pounds (1.04×10^6 t) reported by Wells (1979). The second biggest application area is in the brewing industry, where 1.85 billion pounds (0.84×10^6 t) of corn grits and meals were used in brewing adjuncts. This agrees well with a figure of 1.77 billion pounds (0.80×10^6 t) compiled from reports in *The Brewers Digest* (Anonymous, 1974–1984).

The volume of 1.61 billion pounds (0.73×10^6 t) used in food applications (1.125 billion in general foods plus 0.485 billion in fortified foods) is reasonably close to the figure of 2.0 billion pounds (0.91×10^6 t) reported by Brockington (1970).[2] The breakdown in the general food area (Table IV) has not been published before, so no basis for comparison exists. The value of 485 million pounds (0.22×10^6 t) of fortified foods is quite similar to the figures shown in Table VI for the years 1979–1982 (Bookwalter, 1983).

The product volume of 530 million pounds (0.24×10^6 t) for nonfood uses is considerably higher than data previously published by Senti (1965) and Alexander (1973). The larger figure was the result of increases in the use of corn flours in gypsum board, foundry binders, and particularly citric acid production (in the fermentation area) during the 1975–1978 period. According to Wells (1979), this volume dropped off to 377 million pounds (0.17×10^6 t) in 1979, which is probably closer to current usage levels. Specific application areas are discussed in the following sections of this chapter.

B. Brewing

THE BREWING PROCESS

Traditionally, the brewing industry has been the largest user of prime products made by the corn dry millers. A brief description of the process will aid in understanding of the use of corn grits in making beer. When grits are used in brewing beer, the first step is cooking the grits. This is frequently accomplished in the "mashing" or "mash tun" (or tub) before treatment with barley malt. Corn grits and water are combined, heated to 90–95° C to gelatinize the starch, and cooled to 67° C. Alternatively, grits may be processed through a jet cooker or a continuous cooker. Malt is added, and starch from both malt and corn grits is hydrolyzed to fermentable sugars by the joint action of α- and β-amylases.

The solubilized carbohydrates are separated from the spent grains by filtering or lautering, and the spent grains are washed or sparged with water at 75° C. The resulting wort is combined with hops and heated to boiling, traditionally in a copper kettle. After filtration, the hopped wort is cooled and adjusted to the proper specific gravity. It is then inoculated or "pitched" with a selected strain of yeast, and the sugars are fermented to alcohol. After fermentation, the immature or "green" beer is allowed to age for seven to 10 days.

Finally, the beer is filtered, pasteurized, and packaged. More details of the brewing process may be found in such excellent reviews as that by MacLeod (1977).

INDUSTRY TRENDS

In 1977, nearly two billion pounds (0.91×10^6 t) of corn grits were employed in making beer. Unfortunately for the corn dry millers, this figure represented the peak year for brewing use. Corn grits have always had to compete with rice and corn syrups as adjuncts in the United States, and both of these cereal-derived products have increased quite dramatically during the past 10 years at the expense of corn grits. The graph in Fig. 2 shows the trends in consumption of the various products. The use of corn grits increased from 1973 to 1977. Between 1977 and 1983, it decreased on an average of 3.7% per year, for a loss of nearly 400 million pounds (0.18×10^6 t). On the other hand, both rice and corn syrups have increased, rice by 350 million pounds (0.16×10^6 t), or 61%, and corn syrups by 360 million pounds (0.16×10^6 t), or a substantial 130%, over the 10-year period. There are several reasons for these changes.

The increased use of corn syrups has been the result of several factors. Probably the most important to the brewers is economic. Corn syrups represent

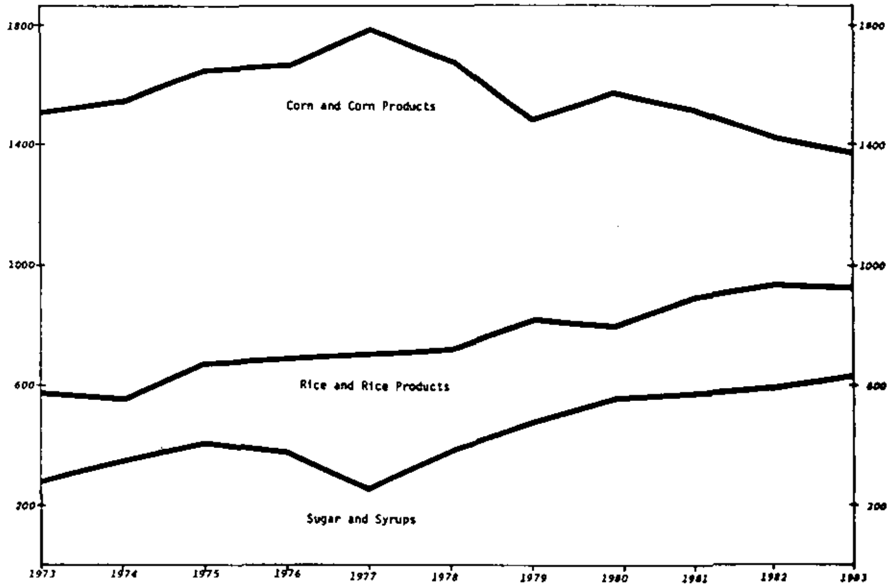

Fig. 2. Consumption of cereal adjuncts by the brewing industry for 1973–1983. Data from *The Brewers Digest* (Anonymous, 1974–1984).

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[1] Factor converting corn with 15% moisture corn to finished products with 11% moisture.

[2] Figure obtained by adding the degermed corn meal (0.75 billion pounds) to grits for human consumption (1.28 billion pounds) (Brockington, 1970, in Table 15.1).

a form of adjunct with a higher concentration of fermentable sugars. Therefore, increases in brewing capacity (Pfisterer et al, 1978) and production rates (Pollock and Weir, 1976; Swain, 1976) have been possible without plant expansions. Swain (1976) also cited lower production costs, whereas others (Rao and Narasimham, 1975; Pollock and Weir, 1976) have indicated that syrups result in fewer production problems plus a more uniform product with equal or higher quality. Moll and Duteurtre (1976) indicated that, when a new plant is built, lower capital costs are possible with the use of corn syrups.

The increased use of rice has not been as well documented. However, certain rice varieties can provide higher-gravity brews (Stubits and Teng, 1983) and thus increased brewing capacity similar to that for syrups. In addition, the popularity of lower-calorie beers in recent years has resulted in the increased use of enzymes, both amylolytic and debranching. One patent (Line et al, 1982) claims to use malted rice as the source of debranching enzyme as well as of starch.

C. General Food Uses

INTRODUCTION

Combining the application areas of brewing, general food uses, and fortified foods from Table IV, one obtains a total of nearly three and one half billion pounds (1.59×10^6 t). This represents 87% of the prime products sold for all uses, indicating the importance of the food-beverage industry to the dry corn milling industry. Next to brewing, the general food category is the second largest market segment, with over one billion pounds.

In recent years, several reviews have covered food applications of dry-milled corn products; these include Brockington (1970), Bailey,[3] and Wells.[4] Processes for making breakfast cereals were well documented by Matz (1959). In addition, the food area is updated and discussed more thoroughly in Chapter 13. Consequently, food uses are not described here to any great extent. However, because of the importance of extrusion-cooking as a processing tool for the corn dry millers in both food and nonfood areas, some discussion is devoted to this relatively new technology.

EXTRUSION-COOKING PROCESS

Large-volume extrusion-cookers first became available for use in the cereal industry in the late 1950s to early 1960s. Two commercial full-scale units are shown schematically in Figs. 3 and 4. Basically, the process involves feeding a dry or semimoist (15–25% moisture) corn or other cereal product into the hopper end or feed section of an extruder. At this point, the extruder screw and starting material are usually at ambient temperatures, although the mixing chamber shown in Fig. 4 provides a vehicle in which the cereal product can be heated.[5] Also, at this point in the process, the flights of the extruder screw are the widest apart. As the cereal product is conveyed down the length of the extruder (compression section), the flights get closer and closer together, so that by the time the cooked product exits the end of the extruder, the material is under a pressure of 200–1,000 psi (1,300–6,900 kPa).

As the cereal product is moved through the extruder, the temperature in the extruder barrel increases, primarily as a result of 1) the internal shear forces, but also from 2) external heat that can be applied with some extruders, and 3) steam

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[3] T. Bailey. Functionality and uses of corn flour. Presented to: Central States Section, Am. Assoc. Cereal Chem., St. Louis, MO, Feb. 16–17, 1973.

[4] G. H. Wells. Cereal flours in fabricated foods. Presented to: Symposium: Fabricated Foods. Central States Section, Am. Assoc. Cereal Chem., St. Louis, MO, Jan. 30–Feb. 1, 1975.

[5] G. L. Johnston. Technical and practical processing conditions with single screw cooking extruders. Presented to: International Seminar on Cooking and Extruding Techniques, ZDS Solinger-Grofroth, West Germany, Nov. 27–29, 1978.

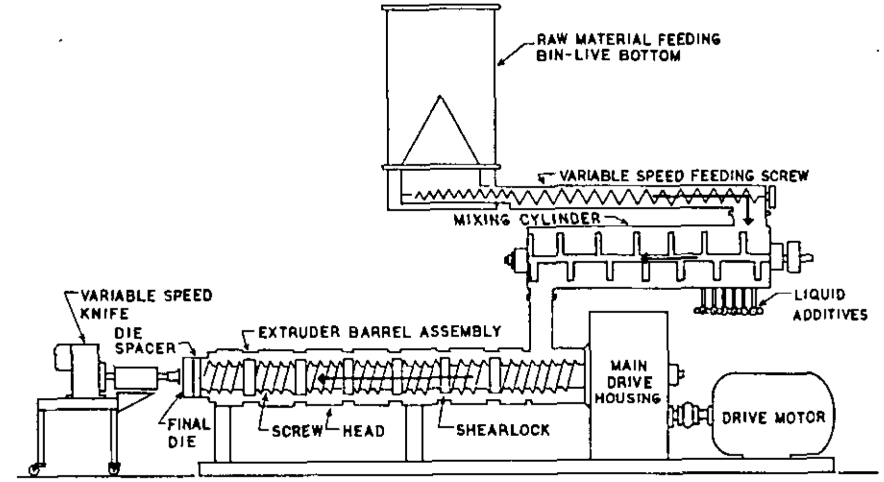

Fig. 3. Cut-away view of a single-screw extrusion-cooker. (Courtesy Anderson International, Strongsville, OH)

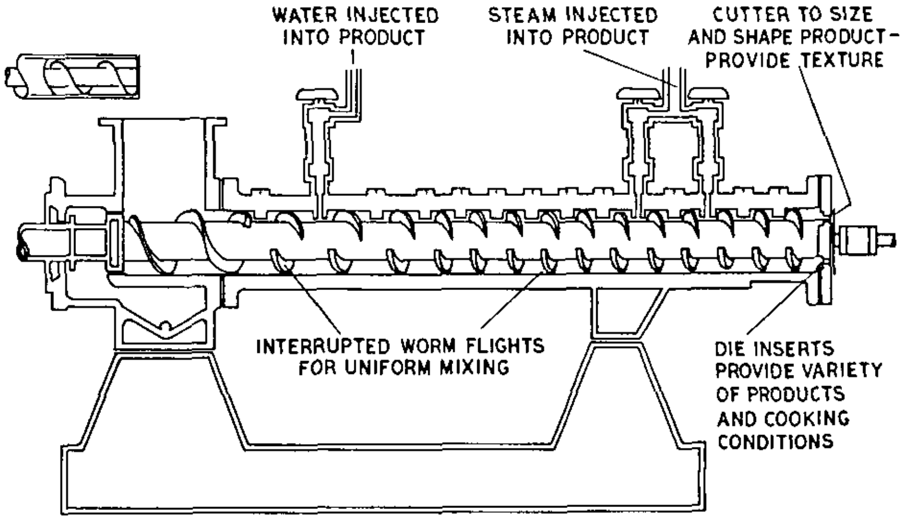

Fig. 4. Cut-away view of a complete extrusion system, including storage bin, screw-conveyor, mixing chamber, and single-screw extrusion-cooker. (Courtesy Wenger Mfg., Sabetha, KS)

injection that is possible in certain models. The heat causes the starch in the cereal product to gelatinize and swell, and the resulting extrudate becomes quite viscous. This creates additional pressure, shear, and heat at the head end of the extruder barrel.

The extrudate exits the extruder through holes in a die plate. These holes can be varied in size, shape, and number. At the end of the extruder is a variable-speed knife, which cuts the extrudate into smaller pieces called "collets," which are conveyed to a cooler/dryer. If the collets are intended for second- or third-generation snack foods, as defined by Hauck (1980) or Matson (1982), the product is packaged and made ready for shipment. If the final end use is as a precooked cornmeal or corn flour, the dried collets are ground in a hammer mill, entoleter mill, or the like, to the desired particle size before bagging and shipment.

A number of variables in screw design, extruder shape, die configuration, numbers of extruder screws, etc., are possible. For instance, in the machine in Fig. 3, water or other liquids or reagents can be added directly into the extruder barrel, and external heat can be added by steam injection into the barrel. In the machine in Fig. 4, liquid additives are added in the mixing cylinder ahead of the extruder, and part of the heat can be provided through the use of jackets suitable for circulation of water, steam, or other liquid. In addition to the Anderson and Wenger units, single-screw industrial extrusion-cookers are available from Bonnot Company and the Sprout Waldron Division of Koppers and double-screw extruders from Werner-Pleiderer Corporation and Wenger Manufacturing, just to mention a few.

Along with equipment design, cereal properties, such as degree of cooking, density, viscosity, or water absorption properties can be controlled and modified by such process variables as extrusion moisture, temperature, screw speed, and, perhaps most importantly, die configuration. This flexibility has helped make extrusion cooking the important processing tool that it is today in the food industry, and, especially for the corn dry millers, it provides a means of converting corn flour from a by-product into premium products (Roberts, 1967).

EXTRUSION APPLICATIONS

The early patent literature (Bradley and Downhour, 1970; Stickley and Griffith, 1966) describes the use of extruders in producing precooked corn and sorghum flours for use as foundry binders. Subsequent publications reported their use in breadings and croutons (Anonymous, 1983), fabricated foods,[6] fortified cereal products (Anderson et al, 1969, 1970; Bookwalter et al, 1971), and as bases for certain specialty confections and protein-fortified beverages (Hauck, 1980).

The snack food industry seems to have benefited the most from the variety of products, shapes, densities, etc., possible with modern extruders. Cornmeals or corn flours have been found to be particularly useful raw materials (Sanderude, 1969; Matson, 1982) in the production of corn chips (Sanderude, 1969; Scales, 1982; Stauffer, 1983), puffs (Williams, 1977; Toft, 1979; Scales, 1982), onion rings (Sunderude, 1969; Williams, 1977), and several second- and third-generation snacks (Toft, 1979; Hauck, 1980; Matson, 1982). Products made by direct extrusion compete with snacks made from masa flour, which involves treatment with lye before milling (Scales, 1982; Stauffer, 1983; Przybyla, 1984). Corn processed by the traditional masa process has been recently described by Bedolla and Rooney (1982) and is discussed in more detail in Chapter 13.

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[6] See footnote 4.

D. Corn-Based Fortified Foods

INTRODUCTION

During the late 1950s and early 1960s, a number of changes occurred within the government food aid programs that had a major effect on the corn dry-milling industry. In this period, the shortage of nonfat dry milk (NFDM) resulted in the search for alternate sources of low-cost protein (Senti et al, 1967). The government assisted industry with the passage of the Food for Peace Act of 1966, which broadened the range of commodities eligible for donation to underdeveloped countries. Even before passage of the new legislation, the corn dry millers had developed several corn-based prototypes (Tollefson, 1967), so that in 1966 they were ready to produce the first of several protein-fortified foods.

The first product that received worldwide distribution and acceptance was corn-soy-milk (CSM). The original formula for this material consisted of 64% partially cooked cornmeal (PCM), 24% defatted, toasted soy flour, 5% NFDM, 5% soy oil, and 2% vitamins and minerals. The product was well balanced from a carbohydrate-protein-fat standpoint, and the protein contained a particularly good amino acid profile (Cantor and Roberts, 1967). The combination of corn, soy, and milk proteins resulted in a protein efficiency ratio essentially equivalent to that of casein. It is believed that the combination of functional, flavor, and nutritive properties resulted in the success of CSM.

PURPOSE OF FOOD FOR PEACE PROGRAM

The main objective of the Food For Peace legislation (PL480) has been to provide nutrition, in the form of both total calories and high-quality protein, to the millions of people in the Third World who do not have enough food. Indications are that as many as 10,000 people die each day from malnutrition (Anonymous, 1970), while irreversible physical damage is incurred in thousands more. The emphasis has been directed, in most cases, to weaning and preschool children, in whom protein malnutrition takes its greatest toll.

To accomplish this goal, the various cereal products purchased for the program have been distributed to most of the countries in the world through the Agency for International Development, local governments, and various volunteer agencies, such as CARE, UNICEF, Catholic Relief Agency, and Church World Services. The products get to the people through various programs, including church-related schools, school-lunch programs, and mother-child care centers.

DEVELOPMENT OF CORN-BASED PRODUCTS

In the author's opinion, the development of CSM and the subsequent cereal-based products that have become part of the PL480 program was truly a cooperative effort. It involved industry and government, as represented by the

U.S. Department of Agriculture and the Agency for International Development, plus a variety of scientists, nutritionists, etc., from private industry, academia, and a variety of government and volunteer agencies. The corn industry (Tollefson, 1967) provided the process capabilities, some of the product development effort (Cantor and Roberts, 1967), and the ability to process and move the large volume of commodity ingredients involved in the manufacture of these products. The U.S. Department of Agriculture was involved in product and process development (Anderson et al, 1969, 1970; Bookwalter et al, 1971; Conway, 1971a, 1971b; Bookwalter, 1977) and in defining specifications and requirements for the products (Senti et al, 1967; Bookwalter et al, 1968, 1971; Bookwalter, 1981).

The corn-based materials developed for PL480, when they were introduced, and their compositions are shown in Table V. Quantities of the products sold to the government from 1970 through 1982 (Bookwalter, 1983) are recorded in Table VI.[7] The size of the figures points up the significant effect this program has had on the corn industry.

Before about 1967, the PCM used to make CSM was generally produced on hot rolls (Anderson, 1982), the commercial products being made on gas-fired rolls. Since 1967, most of the PCM and instant PCM (used to make instant CSM) have been made in extrusion-cookers of the type described in the preceding section and by Conway (1971a, 1971b). Other forms of cooking have been described by Anderson et al (1969, 1970), although the extruder appears to be the most versatile and practical cooking equipment for dry-milled corn products.

TABLE V
Corn-Based Fortified Foods Developed for PL480 Programs

Product	Year Introduced	Composition
Cornmeal, enriched[a]	1957 (approx.)	99+% cornmeal, ¼ oz vitamin mineral premix per hundredweight.
Processed cornmeal, enriched[b]	1963	99+% PCM,[c] ¼ oz vitamin-mineral premix per hundredweight.
Ceplapro[b]	1965	58% cornmeal, 25% soy flour, 10% durum flour, 5% NFDM, 2% vitamin-mineral premix.
CSM (corn-soy-milk)	1966	59.2% PCM, 17.5% soy flour, 15% NFDM, 5.5% soy oil, 2.8% vitamin-mineral premix.[d]
Instant CSM	1971	63% instant PCM, 23.7% soy flour, 5% NFDM, 5.5% soy oil, 2.8% vitamin-mineral premix.[d]
Instant sweetened CSM	1971	53% instant PCM, 27.5% soy flour, 7.35% sucrose, 5% NFDM, 5% soy oil, 2% vitamin-mineral premix, 0.15% vanilla flavor.
Soy-fortified cornmeal	1972	85% cornmeal, 15% soy grits.
CSB (corn-soy blend)	1973	67% PCM, 25% soy flour, 5% soy oil, 3% vitamin-mineral premix.

[a] According to Tollefson (1967), between 1957 and 1967 approximately 140 million tons was sold for U.S. aid programs.
[b] Product was tested in more than thirty countries, but never purchased under PL480.
[c] PCM = processed cornmeal, NFDM = nonfat dry milk.
[d] The original formulas for these products called for 64% PCM, 24% soy flour, 5% NFDM, 5% soy oil, and 2% vitamin-mineral premix. Present requirements were described by Bookwalter (1981).

Although soy flour and soy grits have been the main protein supplement used in PL480 products (alone or in combination with NFDM), other protein sources have been investigated. Cantor and Roberts (1967) described the use of fish protein concentrate in producing materials equivalent to CSM in protein efficiency ratio. They also discussed the possible use of amino acid fortification. Hayes et al (1978, 1983) examined the replacement of soy flour in both corn- and wheat-based products with both defatted cottonseed and peanut flours. Whey protein concentrate was also tested and eventually approved as a replacement for NFDM and for use in a whey-soy drink mix (Bookwalter, 1981).

RESULTS OF PL480 PROGRAM

The main thrust of the PL480 program has never been to continue indefinitely the donation of food products to less developed countries, but to provide a stop-gap measure until adequate agricultural and processed food products could be produced by local governments. However, this stop-gap program has been going on for over 30 years and will probably continue into the foreseeable future.

Nevertheless, the efforts expended in this and other programs have been quite fruitful. The author is aware of at least 60 different products developed by various companies, governments, and foundations, many of which are being sold directly to people or local governments by private industry (Anonymous, 1970). Products with such names are Areparina, BalAhar, Duryea, Incaparina, Modern Bread, Pronutro, Saridele, Superamine, Golden Elbow Macaroni, and Yoo Hoo are but a few of the cereal-based foods that have helped to relieve part of the hunger problem. Add to these the 15–20 fortified cereal products, plus the many other commodity-based foods sold to and distributed by the U.S. government, and one begins to get a picture of the total energy and resources spent in this area in the last 30 years.

TABLE VI
Quantities (million lb)[a] of Corn-Based Fortified Foods Sold to Government Agencies under PL480

Product	1970[b]	1974[b]	1977[c]	1979[d]	1980[d]	1981[d]	1982[d]
Cornmeal, enriched	···	···	···	0.3	8.1	57.4	54.3
Soy-fortified cornmeal	···	25.5	···	105.6	108.2	133.9	83.1
Corn-soy blend	···	191.6	···	7.3	···	2.4	2.0
Corn-soy-milk (CSM)	383.5	···	···	226.5	247.3	282.9	215.4
Instant CSM	···	40.7	···	65.3	82.4	70.7	45.6
Instant sweetened CSM	···	31.4	···	···	···	···	···
Totals	383.5	289.2	485.0	405.0	446.0	547.0	400.4

[a] Divide figures in this table by 2205 to convert to million metric tons.
[b] Data from R. J. Alexander, Creating new foods from corn and other grains, paper presented to A Workshop on Food Engineering, Texas A&M University, May 19–21, 1975.
[c] Unpublished data; no information available on specific products.
[d] Data from Bookwalter (1983); values converted from metric tons to pounds.

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[7] R. J. Alexander. Creating new foods from corn and other grains. Presented to: A Workshop on Food Engineering, Texas A&M University, May 19–21, 1975.

E. Nonfood Uses

The importance of nonfood or industrial uses of dry-milled corn products has grown rather dramatically in recent years. Data for 1977 (Table IV) suggested a total volume of 530 million pounds (0.24×10^6 t). This is much higher than the figures reported by Senti (1965), Senti and Schaefer (1972), or Alexander (1973), indicating a substantial growth in the pharmaceutical-fermentation area, products for the construction industry, and foundry and charcoal briquetting applications.

This growth is undoubtedly the result of research and product development activities conducted in the 1950–1975 period, which led to an increased demand for corn flour and modified corn flours made by a variety of methods, as suggested by Roberts (1967). It is also a result of the fact that corn flour is an inexpensive starch source and can be used interchangeably with the more expensive corn starch in a number of end uses. This trend has been accentuated by the cost of cereal products, which have doubled, and in some cases tripled, in the last 20 years.

Most of the specific nonfood applications have been covered to some extent in recent years by Brockington (1970), Alexander (1973), and Rankin (1982). Nevertheless, the main nonfood uses are briefly reviewed here with special emphasis on the more recent developments.

GYPSUM BOARD BINDERS

Acid-modified, dry-milled corn and sorghum flours have been the most common starch-based binders employed in the production of dry wall or gypsum board for a number of years. Traditional products have been described by Slotter (1952) and Wimmer and Meindl (1959). Chemically modified, acid-modified flours with improved properties have been described by Rankin et al (1963) and more recently by Ferrara (1976).

The acid-modified flours seem to be preferred in many gypsum board plants over related acid-modified starches because of both price advantages and differences in functional properties. Because of process differences, dry-milled flours have more residual soluble carbohydrates, which aid in the manufacture of gypsum board.

The starch-containing corn flour is gelatinized in situ during the manufacture of gypsum board; it functions by controlling the rate of water loss during drying of the board (Alexander, 1973). The soluble carbohydrates migrate to the surface and control the rate of crystallization of the gypsum, providing a strong bond between gypsum and liner.

OTHER BUILDING MATERIALS

Corn flours have also been used in a variety of applications associated with the building products or construction industry. These include insulation or fiber board (Naffziger et al, 1963; Alexander, 1973), plywood and related laminating adhesives (Senti, 1965), and compression-molded particleboard (Alexander and Krueger, 1976) and wafer board. They have also been used in ceiling tile, as edge pastes in gypsum board production, and as binders in gypsum-based taping compounds (Cummisford, 1973).

PHARMACEUTICAL FERMENTATION

As noted in Table IV, the largest volume of dry-milled corn products in the nonfood area was in the pharmaceutical-fermentation area. This volume was principally that of corn flour used in the production of citric acid and other pharmaceuticals by fermentation procedures. The large increase in volume between 1973 (Alexander, 1973) and 1977 was related to the price structure of competing starch-based ingredients during that time, as evidenced by the peak use of corn grits in brewing during the same period (Fig. 2). Based on the general decline of nonfood uses of dry-milled corn products in 1979 (Wells, 1979), use in this category today is probably less than 200 million pounds.

Fermentation of corn products is also employed in processes for making industrial alcohol, while grain neutral spirits and whiskey production generally use whole corn. The potential use of dry-milled corn products for the production of various corn-based sweeteners using enzymatic processes has never been economically feasible in this country because of the dominance of the corn wet-milling industry. In Europe, however, commercial processes have been developed and are summarized by Kroyer (1966).

FOUNDRY BINDERS

Although the market for cereal-based binders has been eroded over the past 30 years by a number of different products, particularly petroleum-based binder systems, precooked corn flours still command a sizeable percentage of foundry binders. These precooked flours are used particularly as core binders in a sand-cereal-linseed oil system, in which the flour serves as the primary binder before the core is baked (Alexander, 1973). It provides a so-called "green strength" to the core while it is being conveyed from the core room to the baking ovens. During baking, the linseed oil takes over as the primary binder.

Typical precooked corn flours described by Burgess and Johnson (1961), Farrel,[8] and Smith[9] compete with similarly processed sorghum flours (Stickley and Griffith, 1966), both manufactured with extrusion-cookers. Certain wet-milled, hot-rolled starches have also been used in this application (Kowall and Hadyn, 1960), although the extruded flours appear to be preferred (Wenninger, 1966; Caine and Toepke, 1969) in many core systems. Chemically modified products (Penny and Harrington, 1951; Sietsma, 1961; Fortney and Hunt, 1966) have also been prepared, with reportedly improved properties as foundry binders.

A totally new corn-flour-based core binder was recently described by Cummisford et al (1977), in which an acid-modified, extruded flour was combined with glyoxal, or related polyaldehydes, under certain conditions to provide a thermosetting resin. In this sytem, no core oil was needed, and the mixture of cereal flour and dialdehyde functioned as the binder for the sand particles both before and after drying in the core ovens.

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[8] R. Farrel. Extrusion equipment—Types, functions, and application. Presented to symposium: Extrusion: Process and Product Development. Central States Section, Am. Assoc. Cereal Chem., St. Louis, MO. Feb. 12–13, 1971.

[9] O. Smith. Why use extrusion? Presented to symposium: Extrusion: Process and Product Development. Central States Section, Am. Assoc. Cereal Chem., St. Louis, MO, Feb. 12–13, 1971.

CHARCOAL BRIQUETS

Corn flour has been reported (Senti, 1965; Alexander, 1973) as the primary adhesive or binder in the production of charcoal briquets. In 1977 (Table IV), the volume was still reasonably high at 75 million pounds. Very few, if any, significant technical advances or product improvements have been generated in this area in recent years, as evidenced by the lack of technical publications and patents. A brief discussion of the process used to make briquets is reported by Alexander (1973).

OTHER USES

Paper. Judging from the literature, the largest area of new product development among the various "other" uses of dry-milled corn products is in paper applications. This is a fairly logical extension of the research conducted in the wet corn milling industry, since the paper industry is the largest nonfood user of starch and modified starches. Several specialized applications within the paper area have been investigated.

The first area is that of wet-end additives used in the improvement of either dry strength (Russell et al, 1962; Jones et al, 1966) or wet strength through the use of cereal flour xanthates (Russell et al, 1962, 1964). Dry-milled flours have also been used in fiber board produced from waste paper (Alexander, 1973) and as a surface size in Kraft liner board.

Another application area is that of cationic corn flours useful in improving both dry strength and pigment retention. Modified corn flours made with tertiary amino- or quaternary ammonium-etherifying agents were claimed by Alexander and Cummisford (1971). Several authors have described the preparation and properties of cereal flours treated with ethylenimine (Rankin and Russell, 1970; McClendon and Berry, 1973; McClendon, 1974), a reagent first reported by Kerr and Neukom (1952) for modifying corn starch.

The last area is that of surface sizing of paper, which has usually required an acid modification of the starch-based material. Processes for the dry acid modification of cereal flours have been reported by Rankin et al (1963, 1964) and Lancaster and Griffin (1965). Further improvements in surface sizing properties can be accomplished by treating the acid-modified flour with ethylene oxide, as described by Rankin et al (1973).

Because of paper industry requirements, significant quantities of corn flour are probably not being used in paper applications today. The demand for high-brightness papers as well as starch sizes and adhesives with low levels of sludge (usually after enzyme conversion) preclude the use of yellow corn flours containing as much as 10% nonstarch components.

Corrugating Adhesives. A number of special processes for making corrugating adhesives from corn flours have been reported. Wimmer (1959a) used corn flour plus sodium chloroacetate in the carrier portion of the adhesives to make an improved product. Horner (1961) described the use of waxy starch or flour in the carrier in combination with a cereal flour, preferably from sorghum, to produce a nonthixotropic adhesive. A more recent process (Fortney and Hunt, 1966) employs fine-grind corn flours with a special granulation profile to produce a superior adhesive. The author is aware of at least one corrugating plant that was using corn flour made according to this latter patent, although the quantities of flour employed today are not known.

Adhesives (General). The potential use of corn flour and modified corn flours as general starch-based adhesives has been described by several investigators. Rankin and Mehltretter (1959), Rankin et al (1959), Smith et al (1962, 1969), and Alexander (1974) have prepared chemically modified flours with excellent viscosity and adhesive characteristics. Waggle (1971) claims a process for producing a modified cereal flour useful in pelletizing animal feed. Bailey[10] suggests the use of corn flour as an adhesive for bag bottoms, and Senti (1965) indicates its utility in laminating adhesives. Other adhesive uses were discussed earlier in this chapter.

Ore Refining. Although Senti (1965), Senti and Schaefer (1972), and Wells (1979) have suggested that as much as 60 million pounds of corn flours have been used in ore-refining operations, Alexander (1973) has indicated that this quantity of flour is probably derived from sorghum rather than corn. The author is aware of three companies that sold unrefined sorghum flours for the beneficiation of aluminum ore (bauxite) during the 1960s and 1970s. Such products and processes have been patented by Jones (1960). Also, extruded sorghum flours have been patented as binders in pelletizing iron ore (Stickley et al, 1964).

Oil Well Drilling. This is one application area for corn flours that has definitely increased in volume since the market statistics reported in 1965 (Senti) and 1973 (Alexander) and since the 1977 estimates in Table IV. Although domestic use of crude oil was on a steady incline until the formation of OPEC in 1973–1974, the drilling of new wells in this country was on steady decline until 1979. In June of 1979, President Carter deregulated the price of domestic crude oil and natural gas. This created the setting for the biggest drilling boom in history and the need for increased quantities of precooked starch-based materials.

The total market for precooked starch for oil drilling uses increased to nearly 120 million pounds in 1981. About 40%, or 50 million pounds, was corn-flour-based materials. In 1982–1983, the number of new wells dropped considerably as a result of the recession, combined with a surplus of petroleum-based products. The volume today is thought to be around 30 million pounds.

In the oil-well-drilling application, the precooked starch or flour functions to minimize water loss in the drilling mud. The mud cools and lubricates the drill bit, suspends and removes the cuttings from the bottom of the hole, and coats the hole with an impermeable layer. It also controls subsurface pressures in the hole, supports part of the weight of drill pipe and casing, and minimizes adverse effects on the formation adjacent to the hole.

The precooked flours used in this application have been produced using either drum dryers or hot rolls (Roemer and Downhour, 1970a, 1970b) or extrusion-cookers (Bradley and Downhour, 1970; Roemer and Downhour, 1970a, 1970b). Chemically modified flours, such as described by Smith et al (1962, 1969), have been suggested to be improved agents for decreasing water loss because of their increased water-holding capacities. In extremely deep holes, where mud temperatures in the 200–300° C range are reached, corn flours (Wimmer, 1959b) or starches (Hullinger, 1967) that have been crosslinked are preferred.

Thermoplastics and Polyurethanes. A number of different corn-flour-based

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[10] See footnote 3.

products have been developed for use with petrochemical-based synthetic polymers. Russell[11] discussed the use of flours as extenders in polyvinyl alcohol and polyvinyl chloride films used as agriculture mulches. Cereal flours have also been used as polyol-extenders in rigid polyurethane foams (Bennett et al, 1967), in flexible polyurethane foams (Hostettler, 1978), and in polyurethane resins (Otey et al, 1968), which can be molded and machined into furniture parts and the like. In certain polyurethane foams (Anonymous, 1967; Bennett et al, 1967), the flour appears to function as a fire-retarding agent as well as an extender.

Miscellaneous. A number of other minor uses for dry-milled corn products have been reported, including explosives, carriers for vitamins in animal feeds and for certain pesticides, and abrasive agents in industrial hand soaps (Alexander, 1973); as textile sizes (Rankin et al, 1963); and as a dry carrier in solvent-based dry cleaners.[12]

F. By-Products and Animal Feed

As indicated in Section II of this chapter, the various by-product streams from the corn dry-milling process are most frequently combined to produce a single by-product known as hominy feed. The volume of this product, the largest for the products sold by the dry corn millers, is annually about 2.2 billion pounds (Brekke, 1970a; Alexander, 1973). This material competes with similar corn by-products, such as corn gluten feed and spent brewer's grains (Shroder and Heiman, 1970), as ingredients in animal feed. This area has been the subject of fairly comprehensive reviews (Morrison, 1959; Smith, 1959; Shroder and Heiman, 1970; Ensminger and Olentine, 1978) and is not reported here in any detail.

Hominy feed provides the U.S. feed industry, as well as numerous countries throughout the world, with an inexpensive, high-fiber, high-calorie ingredient. The material is high in carotenoids (the yellow pigments in corn) and in vitamins A and D. The high carotenoid content is particularly desirable in chicken feed for providing eggs with bright yellow yolks.

In recent years, a number of investigators have taken a close look at alternative, potentially more profitable uses for some of the by-product streams, in particular, corn bran and oil-free corn germ. Corn bran has been of particular interest because of its potential as a source of dietary fiber (Wells, 1979). One researcher (DuVall, 1982) incorporated dry-milled corn bran of a certain specific particle size into an extruded, high fiber, corn-based breakfast cereal. At least one dry-milled product (Anonymous, 1977; Tabor Milling Company, 1977) was introduced as a high-fiber ingredient for food applications. Others (Alexander and Krueger, 1978) have taken advantage of corn bran's superior water absorption properties in providing an extender-viscosifier for use in urea-formaldehyde plywood adhesives.

Oil-free, dry-milled corn germ, especially that produced by hexane extraction, is a good source of high-quality protein (Blessin et al, 1972, 1973; Garcia et al, 1972), plus a fairly good source of dietary fiber. Such material has recently received considerable attention as an ingredient in protein-fortified cookies (Blessin et al, 1972, 1973; Tsen 1976), bread (Tsen et al, 1974), and other food products, such as corn muffins and meat patties. At least one dry corn milling company reportedly produced pilot plant quantities of a corn germ flour for evaluation during the mid-1970s. The current status of this venture is not known.

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[11] C. R. Russell. Cereal starches and flour products as substitutes and extenders for petroleum-based polymers and plastics. Presented to: American Corn Milling Federation meeting, Northern Regional Research Laboratory, Peoria, IL, June 1975.

[12] See footnote 3.

By the use of alkaline extraction and dialysis techniques, Nielsen and coworkers (1973, 1977) prepared protein isolates from oil-free corn germ. Products with nutritionally valuable amino acid profiles for potential fortification of food products were described.

Typical analyses of the various by-product streams are shown in Table VII. Composition of hominy feed can vary somewhat depending on whether the corn miller incorporates germ cake into the feed, sells corn germ to another company that processes germ, or finds other ways of upgrading the various streams.

V. FUTURE OF CORN DRY MILLING

Considering the current situation with corn dry milling, it is somewhat difficult to predict what will happen to the industry in the next 10–15 years. On the negative side, the industry has not really grown in recent years. The amount of corn processed by dry millers in 1977–1982 (Anonymous, 1982) is about the same as that reported by Brekke (1970a) for the 1965–1969 period, or about 120–140 million bushels ($3.0–3.5 \times 10^6$ t). Increases in product volumes achieved in certain food and nonfood applications have been offset by decreases in brewing.

On the positive side, some new developments, especially in the food area, could lead to increases in the near future. One area of particular importance has been that of ethnic foods, specifically Mexican and Latin American food products. The number of alkali-processed corn products in both the supermarket and the fast-food and Mexican food restaurants has definitely shown an increase. New corn mills devoted exclusively to the production of masa flour (Rice, 1983) have been built since 1980, and masa flours produced by

TABLE VII
Typical Composition (%, as-is basis)
of Dry-Milled Corn By-Product Streams[a]

Component	Standard Meal	Corn Germ[b]	Corn Bran	Hominy Feed
Moisture	14.0	9.6	10.0	13.5
Protein	11.0	15.8	8.0	8.0
Fat	4.5	23.8	4.5	3.4
Crude fiber	2.5	5.7	12.0	4.7
Ash	2.0	6.7	2.5	2.0
Starch	60.0	18.4	35.0	61.0
Other polysaccharides	6.0	20.0	28.0	7.4

[a] Except for hominy feed, the product streams normally do not exist as separate finished products but are combined with broken corn and subsequently dried and hammer milled together to produce hominy feed.

[b] Represents composition before oil expelling or extraction.

traditional dry millers have been described in recent years (Wimmer and Sussex, 1968; Anonymous, 1984a).

Although the use of corn products in more traditional food applications has probably declined, the production of processed corn flours has increased. As discussed earlier, this is in large part the result of the use of extrusion-cookers, which has resulted in increases in the snack food, fortified food, and specialty breakfast food areas. Nonfood areas, such as foundry binders and oil well drilling, have also benefited from the use of extrusion.

The author's prediction is that the industry will remain fairly static during the next 10–15 years, with increases in food uses being counterbalanced by decreases in brewing. The industry will probably grow at about the same rate as the population.

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CHAPTER 12

WET MILLING: PROCESS AND PRODUCTS

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I. INTRODUCTION

Corn is abundant and relatively low in price; it has a high starch content an protein of acceptable quantity and quality. Hence its primary use is for anima feed. It is also useful for processing into valuable food and industrial products such as ethyl alcohol by fermentation, cornmeal by dry milling, and highl refined starch by the wet-milling process. The greatest volume is processed b wet milling to produce starch products (Chapter 16) and sweetener products fo foods (Chapter 17). Nonfood products such as industrial starches, corn glute feed, and corn gluten meal are also manufactured.

The wet-milling process involves an initial water soak under carefull controlled conditions to soften the kernels. The corn is then milled and it components separated by screening, centrifuging, and washing (Fig. 1), to produce starch, oil, feed by-products, and sweeteners (by starch hydrolysis). Applications for these products have shown steady growth, which ha necessitated major investment to expand production facilities in recent years.

II. THE PROCESS

A. Steeping

The first critical step in the wet milling of corn is steeping—the soaking of the corn in water under controlled processing conditions of temperature, time, sulfur dioxide (SO_2) concentration, lactic acid content, etc. These conditions have been found necessary to promote diffusion of the water through the tip cap of the kernel into the germ, endosperm, and their cellular components. Steeping softens the kernels, facilitating separation of the components.

Corn is shipped in bulk to the wet-milling plants by truck, hopper car, and barge. It is then cleaned on vibrating screens to remove coarse material (retained on 12.7-mm [1/2-in.] openings) and fine material (through 3.18-mm [1/8-in.] openings). These screenings are diverted to animal feed. If they are allowed to remain with the corn, they cause processing problems such as restricted water flow through steeps and screens, increased steep liquor viscosity, and quality problems with the finished starch.

Steeping is accomplished by putting corn into tanks (steeps) that have a capacity of 50–330 t (2,000–13,000 bu) each. The corn is then covered with steepwater, heated to 52°C (125°F) and held for 22–50 hr. Steeps have cone bottoms with screens so that the water can be separated from the corn and pumped elsewhere or recirculated back into the top of the steep. To maintain steeping temperature, the recirculated flow is heated with steam directly by sparge injection or indirectly by using a heat exchanger. The water should not exceed 55°C (131°F) to avoid destroying the bacteria needed to produce lactic acid.

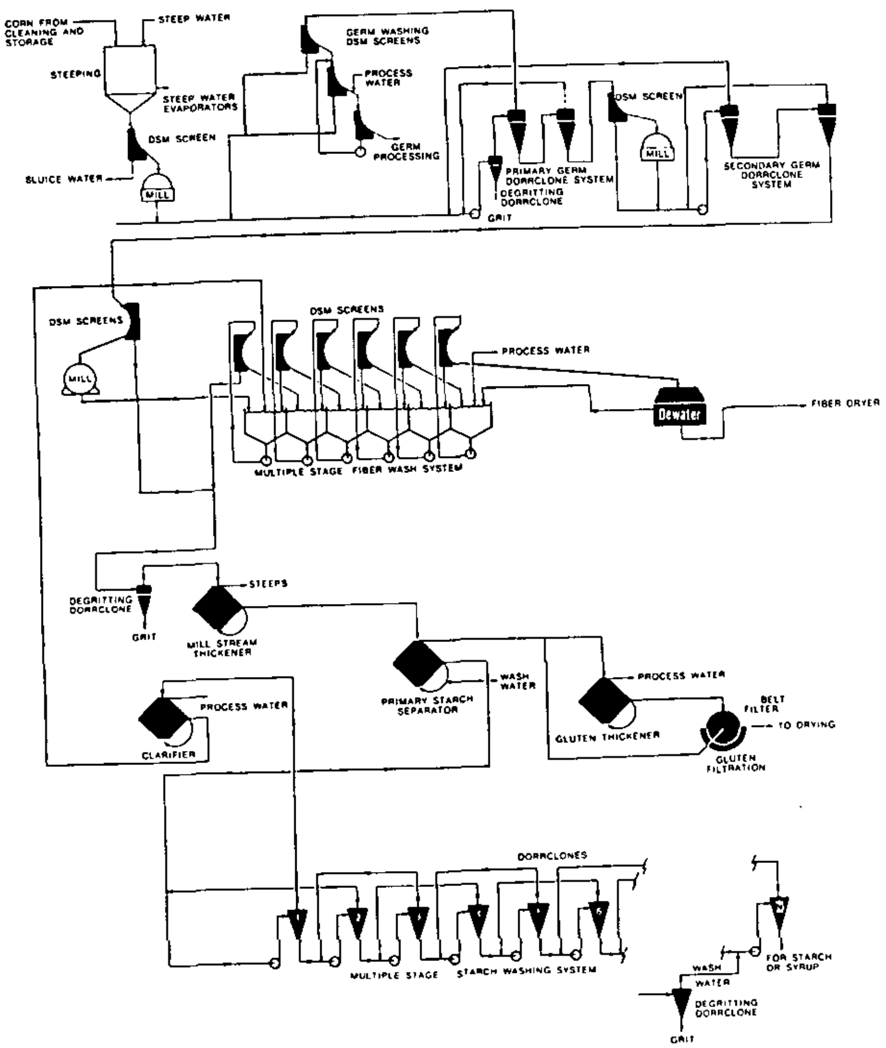

Fig. 1. Wet-milling process flow diagram, showing equipment arrangement for the separation of the major components—steepwater, germ, fiber, gluten, and cornstarch. (Courtesy Dorr-Oliver, Inc., Stamford, CT)

Steeping is a countercurrent system, utilizing a battery of six to twelve or more steep tanks. Steeps are filled one at a time as they become empty. The corn does not move—just the water, which is transferred from one steep to the next. However, steeping is accomplished in one plant by continuously adding dry corn at the top of the steep while continuously withdrawing steeped corn from the bottom (Randall et al, 1978).

Water for the steeps originates in the wet-milling process, where it accumulates corn solubles. It is treated with SO_2 to a concentration of 0.12–0.20%. The SO_2 is purchased as a liquid or manufactured on-site by burning elemental sulfur. The SO_2 increases the rate of water diffusion into the kernel and assists in breaking down the protein-starch matrix, which is necessary for high starch yield and quality.

The SO_2-treated water is added to the steep containing the oldest corn. As the water is advanced from steep to steep, the SO_2 content decreases and bacterial action increases, resulting in the growth of lactic acid bacteria. The desired lactic acid concentration is 16–20% (dry basis) after the water has advanced through the system and been withdrawn as light steepwater. Meanwhile, the SO_2 content drops to 0.01% or less.

The volume of water available for steeping is normally 1.2–1.4 m^3/t of corn (8–9 gal/bu). About 0.5 m^3/t (3.5 gal/bu) is absorbed by the corn to increase its moisture from 16 to 45% during the steeping. The remaining 0.7–0.8 m^3/t

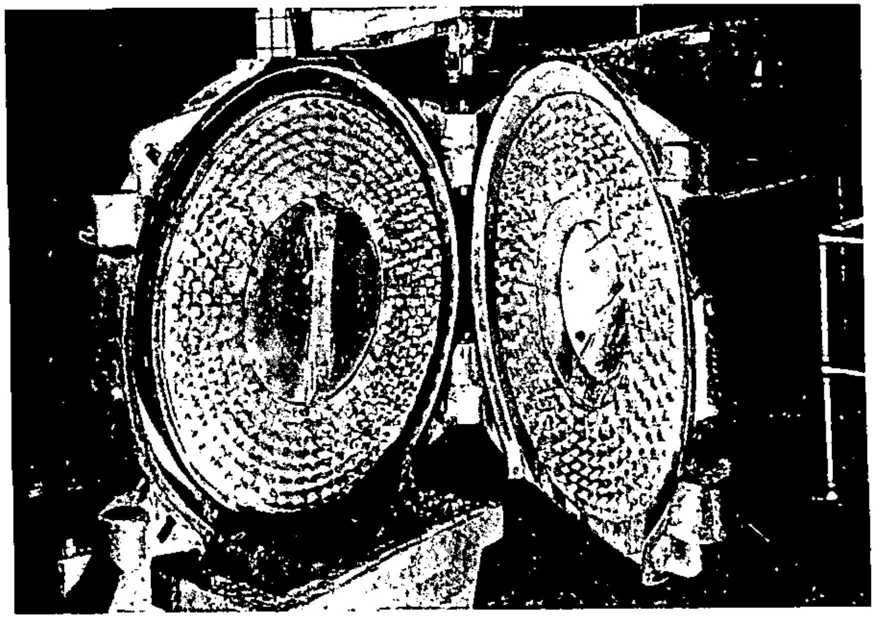

Fig. 2. Degerminating mill opened up to show the knobby disks. Feed enters the center portion. One disk rotates while the other remains stationary. (Courtesy Dorr-Oliver, Inc., Stamford, CT)

(4.5–5.5 gal/bu) is the *quantity withdrawn from the steeping system*. This water contains the solubles soaked out of the corn, which is 0.05–0.06 t of solids per tonne of corn processed (2.8–3.6 lb of solids per bushel). It is evaporated to 40–50% solids, mixed with corn fiber, dried, and sold as corn gluten feed. Watson (1984) gives an in-depth presentation of the chemistry associated with the steeping process.

B. Separation of Kernel Components

GERM

A water sluice system is generally used to transport steeped corn from the discharge of a steep tank to a surge bin. The water used for transportation is screened out of the corn before the corn is put into the bin and is returned to sluice more corn. The required volume is 4.5–6.0 m^3/t of corn grind (30–40 gal/bu). Dewatered corn is metered from the wet corn bin into coarse grinding mills having one stationary and one rotating disk (Fig. 2). The disks have knobs that break up the corn kernel. Clearance between the disks is adjusted so that a few whole kernels but few broken germs are in the mill discharge. Some dilution water is added to the mill feed, as well as to the mill discharge. *The diluted slurry* from the mills is pumped to flotation tanks or hydroclones (Fig. 3), where the oil-bearing germs are floated off the top. These are routed to a series of 50° wedge-wire screens (Fig. 4) that are used to wash the germs, with the addition of 1.2–1.3 m^3 of wash water per tonne of corn (8–9 gal/bu) (Anderson, 1970; Watson, 1984). The recovered *germs are then dewatered in* screw presses, dried, and further processed to recover the corn oil.

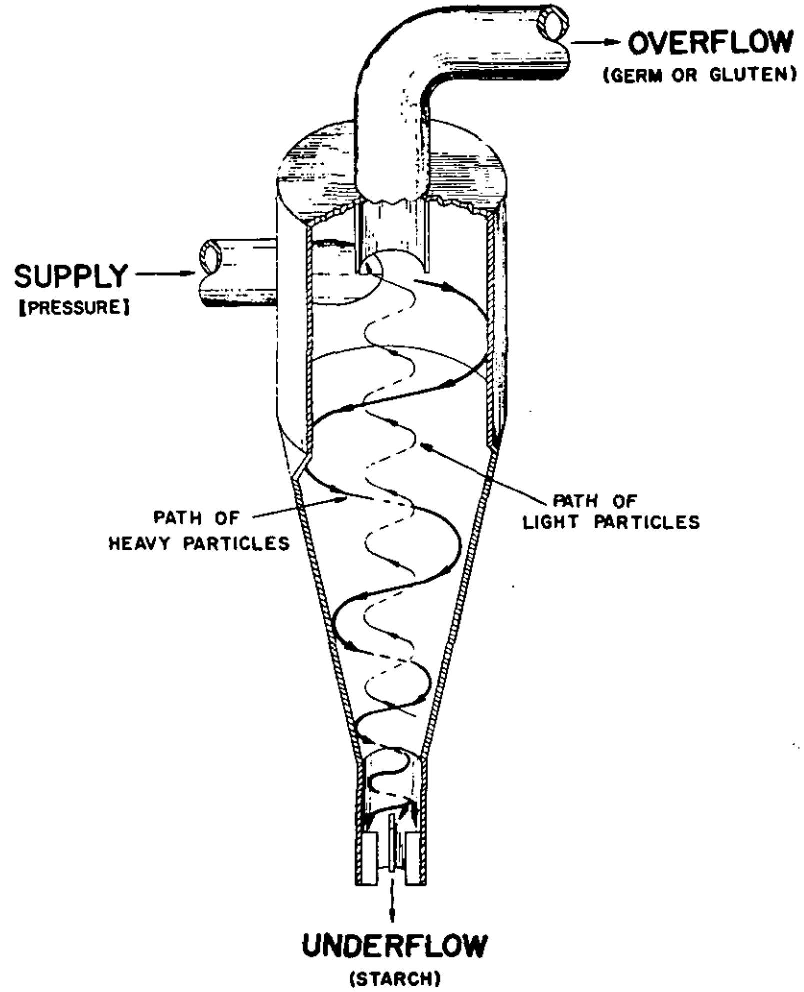

Fig. 3. Cutaway diagram of hydroclone separator. (Reprinted, with permission, from Watson, 1984)

The water-starch slurry from the germ wash is used to dilute the milled corn slurry being fed to the germ separation step. Other dilution water may also have to be added because the carrying medium must be carefully controlled within an optimum range of 15–17% *solids for optimum germ recovery. The carrying* medium is the corn slurry, with the fiber screened out for density measurement. Banks of hydroclones (Fig. 5) that are 150–200 mm (6–8 in.) in diameter are now preferred over flotation tanks because they are easier to control and more sanitary than the open-vat flotation system. This operation is controlled to obtain *germ purity of 45–50% oil in washed, dried germs and* optimum germ recovery by adjusting the overflow rate from the separation equipment. The lower the flow, the higher the oil content, but fewer germs are recovered and oil yield is reduced.

The underflow material from the flotation tanks or hydroclone separators is usually passed through a second disk mill with closer *adjustment to release more* germs with a second separation, which usually duplicates the first separation. The freed germs are routed back to the first germ separation for final recovery. The germ recovery flow system is diagrammed in Fig. 1.

FIBER SEPARATION

After germ separation with flotation or hydroclones, the corn slurry is screened, using 50 μm, 120° wedge-wire (Fig. 4) to separate fiber (mostly

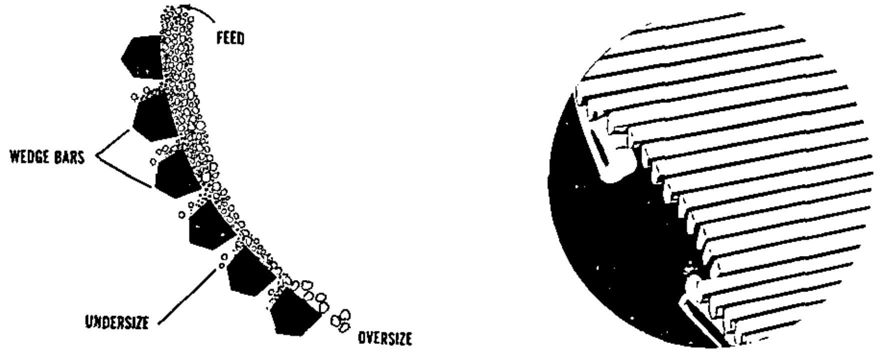

Fig. 4. Simulation of unique slicing action of wedge-bar screen surface. (Courtesy Dorr-Oliver, Inc., Stamford, CT)

pericarps) from the starch and gluten. About 30–40% of all the starch is separated out and routed to mill starch.

The remaining stream includes fiber with some attached starch. Entoleter mills that sling the material against pins at high speed are used to free the starch with minimum fiber breakup (Fig. 6). Counterrotating disk mills are also used, in which the disks turn at 1,500–1,800 rpm in opposite directions (Fig. 7). Recently developed mills, 1.3 m (50 in.) in diameter, with only one disk rotating at 1,800 rpm and with 800–1,000 connected horsepower are being used for capacities as high as 1,269 t (50,000 bu) of corn milling per day. All the disk mills have knoblike protrusions or grooves that are capable of reducing the percent of starch bound to the fiber from 35% to 5–15% with minimum attrition of the fiber.

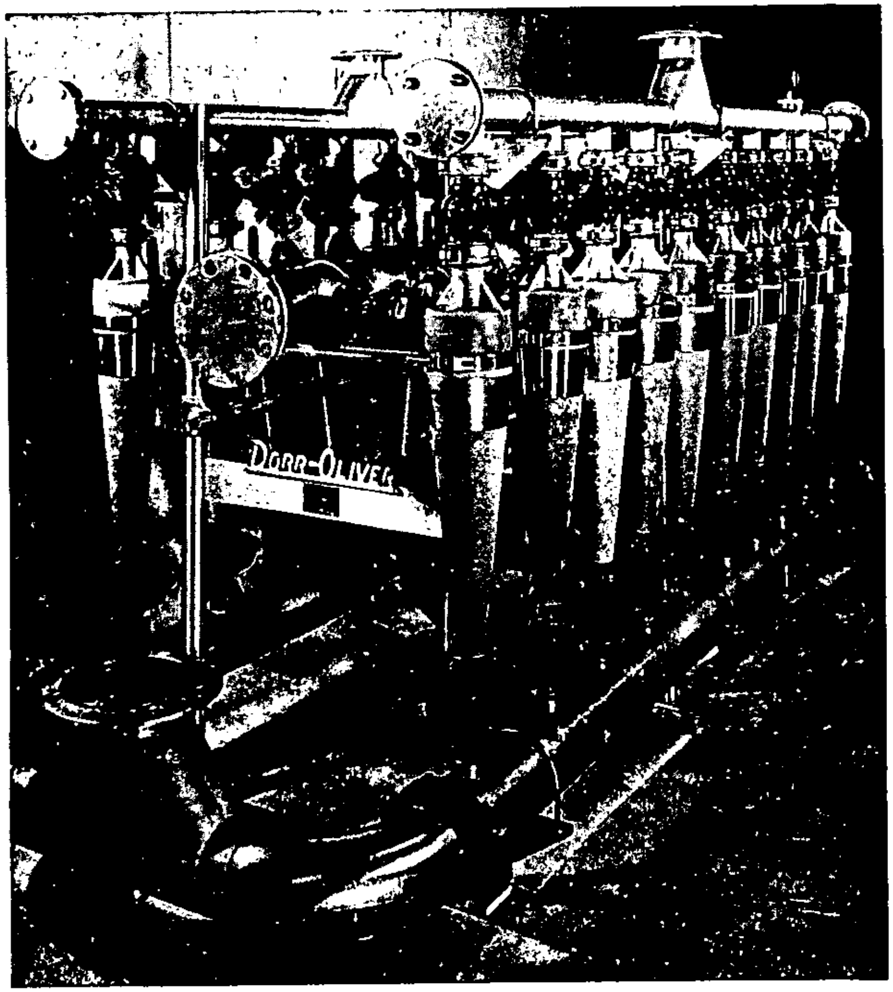

Fig. 5. Battery of hydroclones used for separation of germs from milled steeped corn. (Courtesy Dorr-Oliver, Inc., Stamford, CT)

The milled slurry is then washed and screened to separate the starch from the fiber. The most common washing equipment consists of 120° wedge-wire screens with five to seven separate stages operating in series (Figs. 1 and 4). Wash water, about 1.8–2.1 m^3/t of corn (12–14 gal/bu), is introduced ahead of the last stage, where it flows countercurrent to the fiber, finally emerging from the first stage with its accompanying starch and then being routed to mill starch. Wedge-wire screens (50 μm) have been found satisfactory for the first washing stage, and 70-μm screens can be used effectively on other stages. Screens must be thoroughly washed frequently to maintain good performance. Each stage has a separate pump and tank. Large compartmented tanks are also used. The design is such that water can cascade from one level to another as required to reduce the need for automatic controls.

Washed fiber from the last wash stage is only 10% solids, 15% at maximum. Further dewatering is necessary and is accomplished by mechanical means. Solid bowl centrifuges have been used to attain 40% solids. A disadvantage is poor starch recovery because all the free starch goes with the fiber to the feed. All other types of equipment have screens or bar spacings, allowing starch to escape with the water that is being forced out. This starch is recovered by recycling the flow upstream.

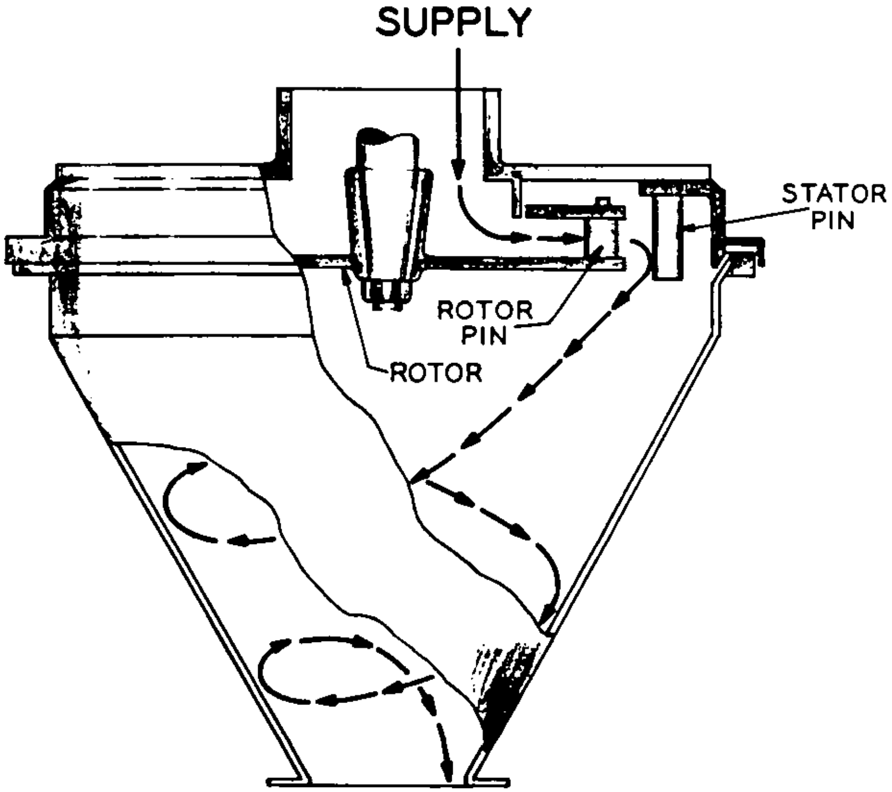

Fig. 6. Cutaway diagram of Entoleter mill used for fine milling of degerminated residue. (Reprinted, with permission, from Watson, 1984)

Dewatering is commonly done in two steps. The first is with screen centrifuges or screened reels to increase the solids to 20–30%. The advantage is greater capacity and somewhat drier cake from the second step, which utilizes screw presses (or recently introduced horizontal belt presses). Final dryness achieved is in the 42–48% range. The dewatered fiber is mixed with evaporated steepwater, and then normally dried and sold as corn gluten feed. Efforts are being made to expand sales for the wet feed.

The performance of the fiber system is frequently affected by the percentage of fine fiber present. Fine fiber is pulpy and washes (screens) poorly, resulting in wet fiber with a high starch content. The fine fiber is generally created by intensive milling, which is done to dislodge as much starch as possible. Frequently, milling is reduced somewhat to reach a compromise between starch recovery and dewatering performance. This problem is more commonly associated with plants that use disk rather than pin mills.

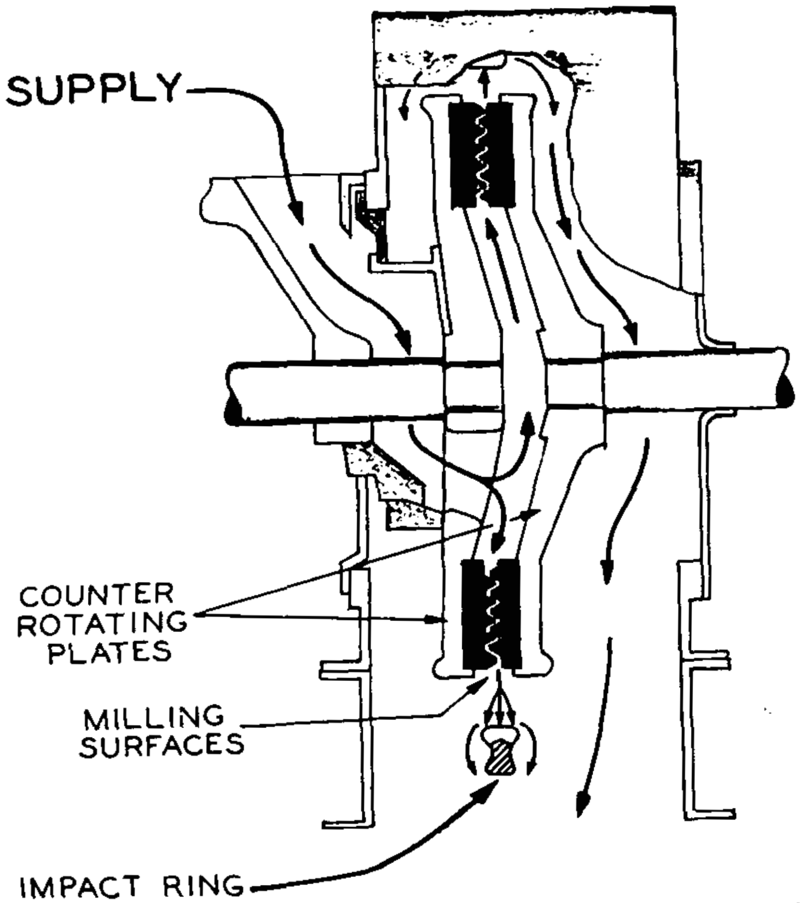

Fig. 7. Cutaway diagram of Bauer attrition mill for fine milling of degerminated residue. It is also used for degermination (first break) milling, with one rotor fixed, reduced rpm, no impact ring, and wider spacing of interlocking teeth. (Reprinted, with permission, from Watson, 1984)

PRIMARY STARCH SEPARATION

After the germs and fiber have been screened from the ground corn, only high-protein substances, gluten and corn soluble impurities, remain with the starch slurry. The gluten is separated from the starch by taking advantage of its lower density (1.06, in contrast to 1.6 sp. gr. for starch). Disk-nozzle types of centrifuges designed to separate the insoluble gluten particles by classification are used to obtain high-protein gluten (>68% total protein, solids basis).[1] This high protein level is necessary to meet finished product specifications. Some protein and impurities stay with the starch stream, which is further processed in the subsequent starch washing step.

The gluten from the primary centrifuge is dewatered with other disk-nozzle centrifuges to increase solids from 3 to 12%, then vacuum filtered to 42% solids, and finally dried to 88% solids. This corn gluten meal is sold for animal feed formulations (Chapter 15). The water separated from the dewatering operations is used as wash water in the wet-milling process.

Equipment used to dewater gluten, besides rotary, cloth-belt, vacuum filters, are plate-type pressure filters (used where labor costs are low) and solid bowl centrifuges. The dewatering ability of the centrifuge is increased by such means as heating the feed and raising its pH from the normal level of 4.5 to as high as 7.0 pH.

STARCH PURIFICATION

Starch from the primary centrifuges contains 3–5% protein. It is washed with water in countercurrent fashion, using hydroclones 10 mm in diameter that are grouped into clusters and enclosed in housings capable of holding as many as 720 cyclones. These units are then arranged into 10–14 separate stages operating in series (Fig. 8). The installations are compact and sanitary, have no moving

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[1] Throughout this chapter, percent protein = percent nitrogen × 6.25.

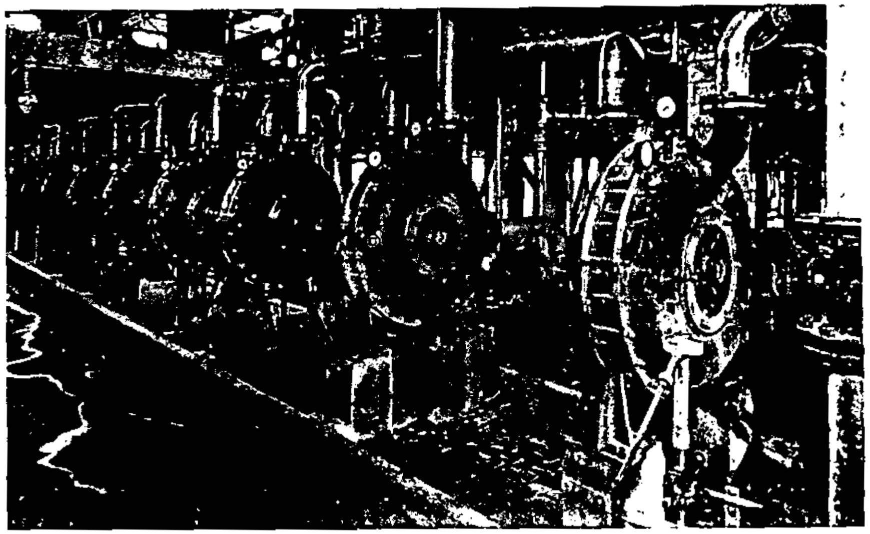

Fig. 8. Hydroclone starch washing-separating units. Each clamshell contains as many as 480 individual hydroclone tubes 10 mm in diameter. (Courtesy Dorr-Oliver, Inc., Stamford, CT)

parts (except pumps), and are easy to automate. They replace the tables, centrifuges, and vacuum filters previously used for this operation.

About 2.1–2.5 kg of fresh water per kilogram of dry starch is used to wash out the soluble impurities in the starch; the hydroclone action separates out the remaining insoluble gluten. The washed starch can be expected to contain 0.3–0.35% total protein and 0.01% soluble protein. These results are attainable with normal dent corn and conventional steeping, milling, screening, centrifuging, and washing.

The water used for starch washing is generally deionized. It can be supplemented with a suitably pure condensate; condensates such as that from the steepwater evaporator, which can impart off-flavor to finished sweeteners, are not used. The water is heated for optimum soluble removal. The temperature is limited to 38–43°C (100–110°F). The lower temperature is now more prevalent because more stages of hydroclones are being used and more heat is generated from the additional pumps. Temperature sensors in the hydroclone systems keep temperatures well below the starch slurry pasting temperature of 63°C (145°F).

The wash water enters the washing system at the last stage, where the washed starch is exiting. The water and impurities leave the system at the first stage, along with about 25% of the starch being fed in. This stream, termed "middlings," contains solubles and gluten but is predominantly very small starch granules, some of which may have some protein attached. The middlings are generally concentrated in centrifuges, and the underflow is recycled back to the primary separation. The overflow water removed by the centrifuges is low in solubles and ideally suited for use as wash water for the primary separation.

C. Corn Varieties Processed Commercially

Normal dent corn is the predominant corn processed. Its starch has 27% amylose, a linear glucose polymer, and 73% amylopectin, a branch-chain glucose polymer.

The proportion of these fractions is constant in the starch recovered from any single variety of normal dent corn. Flint corn, a variety of normal corn grown in South America, is processed successfully even though it does not soften much, even with 50–60 hr of steeping. Its starch yield is slightly less than is regular, but its quality is good and the amylose-amylopectin ratio is the same as that of normal dent corn. No flint corn is processed in the United States.

Waxy corn, a genetic mutant, contains starch composed entirely of amylopectin. It can be processed in the same way as regular corn, with minor adjustments. The pasting temperature of the starch is lower, so the process must be cooler by about 3°C (5°F). Separation of the starch and gluten is easier, but the starch yield is only 90% of that of regular corn. About 1.5% of the corn processed by wet milling in the United States is the waxy type. The starch may be somewhat more difficult to filter because of the presence of a small amount of phytoglycogen (Freeman et al, 1975).

Another genetic mutant variety that is processed commercially is high-amylose corn, with starch that is 60–70% amylose. Like waxy corn, it commands a premium price, because the farmer must grow it in fields isolated from other varieties to prevent cross-pollination and then handle it separately after harvest to avoid contamination (Chapter 2). Unlike the lower temperature for waxy corn, the processing temperature should be 3°C higher than that for regular corn. More steep time is required, starch-gluten separation and starch filtration are more difficult, and the starch yield is only 80–90% of that of regular corn. Careful attention is necessary to prevent high-amylose starch from contaminating the regular variety because it affects syrup and starch quality (for instance, it is difficult to "paste"). Only about 0.2% of the corn wet milled in the United States is the high-amylose variety. Unique properties of the cornstarch from these genetic varieties are discussed in Chapter 16.

D. Feed Production Process

STEEPWATER EVAPORATION

Solubles extracted from the corn during steeping are routed to evaporators, where 0.6–0.7 m^3 of water per tonne of corn (4.0–5.0 gal/bu) is removed to increase the solids from 5–10 to 40–50%. The solids are then mixed with corn fiber and processed into corn gluten feed (see Chapter 15).

Falling-film recirculating evaporator systems are used to increase the light steepwater solids to 30%, using steam at a pressure of 1.2 kg/cm^2 (17 psia) or less (Fig. 9). Multiple effect design, in which 1 kg of steam can evaporate several

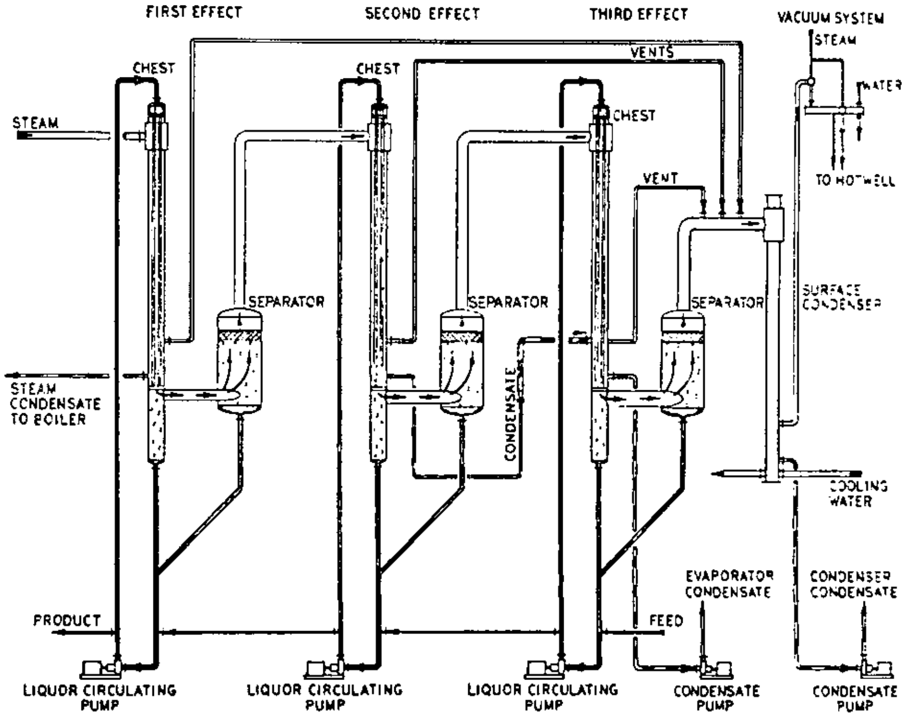

Fig. 9. Falling-film evaporator with continuous recirculation for each of its three effects. (Courtesy Dedert Corp., Olympia Fields, IL)

kilograms of water, is necessary to minimize energy costs. Energy can be further reduced with mechanical recompression, which completely recycles the vapors, compresses them, and discharges them into the evaporator steam chest (Fig. 10). Efficiencies of 167 kcal/kg (300 btu/lb) of evaporation for quadruple-effect steam evaporators can be reduced to 17–28 kcal/kg (30–50 btu/lb) at the expense of high capital investment. Compressors are radial-flow centrifugals with mechanical efficiencies in the 75% range. Electric motor drives are conventional, but steam-driven turbines are also used.

Forced-circulation multiple-effect steam evaporators are used to increase solids to 50%. These units differ from the falling-film design in that 7–11 m^3/hr (30–48 gal/min) of the steepwater is recirculated per tube instead of 0.7 m^3/hr (3 gal/min). (Tube sizes generally used are 38 mm [1.5 in.] in diameter and 3.7–9.1 m [12–30 ft] in length.) Evaporators must be boiled out with alkali to remove a proteinaceous coating that increases in thickness with time, primarily on the heating surfaces. Biweekly boilouts are common for falling-film, monthly for forced-circulation evaporators.

Condensate from the evaporators is very corrosive, about 3.0 pH, and contains condensed organic volatiles and alcohols that require extensive waste treatment before disposal.

FEED DRYING

Corn gluten feed is produced by mixing wet corn fiber with evaporated steepwater and drying to 8–11% moisture to give a finished product of 21% protein content. Corn cleanings and defatted corn germ meal are frequently added. Various types of dryers are used, such as direct-fired rotaries with inlet temperatures of 300–700° C (572–1,292° F) and outlet temperatures of 65–145° C (149–293° F). Rotary steam tube dryers are also effective, provided enough product recycling is used to keep the material from adhering to the tubular heating surfaces.

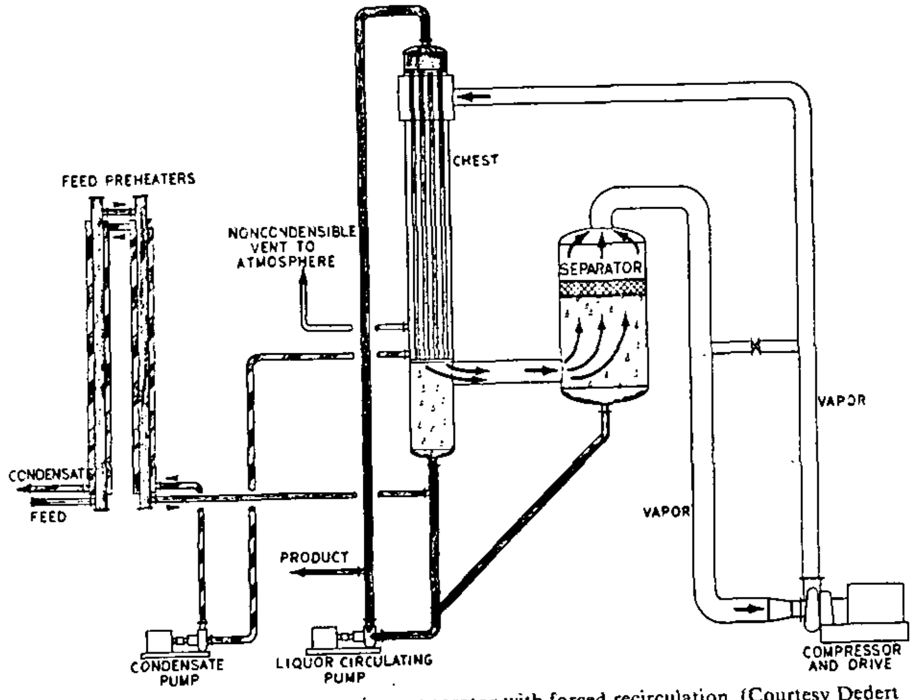

Fig. 10. Mechanical vapor recompression evaporator with forced recirculation. (Courtesy Dedert Corp., Olympia Fields, IL)

The dried feed is cooled to 43° C (110° F) to make it friable for milling. Pneumatic cooling-conveying systems are used in small facilities. Rotary coolers are used in the larger plants. Air, with either concurrent or countercurrent flow, is effective with 30–50% of the cooling, due to the evaporation of 1–2% moisture from the feed. Rotary water tube coolers are also utilized.

Standard swinging hammer mills with screens that have 3–8 mm (1/8–5/16 in.) openings are used to reduce the particle size of the feed. The ground feed can be sifted to assure that it meets the specifications of being finer than 12 U.S. mesh but no coarser than 10% through 100 U.S. mesh. Feed is sometimes cooled further to avoid caking and self-heating in storage and in transit, especially in hot, humid areas.

Most gluten feed manufactured in the United States is pelleted to increase its density and improve its handling characteristics for shipment to the European Economic Community. Requirements for making good pellets are proper feed moisture, small particle size, steam conditioning, pellet dies of 6–10 mm (1/4–3/8 in.) diameter, energy input (20 connected horsepower per ton of feed per hour), and cooling to 38° C (100° F).

GLUTEN DRYING

After the gluten has been dewatered as much as possible by mechanical means (to 55–60% moisture), it is dried in direct-fired, flash or rotary dryers to 12% moisture. Product recycling is necessary to overcome the sticky nature of the wet gluten. Drying temperatures should be limited to 400° C (752° F) to avoid a dark-colored product, burnt particles, and offensive odor and haze in the dryer exhaust. The rotary dryer has the advantage of making a product that is not considered dusty, whereas the flash dryer product is less dense and has the advantage of brighter color due to less dryer retention time. The natural golden pigmentation, xanthophyll, is important to poultry feeders. The pigment can be destroyed by excess dryer heat but may be partially protected by the introduction of heavy steepwater during the drying cycle. A minimum of 60% protein in the product is sometimes difficult to achieve in the wet-milling process. The causes are frequently improper steeping, excess fine fiber in the mill starch, and poor primary centrifuge operation. Dried gluten meal should be finer than 12 U.S. mesh but no more than 20% through 100 U.S. mesh.

Very small plants find it more economical to avoid investing in separate gluten drying facilities but to mix the gluten cake with wet fiber and evaporated steepwater to produce a combined feed with a 30% protein level.

E. Germ Processing

Germs separated from the corn slurry by the wet-milling process are dewatered to 50% solids in a screw press. They are then dried in rotary steam tube dryers to 3% solids and cooled in rotary water tube coolers or pneumatic cooler-conveyors to 38° C (100° F) to avoid heat degradation and self-ignition. Smaller plants frequently sell their dry germs instead of processing them on-site for oil recovery.

Pressure and heat are required to rupture the oil cells in the germ to obtain the oil. The germs should be softened by heating to 120° C (248° F) and steamed before being mechanically squeezed in conventional oil-expeller equipment. The oil content can be reduced from 45 to 6% for "full pressing," where no further processing is done to recover the remaining oil. In larger installations, the germs are squeezed only enough to break the oil cells, which reduces the oil content to 13–20% (Bredeson, 1983). They are then flaked with rolls and solvent-extracted with hexane to lower the oil content to 1.5%.

Extruders are showing promise as a lower-cost means for germ preparation before extraction. Another commercially operating process eliminates expellers by preconditioning, solvent extraction, flaking in the presence of the solvent, and then further solvent extraction.

The solvent extraction process involves soaking the oil out of the oil-bearing material. The oil-free material that is saturated with solvent must be desolventized, i.e., heat is used to drive off the solvent with direct and indirect steam. The oil-bearing solvent, called miscella, is evaporated, and the solvent is driven off the oil by the action of heat, direct steam, and vacuum. The process is relatively simple, but safety and control are critical for satisfactory operation with the flammable solvent (see Chapter 18).

The germ oil meal, containing 23–25% protein on a dry basis, is a corn gluten feed component. The crude corn oil is shipped to refiners to be degummed, stripped of free fatty acids by alkali refining, bleached with clay, deodorized, and chilled to remove waxes.

III. YIELDS, PRODUCTION, AND MARKETING OF PRODUCTS

Product yields from corn wet-milling operations (Table I) have remained constant for many years at 66% starch and 30% animal feeds. The bulk of the starch is further processed into sweeteners and ethyl alcohol (Table II). Twenty-eight wet-milling plants operate across the United States, with the bulk of them in the Corn Belt. There are probably more wet-milling plants outside the United States, but their total output about equals the capacity of all the wet-milling plants in the United States because many of them are quite small. Many are owned and operated by U.S. wet-milling companies. One company, CPC International, Inc., operates 30 corn wet-milling plants outside the United States. Japan has become a major importer of corn for processing into starch and sweeteners (Jones, 1983).

Production of conventional starch, glucose, and dextrose products increased a modest 39% between 1972 and 1985 in the United States (Table III), but the industry capacity increased by 335% due to alcohol and to the explosive growth of high-fructose corn syrup (HFCS), first at 42% fructose and then at 55% (Chapter 17). The latter allowed near one-to-one substitution for sucrose. The HFCS market in the United States increased by as much as 50% per year in the early 1970s, dropping into the 13–22% range in the early 1980s. This growth rate is now decreasing as HFCS nears 100% replacement of sucrose in soft drinks. The remarkable growth since 1972 can be attributed to the following: 1) technical breakthroughs in the HFCS process, 2) a sugar shortage in the early 1970s, 3) high U.S. sugar price supports in recent years, 4) the availability of abundant low-cost corn, and 5) the willingness of the wet-milling industry to capitalize on the above opportunities.

It is anticipated that HFCS market growth in the future will parallel the modest growth pattern experienced by corn starch and sweeteners over the years due to a growing market and new applications developed by wet-milling industry research. Growth outside the United States can be expected to vary,

TABLE I
Yield Distribution of Products Obtained by the Wet-Milling Process as a Percentage of the Raw Corn[a]

Product	As Sold[b]	Moisture-Free Basis
Starch	74	66.0
Oil[c]	3.9	3.9
Gluten feed, 21%[b] protein	27	24.0[d]
Gluten meal, 60%[b] protein	6.4	5.7
Unaccounted-for loss	...	0.4

[a] Adapted from Long (1982).
[b] Calculated at 11% moisture content.
[c] Unrefined.
[d] Includes fiber (pericarp), steepwater (solubles, ~7% db), and germ residue (4% db).

TABLE II
Shipment of Products (thousand pounds) of the Corn Refining Industry in the United States[a,b]

	1983	1984	1985
Starch products			
(Includes corn starch, modified starch, and dextrin)	4,018,905	4,182,866	4,225,171
Refinery products			
(Includes glucose syrup, high-fructose corn syrup, dextrose, corn syrup solids, and maltodextrins)	16,005,529	17,921,126	20,341,535
High-fructose corn syrup	9,707,041	11,502,324	13,920,406
Other products			
Corn oil crude	72,612	116,142	164,382
Corn oil refined	399,919	407,456	382,234
Corn gluten feed	7,391,069	8,739,730	8,811,476
Corn gluten meal			
41% protein	19,115	20,272	18,503
60% protein	1,383,129	1,635,228	1,609,112
Corn oil meal	28,728	29,465	48,585
Steepwater	211,937	300,770	282,333
Hydrol	208,807	216,558	228,742
Ethanol (thousand gallons, 100%)[c]	325,000	375,000	425,000

[a] Source: Anonymous (1986b); used by permission.
[b] To convert to tonnes, multiply by 4.535×10^{-4}.
[c] Ethanol values calculated from values for wet-milled alcohol in Table II, multipled by ethanol yield of 2.5 gal (100%) per bushel of corn (Gill and Allen, 1985).

depending upon local economic conditions.

Industry products are mostly shipped in bulk. Liquids are handled in railroad tank cars and tank trucks. Dry products are shipped in special hopper railroad cars and trucks, although much is still handled in 100-lb paper bags. In recent years, *most of the corn gluten feed manufactured* in the United States has been shipped to the European Economic Community. The increasingly use of larger shipping containers for products necessitates ever-increasing sanitary and product quality standards to avoid excessive economic losses associated with off-grade shipments.

IV. FINISHING OF WET-MILLING PRODUCTS

A. Starch

A relatively pure starch slurry from the wet-milling operation contains 40% solids. It may be dried directly or treated with an array of chemicals such as bleaches and acids to modify the starch properties to meet customers' requirements. The chemical residuals are washed from the starch in nozzle-type centrifuges or vacuum filters (with sprays), using 1–2 m^3 of water per tonne (0.12–0.24 gal/lb) of dry starch. Cake from the vacuum filters at 40–50% solids is fed into belt-type dryers with 65–150° C (150–302° F) steam-heated air rising up through the dryer belt perforations. The product is agglomerated somewhat but is free flowing and easy to handle. Flash dryers are also used, generally fed from large basket-type centrifuges that dewater to 55–67% solids. The dryer heating medium is steam from coils or direct-fired gas furnaces furnishing 220°C (428° F) air. The products are generally ground in air-swept mills, blended, and shipped in bags, hopper trucks, and railroad hopper cars. They are used in paper, textiles, adhesives, and food. The dry starch is sometimes processed *further by dry roasting, cooling, blending,* and packaging for use as adhesives. Starch is cooked on hot, steam-heated rolls, cooled, and ground for use in food and adhesives. A less severe treatment using extruders results in instant laundry products (see Chapter 16).

TABLE III

Annual Use of Corn (million bushels) in the Production of Starch and Starch-Derived Products from Wet Milling[a,b]

Year Beginning October 1	HFCS[c]	Glucose and Dextrose	Starch	Wet-Milled Alcohol	Total Wet-Milled[d]
1971/1972	10	125	100	10	245
1972/1973	15	145	110	10	280
1973/1974	20	155	110	10	295
1974/1975	30	160	115	10	315
1975/1976	45	165	115	10	335
1976/1977	65	165	120	10	360
1977/1978	80	170	130	15	395
1978/1979	105	170	135	15	425
1979/1980	140	175	130	30	475
1980/1981	165	185	125	40	515
1981/1982	190	185	135	85	595
1982/1983	215	185	135	130	665
1983/1984	255	190	145	150	740
1984/1985	310	190	150	170	795
1985/1986[e]	320	190	150	170	830

[a] Reprinted from Livesay (1985).

[b] To convert to tonnes, multiply by 2.54 × 10^{-3}.

[c] High-fructose corn syrup.

[d] Use yield data in Table I to calculate actual volumes of starch and by-products.

[e] Preliminary (Anonymous, 1986a).

B. Ethanol

Ethyl alcohol (ethanol) produced by the fermentation of starch from the wet-milling process has a unique economic advantage because the yeast can be recycled (there are no other solids to *interfere with the separation after* fermentation). Another advantage is that the light steepwater from wet milling can be used as dilution water for the fermenters to save overall evaporation (energy) costs. Although some alcohol is used in the beverage industry, about 85% of the ethanol produced from corn is blended with gasoline. Besides serving as a fuel extender, it also is an octane enhancer for unleaded fuel. In the past, wet millers have produced 65–75% of the grain ethanol, but in the 1984/85 crop year, the amount dropped to 60%. This downward trend is expected to continue in future years because most new plants use the dry (whole-corn) milling process (Anonymous, 1985). The ethanol fermentation process is covered in more detail in Chapter 19.

C. Feed By-Products and Miscellaneous

Corn steepwater (condensed fermented corn extractives) is the soluble portion of the corn kernel that is evaporated to as high as 50% solids and sold in liquid form for cattle and dairy feeding. At this concentration and its normal pH of 4.2–4.5, it is biologically stable. It is also used as a nutrient supplement in antibiotic and other fermentations. Most of the steepwater, however, is utilized in the manufacture of corn gluten feed.

Corn germ meal, the fraction remaining after the oil is removed from the germ, is frequently used as carrier of nutrient supplements such as vitamins, minerals, and medicants in animal feeds. The bulk of the meal, however, goes to corn gluten feed, where its ability to absorb oils and water is utilized.

Hydrol, or corn sugar molasses, is a by-product in the production of crystalline dextrose (D-glucose). It is used as an animal feed supplement and as a raw material for the manufacture of food ingredients such as caramel color.

The production and finishing of corn sweeteners is discussed in Chapter 17 *and the processing of crude corn oil into food grade oil in Chapter 18.*

V. POLLUTION CONTROL

A. Waste

The larger wet-milling and sweetener plants can generate as much waste as a medium-large city. Economics dictate the need for waste treatment facilities on the plant site to reduce the high strength to the concentration of municipal wastes. These pretreated wastes plus low-strength streams such as boiler blowdown and sanitary flows can then be routed to municipal facilities. Municipal systems commonly levy surcharges based on excess waste volume and strength.

The combined high-strength wastes are in the range of 1,000–2,000 mg/L of BOD_5 and are reduced to 200–300 mg/L of BOD_5 after pretreatment.[2] The raw waste quantity is approximately 6.3 kg of BOD_5 per tonne (0.35 lb of BOD_5 per bushel) of corn grind, which is reduced to 0.9 kg of BOD_5 per tonne (0.05 lb of BOD_5 per bushel) after pretreatment. This volume amounts to about 3.7 m^3/t (25 gal/bu), of which a third is derived from the wet-milling process and the remainder from product-finishing operations. The on-site treatment facility generally consists of equalization tanks having volumes to handle the residue of 8–24 hr of production. This capacity reduces shock loads due to variations in strength, temperature, flow rate, pH, and nutrient availability. Each of the above factors has a range that must be met by adjusting the pH, cooling or heating, and adding nutrients so that the microorganisms in the aerated, mixed, activated sludge system that follows can remain viable. Effluent mixed liquor from an activated sludge tank is clarified to remove the sludge. This can raise the efficiency of the system from 70 to 80–90%. The dilute clarifier sludge (about 1% solids) may be concentrated to 5–6% solids by the use of solid-bowl or basket-type centrifuges and then can be mixed with light steepwater and further processed as part of the animal feed ingredients.

B. Air Quality

The wet-milling process uses about 1.8 kg of SO_2 per tonne of corn (0.1 lb/bu). It is dissolved in process waters but its pungent odor is present in the slurries, necessitating the enclosing and venting of the process equipment. Vents can be wet-scrubbed with an alkaline solution to recover the SO_2 before the exhaust gas is discharged to the atmosphere. Process building interiors should be well ventilated to dissipate not only fugitive fumes, but also the heat generated by motors and process equipment (the process operates in the 50° C [122° F] range).

The most critical environmental problem associated with air pollution is the exhaust from the drying processes. Cyclones are standard for particulate containment but do not meet stringent air quality standards in some areas, necessitating the use of secondary collectors. Bag collectors are used, but they also become dirty and are fire problems. Wet scrubbers create a liquid waste disposal problem and a wet plume. Incinerators have high energy costs and high capital expenditures.

The greatest problem with dryer exhausts is odor and blue haze (opacity). Germ dryers emit a toasted smell that is not considered objectionable in most areas. Gluten dryer exhausts are satisfactory as long as the drying temperature does not exceed 400° C (752° F). Higher temperatures promote hot smoldering areas in the drying equipment, creating a burnt odor and a blue-brown haze. The drying of feeds where steepwater is present results in environmentally unacceptable odor if the drying temperature exceeds 400° C. Of concern is the formation of a blue haze at elevated temperatures. These exhausts contain volatile organic compounds with acrid odors such as acetic acid and acetaldehyde. Rancid odors can come from butyric and valeric acids, and fruity smells emanate from many of the aldehydes present.

The objectionable odors have been reduced to acceptable levels commercially with ionizing wet-collectors, in which particles are loaded electrostatically with up to 30,000 V. An alkaline wash is necessary before and after the ionizing sections. However, the most conventional approach is incineration at approximately 750° C (1,382° F) for 0.5 sec followed by some form of heat recovery. This hot exhaust can be utilized as the heat source for other dryers or for generating steam in a boiler specifically designed for this type of operation. The incineration can be accomplished in conventional boilers by routing the dryer exhaust gases to the primary air intake. The limitations are potential fouling of the boiler air intake system with particulates, etc., and derating the boiler capacity due to low oxygen content. Another type of system being utilized is recooperative incineration, in which dampers divert the gases across ceramic fill so that exhaust heat is used to preheat the fumes to be incinerated. The size of the incinerator can be reduced 20–40% by recycling some of the dryer exhaust back into the dryer furnace. Recycling of 60–80% of the dryer exhaust is being done by chilling it to condense the water before recycling. The volume of dryer exhaust can also be minimized by reducing the evaporative load. The steepwater can be evaporated to 50% solids. The corn fiber can be predried in a separate dryer, where the exhaust is not a problem as long as temperatures are limited to 450–500° C (842–932° F).

VI. TRENDS

A. Automation

The wet-milling process and associated equipment have matured sufficiently to permit consistent, reliable separation and product quality on a 24-hr basis with minimum operating labor. The most notable achievements are attained in the new large plants where television-like displays and control systems distributed by cathode ray tubes are utilized to start process equipment sequentially on demand and then to monitor and control the system (Martin, 1979) (Fig. 11). Further, the technician can be alerted, by rate-of-change or trend-in-measurement functions, to variables that are about to get out of control. This allows time to make the necessary adjustments to avoid spills and off-quality. These computer systems are the latest development in the search for reduced costs and better product quality. Even better computer applications are probable as improved on-line measuring devices for protein, starch, fiber, and soluble content are perfected.

B. Utilities

Fresh water usage for a typical large sweetener plant is about 4.5–6.0 m^3/t of corn processed (30–40 gal/bu), of which one fourth is consumed in wet milling. Reduction in the requirements for the wet-milling portion is limited because the

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[2] BOD_5 is the strength of waste as analyzed by the five-day biochemical oxygen demand procedure.

usage about equals the need for properly steeping the corn. Greater water consumption for the finishing processes is likely because the trend is toward more sophisticated products that require more water.

Wet-milling operations are high energy users at 1.48 million kilocalories per tonne of corn (150,000 btu/bu), even for the efficient large sweetener plants. About 20% of the total is for electricity, which indicates that most of the energy goes into fuel to make steam. As products continue to become more sophisticated, the use of energy will increase unless new technology can reverse the trend.

The use of mechanical vapor recompression evaporators in new facilities and in the replacement of old equipment is reducing energy usage because it is five to six times as efficient as quadruple-effect steam evaporation. More imaginative use of heat exchangers can recover heat now being lost to the atmosphere via cooling towers. Steepwater evaporators now in service can utilize feed dryer exhausts as their source of energy.

Superheated steam is showing promise for use in drying feed materials (Covington, 1983). Most (60–80%) of the energy for the primary heating of steam is recovered in low-pressure steam for use elsewhere in the process. Not only is a 20–40% energy saving possible, but there is no discharge to the atmosphere, eliminating odor and particulate problems associated with feed drying. Reverse osmosis is improving due to breakthroughs in membrane technology. When operating with a pressure differential of 35–70 kg/cm^2 (500–1,000 psi), they may replace steepwater and sweetener evaporators, achieving a major reduction in energy requirements (Cicuttini et al, 1983).

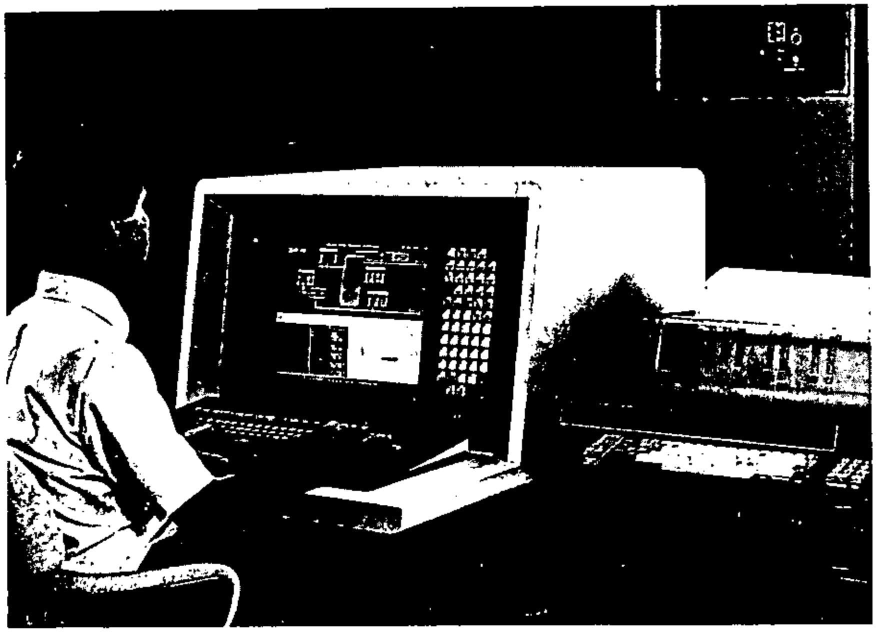

Fig. 11. Television-like displays used to sequentially start and stop process equipment. The processes are also monitored and operated using computer-controlled automation. (Courtesy Foxboro Co., Foxboro, MA)

New steeping technology may be in the offing that improves the possibility of success in concentrating the solids content of steepwater; it works by reducing the low-molecular-weight components such as alcohol that reverse osmosis, up to now, has had difficulty separating. Another benefit is reduced steeping time. A technology being introduced to the industry to treat wastes relies on anaerobic digestion, which has the advantage of using less energy-intensive processes and giving energy credits via recovery of methane gas, which is utilized as a fuel source. The cost of energy is being reduced by installing cogeneration, which was popular in the industry 50–60 years ago. New coal-fired boilers operating at 40–80 atm (600–1,200 psi) drive electric generators. Steam for processing is then extracted in the 10 kg/cm^2 (150 psi) range, and steam for low-temperature heating (of water, for evaporation, etc.) is extracted at exactly 2 kg/cm^2 (30 psi) absolute.

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CHAPTER 16

CORN STARCH MODIFICATION AND USES

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I. INTRODUCTION

Starch is the world's most abundant worldwide commodity. Its use has shown steady, rapid growth over the past several years. Currently, approximately 4.2 billion pounds of starch are produced by the corn wet millers in the United States, who also produce about 20 billion pounds for conversion to sweeteners (Chapter 12, Table III). Future expanded uses for starch may result from the emerging ability to modify starch structure and the relatively inexpensive character of the resulting products.

The utilization and development of corn starches began in about 1844. Commercial cornstarch today is derived by the wet-milling process (Chapter 12), using about 9% of the harvested corn for both starch and sweetener production. About 65% of isolated corn starches is used in a variety of industrial products, primarily in paper, adhesives, and coatings. The remainder goes to foods for thickening and gelation.

Starch usage and demand generally follow the national income and output (e.g., the Gross National Product). A wide range of products are produced, both in native and modified forms. Their various characteristics depend upon their intended applications.

II. Properties Involved in Modification

A. Molecular Characteristics

Starch is a polymer of anhydrodextrose units (Mahler and Cordes, 1971). The basic repeating unit involves the linkage of successive D-glucose molecules by α-D-(1→4) glycosidic bonds. Two distinct structural classes exist: linear chains named amylose and branched chains named amylopectin (Fig. 1). (See Chapter 9 for a detailed description.) The abundant hydroxyl groups on the starch molecules impart the characteristic hydrophilic properties. The polymer

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attracts water and is self-attractive through hydrogen bonding. The self-attraction and crystallization tendencies are most readily apparent for the amylose or straight-chain component (Wurzburg, 1978).

The association between the polymer chains results in the formation of an intermolecular network that traps water. At sufficient starch concentration (>3%), gels are produced, whereas in dilute solutions, the associated forms may precipitate. Precipitation is particularly evident for amylose. Amylopectin association is interrupted because of its highly branched character. However, at low temperature, even amylopectin will associate, resulting in decreased water binding and gel formation.

Starch from common corn contains about 27% amylose and 72% amylopectin (Swinkels, 1985). The genetic mutant varieties of importance are waxy maize, which contains essentially 100% amylopectin, and high-amylose corn, having 50–70% amylose.

The characteristic firm, opaque gel produced by common corn is attributed to the amylose fraction. Properties of waxy maize starch are a result of the amylopectin sols produced having a characteristic soft translucent paste form.

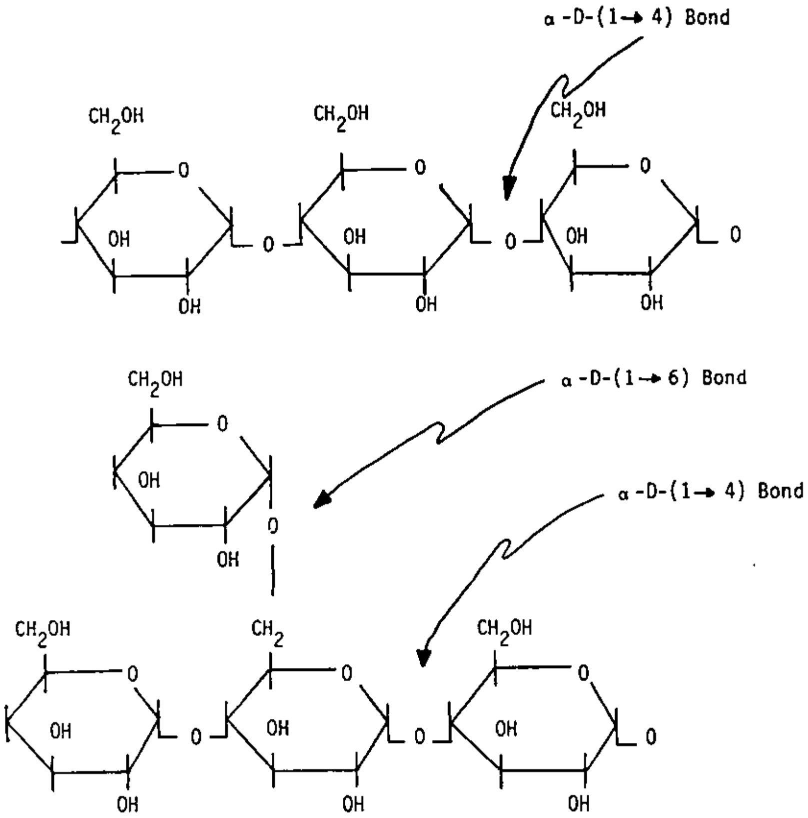


Fig. 1. Chemical structure of amylose (top) and amylopectin (bottom) fractions of the corn starch molecule.

B. Granule Structure and Character

Corn starch is recovered as minute, discrete granules that are an organized aggregation of amylose and amylopectin molecules (Fig. 2) (French, 1984). The granules vary somewhat in shape and range from 5 to 25 μm in diameter (Wurzburg, 1978). They possess a quasicrystalline structure and are insoluble in cold water. When a water slurry of the granules is heated, water is imbibed. With continued heating, the hydrogen bonds holding the granule intact are weakened, and irreversible swelling occurs. The granules eventually burst with continued heating, and solution clarity increases. The viscosity of the solution rises through a maximum and then drops as the granules rupture and disintegrate.

C. Viscosity

The viscosity profile during heating of starch paste is shown in Fig. 3 using a Brabender Visco/amylo/Graph. The pasting of the starch occurs at the major increase in viscosity (Wurzburg, 1978). At the peak viscosity, the swollen granules represent a major factor governing the rheology and viscosity of the cook. Beyond the peak viscosity, the role of the granule disappears, and the characteristics of the dispersion are governed by the size of the molecules and aggregates present (Swinkels, 1985).

Swollen granules exhibit a short, salvelike texture suited primarily for food use, where starch serves as a thickener. Control of granule integrity is dependent on cooking time, temperature, concentration, shear, and pH. As a molecular dispersion, the polymeric molecules develop a cohesive, rubbery texture and have decreased thickening power compared to that of the granular form. Starches for industrial, nonfood applications are generally utilized as molecular dispersions.

III. OBJECTIVES OF MODIFICATION

The objective of starch modification is to alter the physical and chemical characteristics of the native starch to improve functional characteristics

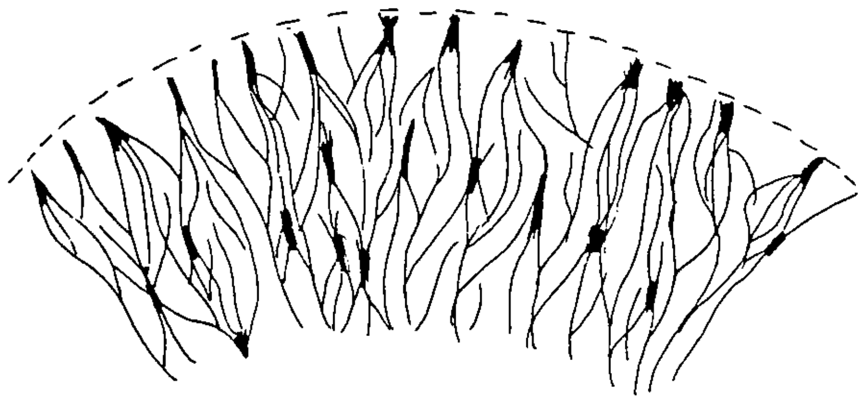


Fig. 2. Concept of the arrangement of starch molecules in a starch granule according to Meyer (1942). Dark areas represent crystalline regions.

(Orthoefer, 1984; Rutenberg and Solarek, 1984). The intent of the modification reaction is to 1) change the character of the dry granule, 2) modify granule integrity, and 3) alter the chemical characteristics. Starch derivatives include modifications that change some of the D-glucopyranosyl units in the molecules. The modifications involve oxidation, esterification, etherification, hydrolysis, and dextrinization (Wurzburg, 1978). The general methods for modification are: acid thinning, bleaching or oxidation, cross-linking or inhibition, substitution or derivatization, and instantizing. A process flow through a corn starch facility is diagrammed in Fig. 4.

Modified starches are defined by source, prior treatment, amylose-amylopectin ratio or content, measure of molecular weight or degree of polymerization, type of derivative or substituent, degree of substitution, physical form, and associated components (Radley, 1968).

Derivatives are prepared to modify the gelation and cooling characteristics of the granular starch, to decrease the tendency toward the retrogradation-crystallization and gelling of the amylose fraction, to increase the water-holding capacity of the starch dispersion, to improve the hydrophilic character, to impart hydrophobic properties, or to introduce ionic groups (Wurzburg, 1978). Modification is important for the continued and increased use of starch to provide thickening, gelling, binding, adhesiveness, and film-forming characteristics.

Multiple treatments may be used to obtain the desired combination of properties. Acid-converted starches, for example, may also be derivatized, and hypochlorite-oxidized starches also may be further converted. Derivatives may

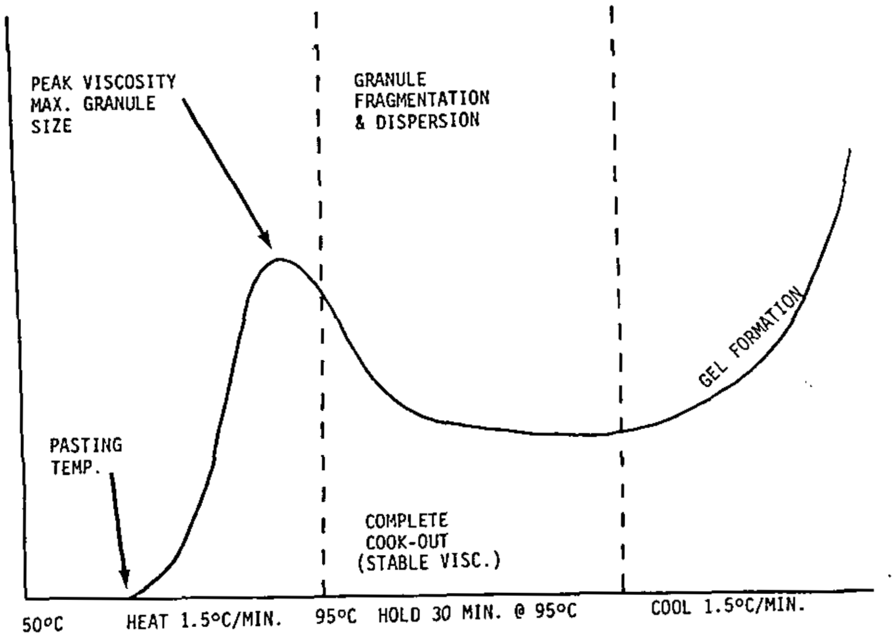


Fig. 3. Amylograph profile of unmodified corn starch.

be dextrinized, acid-converted, or oxidized to obtain the desired viscosity. Cross-linking is often used in combination with derivatization to obtain dispersion viscosity upon processing by high-temperature cooking, high shear, or acid treatment (Orthoefer, 1984).

IV. CHARACTERISTICS OF MODIFIED STARCHES

Modified starches are characterized by a number of factors, which are most often dependent on the type of derivative being produced. Some of these factors are source, molecular weight, type of derivative, nature of the substituent group, and degree of substitution (DS). DS, a characteristic of all derivatized starches, is a measure of the average number, expressed on a molar basis, of hydroxyl groups on each D-glucopyranosyl unit derivatized:

$$DS = 162W/[100\,M - (M - 1)\,W\},$$

where W = weight percent of the substituent and M = molecular weight of the substituent. The maximum number possible for starch is 3 DS since three hydroxyl units are available. Most commercially modified starches have a DS of less than 0.2 (Rutenberg and Solarek, 1984).

During derivatization, the formation of the chemical derivative may be followed chemically. Various viscosity techniques may also be employed that indirectly measure the extent of modification (Fleche, 1985). Viscosity measurements employed include the Brabender Visco/amylo/Graph, fluidity techniques, and Brookfield viscometry. Many of the viscosity methods have been modified to meet the needs of the individual starch processor. The Brabender instrument is probably the one most widely used to obtain complete cooking and cooling curves.

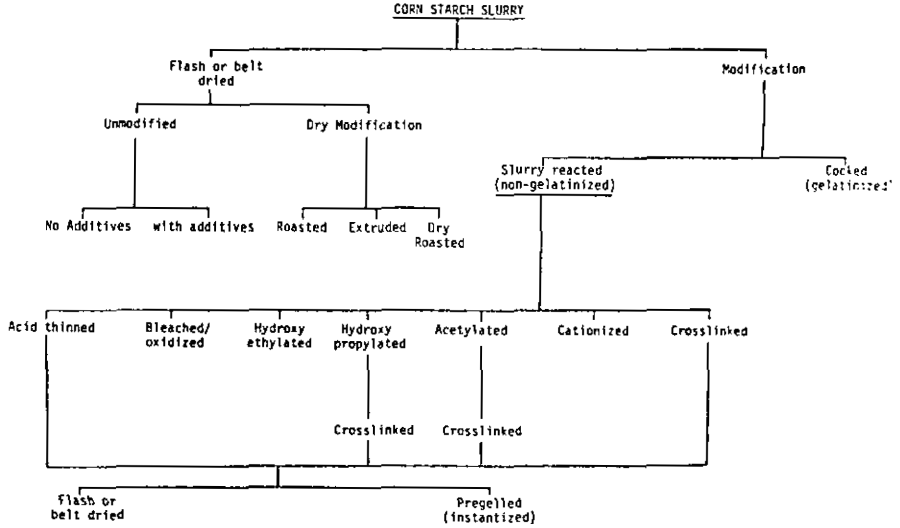


Fig. 4. Process flow chart for preparation of unmodified and modified corn starches.

The curves demonstrate gelatinization temperature, peak viscosities, ease of cooking, stability of breakdown of pastes, setback or gelling, and final viscosities (Fig. 5). Overall, for quality control, the common specifications are: moisture, foreign matter, color, ash, pH, flavor and odor for food, and particular characterization measures for functional properties (Orthoefer, 1984). The common viscosity values utilized are peak, breakdown after peak viscosity, and viscosity after cooling.

V. MANUFACTURE OF DERIVATIVES

The low-DS derivatives are processed in slurry form at 35–45% solids and at pH values of 8–12 (Orthoefer, 1984; Rutenberg and Solarek, 1984; Fleche, 1985). Sodium hydroxide and calcium hydroxide are commonly used to control alkaline pH. Reactions are performed in agitated reaction tanks, called "tubs," having a capacity of 40,000–100,000 lb or higher at temperatures up to about 60° C. Conditions are employed to prevent gelatinization, thus allowing recovery of the modified starch in the granular form. Conversions generally take 4–24 hr. Derivatives are washed, centrifuged, and dried either on a belt or in flash dryers. To prevent swelling under strongly alkaline conditions, salts such as sodium sulfate or sodium chloride are added at a 10–30% concentration. The practical upper limit to the DS is the lowering of the gelatinization temperature by the derivative being prepared.

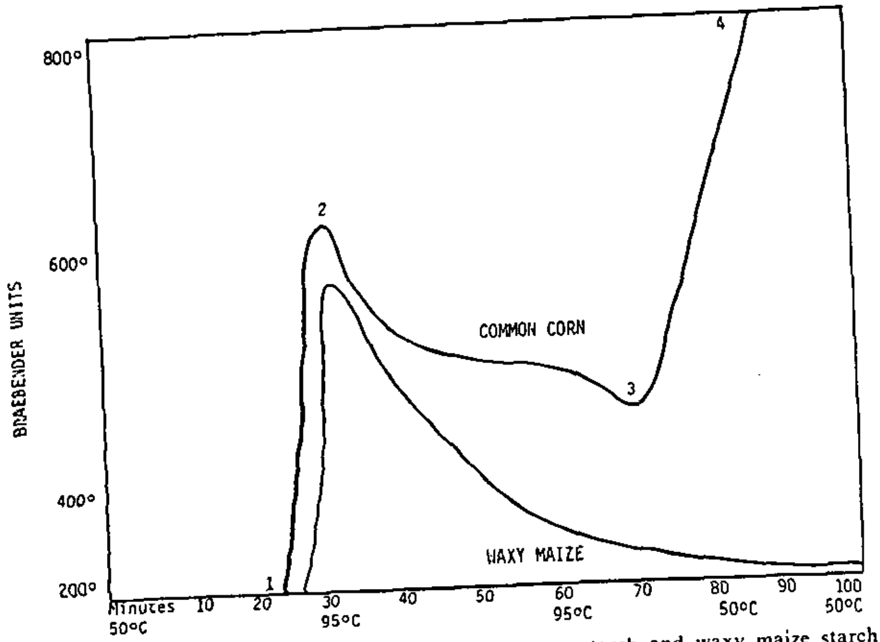


Fig. 5. Amylograph profiles of unmodified common corn starch and waxy maize starch. 1, Gelatinization temperature; 2, peak viscosity temperature; 3, breakdown viscosity; 4, final setback viscosity.

Higher-DS derivatives have been produced using a nonswelling solvent.

Isopropanol, ethanol, or acetone may be used to prepare derivatized starches that gelatinize when dispersed in water at room temperature (Rutenberg and Solarek, 1984).

Dry reacting of starch is also practiced. The dry starch is heated with the reactants to about 150° C in dry or nonaqueous form, yielding granular products that are readily dispersible in cold water. These derivatives generally contain unreacted reagents plus salts. Nonaqueous solvent washing has been applied to remove the excess salts.

Instant or pregelled corn starches are sometimes included on lists of modified starches (Moore et al, 1984). These dry powders hydrate in cold water and develop a thick viscosity. Production of the pregels is a continuation of the processing of starch. The process may be as simple as drum drying of the slurry after modification and washing. Other techniques used include spray drying, extrusion, and more sophisticated swelling of the starch in nonaqueous solvent-water mixtures (Eastman, 1984). Overall, the pregelled starches represent a compromise between ease of use and functional characteristics.

VI. MODIFICATION

A. Acid Thinning

Acid thinning or conversion is used to reduce the hot paste viscosity of raw or native starch (Radley, 1968; Wurzburg, 1978; Fleche, 1985). Glucosidic linkages joining one anhydroglucose unit to another are cleaved, with water being consumed in the process (Fig. 6).

Both wet and dry processes are used for production of acid-thinned starches. Controlled acid hydrolysis in aqueous suspension leads to the thin-boiling types. The thinning reduces the viscosity to permit these starches to be cooked at higher concentrations than the native starches. Textural properties and cold water solubilities are also affected. Dry acid conversions lead to dextrins, which are most often used in adhesives.

In the wet process, hydrochloric or sulfuric acids are used at 1–3% of the starch weight. The temperature is maintained to prevent gelatinization, generally near 50° C. When the desired reduction in viscosity is obtained, the acid is neutralized and the starch recovered by filtration. The acid depolymerization occurs primarily in the amorphous or noncrystalline regions of the granule, with an apparent increase in the linearity of the starch. The degree of hydrolysis by acid is limited, due to the necessity of recovering the modified granules by filtration. A series of products with viscosities suitable for various applications are prepared. Nonfood uses include paper sizing, calendering, and coating applications (Sanford and Baird, 1983; Bramel, 1986).

Overall, as a result of acid thinning, the gel strength of the cooled paste increases and gel clarity improves. In foods, acid-thinned starches are used in confectionery products, particularly starch jelly candies (Moore et al, 1984).

Dextrins are prepared primarily for nonfood uses. To produce dextrins, dry starch powders are degraded by being roasted in the presence of limited moisture and trace levels of acid, generally hydrochloric. Hydrolysis of the glucosidic bond occurs, as well as molecular rearrangement.

Dextrins are usually more soluble and possess lower viscosity than acid modified starches. The products are classed according to color as well as water solubility. These include white dextrins, yellow or canary dextrins, and British gums. The type produced depends on the amount of acid and heat, type of equipment, and conditions used for conversion. Dextrins are used primarily in paste formulations, including box pastes, envelope adhesives, carton sealing, and gums for tapes (Fleche, 1985). In foods, dextrins are used as an adhesive for pan coatings, such as those used in jelly bean production, and as a means to develop a clinging mouthfeel in some foods (Moore et al, 1984).

B. Bleaching or Oxidation

Bleaching, or oxidation, represents a single modification producing two types of products (Rutenberg and Solarek, 1984; Wurzburg, 1978). Those treated with low levels of reagents are referred to as bleached starches. They are prepared with hydrogen peroxide, peracetic acid, ammonium persulfate, chlorine as sodium hypochlorite, potassium permanganate, or sodium chlorite. These reagents may be used to whiten corn starch by bleaching xanthophyll and related pigments. Whiteness is desired when the bleached starch is used as a fluidizing agent for dry powders such as confectioners' sugar. The reagents also allow control of microbial counts, which is particularly necessary for food applications. Low thermophile bacterial counts as well as reduction in yeast and mold counts occur.

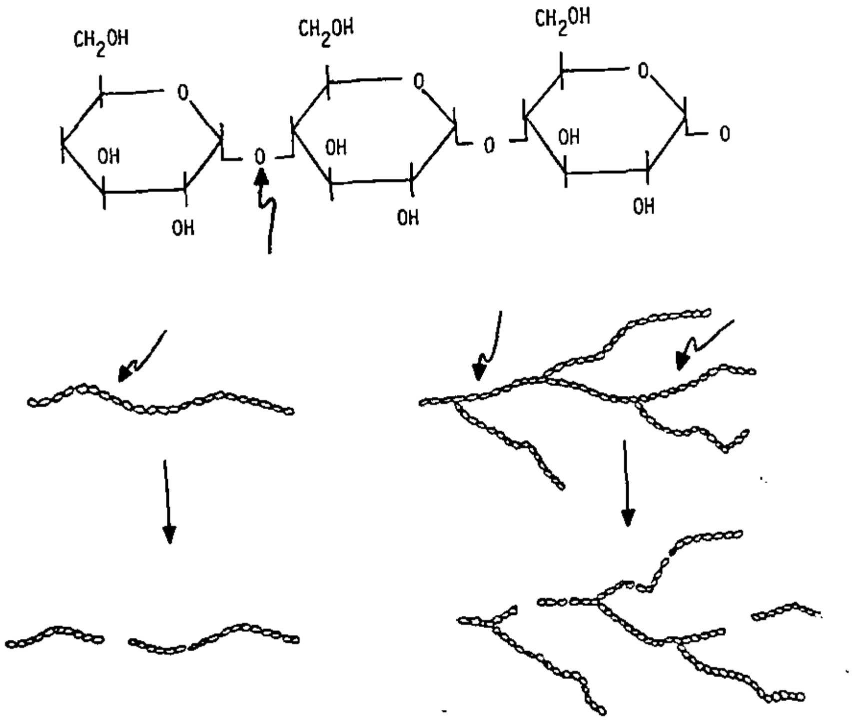


Fig. 6. Mechanism of acid thinning of starch. Arrows indicate points of attack of hydrogen ion.

Bleaching is performed on aqueous slurries. Sodium bisulfite may be used for neutralization. The color bodies solubilized by bleaching are removed during filtering and washing of the starch before drying.

Oxidized starches also are prepared by treatment of aqueous starch slurries. Chlorine as sodium hypochlorite is used at levels of up to 5.5% of the dry starch. The process results in oxidation of hydroxyls, producing a limited number of carboxyl and carbonyl groups along with scission of the glucosidic linkages (Fig. 7). Within the starch granule, oxidation occurs primarily in the amorphous regions. The bulkiness of the carboxyls and carbonyls reduces the tendency of the starch to retrograde. Oxidized starches have less tendency to form a firm gel than do acid-modified starches of comparable hot paste viscosity. Usage is primarily in applications where intermediate to low viscosities are desired and where the acid-converted starches do not show adequate stability.

In foods, bleached corn starch is used for improved adhesion of batter and breading mixes in fried foods (Moore et al, 1984). The carbonyl group probably interacts with the surface of the food, promoting adhesion. Industrially, oxidized starches have been widely used for paper sizing and coating because of their excellent film-forming and binding properties (Bramel, 1986).

C. Cross-Linking

The salvelike texture produced by swollen starch granules is desired particularly in food applications (Orthoefer, 1984). This state is difficult to

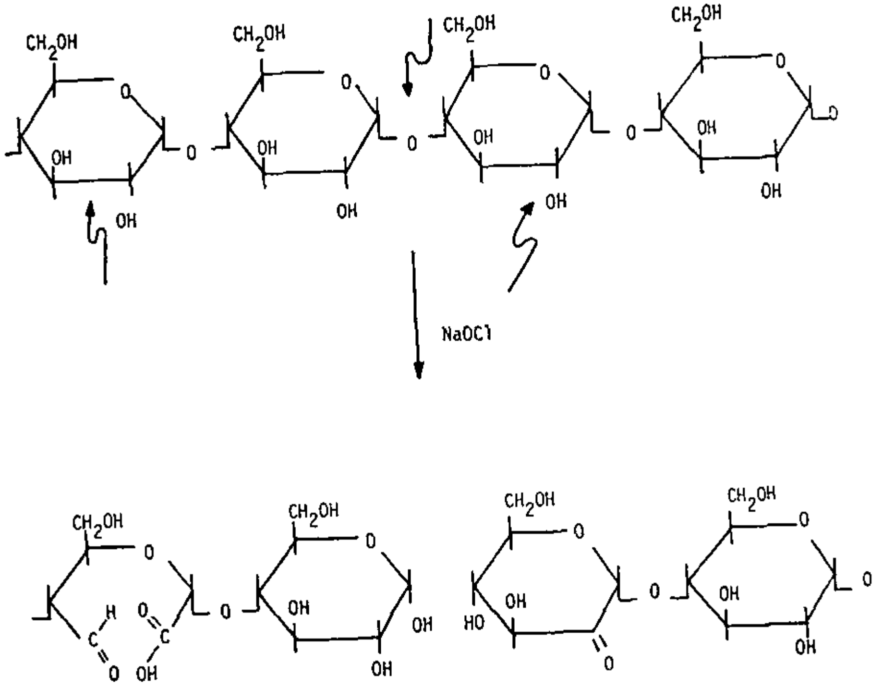


Fig. 7. Hypochlorite oxidation of corn starch, showing carbonyl and carboxyl formation.

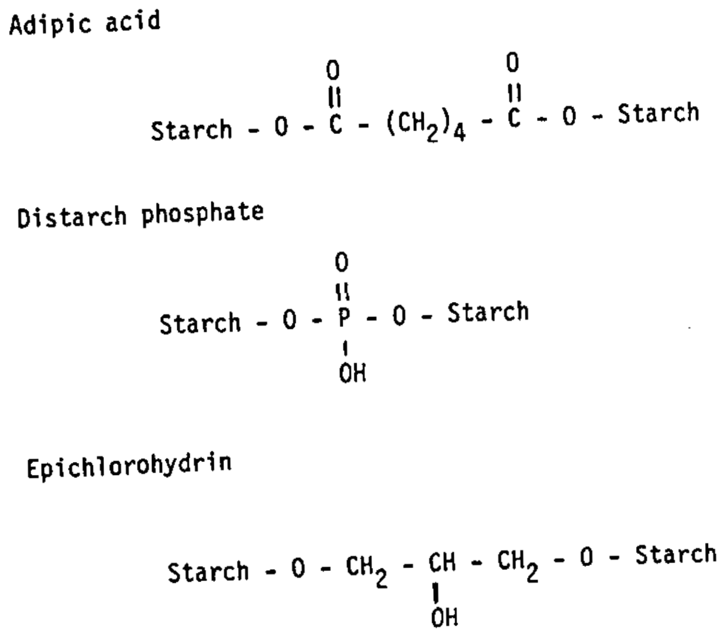
maintain in cooking of native starches. Often the starch is undercooked, or it is overcooked and becomes elastic. Control of cooking time, temperature, concentration, shear, and pH are required.

Cross-linking is used to overcome the sensitivity of the starch granules to disruption (Fleche, 1985). It improves the strength of the swollen granules, providing resistance to rupture. No reduction in digestibility or caloric value is seen.

Cross-linking is accomplished by treating the starch in the granular state with difunctional reagents capable of reacting with hydroxyl groups on two different molecules within the granule (Fig. 8). The cross-linked starch, when cooked in water at temperatures that weaken or destroy hydrogen bonds, exhibits granule integrity by virtue of the chemical cross-links. Brabender viscosity profiles of cross-linked starches are shown in Fig. 9.

Two major types of cross-linking reagents are commercially utilized (Rutenberg and Solarek, 19840). Distarch adipate is produced using a mixture of adipic acid and acetic anhydride. Distarch phosphates are produced with phosphorus oxychloride or by roasting with sodium trimetaphosphate. Epichlorohydrin, previously widely used for cross-linking, now is used to a much lesser extent. The reactions are normally run on granular starch suspended in water in the presence of low to moderately alkaline conditions. After completion of the reaction, the slurry is neutralized and the starch is filtered, washed, and dried.

When adipic acid is the reagent, 0.12% or less is used on a commercial basis. The mixed anhydride reacts almost instantly with the starch or is hydrolyzed, forming the salts of adipic and acetic acids. The reaction with $POCl_3$ is also extremely rapid, forming the cross-linked starch or sodium phosphate and sodium chloride. After the reaction, the slurry is neutralized, washed, and dried.



Adipic acid

$$\text{Starch} - O - \overset{\overset{O}{\|}}{C} - (CH_2)_4 - \overset{\overset{O}{\|}}{C} - O - \text{Starch}$$

Distarch phosphate

$$\text{Starch} - O - \underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}} - O - \text{Starch}$$

Epichlorohydrin

$$\text{Starch} - O - CH_2 - \underset{\underset{OH}{|}}{CH} - CH_2 - O - \text{Starch}$$

Fig. 8. Chemical structure of cross-linked starches.

Epichlorohydrin reacts with aqueous starch suspensions in the presence of caustic. The level required is very low, with 0.05% or less previously having been used for commercial starch. The starch industry voluntarily stopped using epichlorohydrin in the processing of modified food starches when its hazard to the work environment was identified.

The extent of cross-linking utilized varies, depending on the system in which the starch is used, such as pH, time, temperature, and cooking technique. Generally, the level of cross-linking giving the desired thickening is employed. Cross-linked starches designed for a given use have higher viscosities than unmodified starches under the same conditions. The actual amount of cross-linking corresponds to approximately one cross-link per 1,000 anhydroglucose residues (Wurzburg, 1978).

D. Derivatization or Substitution

Derivatization, or substitution, refers to the introduction of substituent groups on the starch by reacting some of the starch hydroxyls with monofunctional reagents (Rutenberg and Solarek, 1984; Fleche, 1985). For foods, acetate, succinate, octenyl succinate, phosphate, or hydroxypropyl groups are introduced. Industrially important starches are produced utilizing hydroxyethyl and cationic substitutes, as well as others.

Acetylated corn starches are produced with acetic anhydride in the presence of an alkaline starch slurry (Wurzburg, 1978). The reaction is terminated by neutralization. Hydroxypropylation utilizes propylene oxide also at alkaline pH.

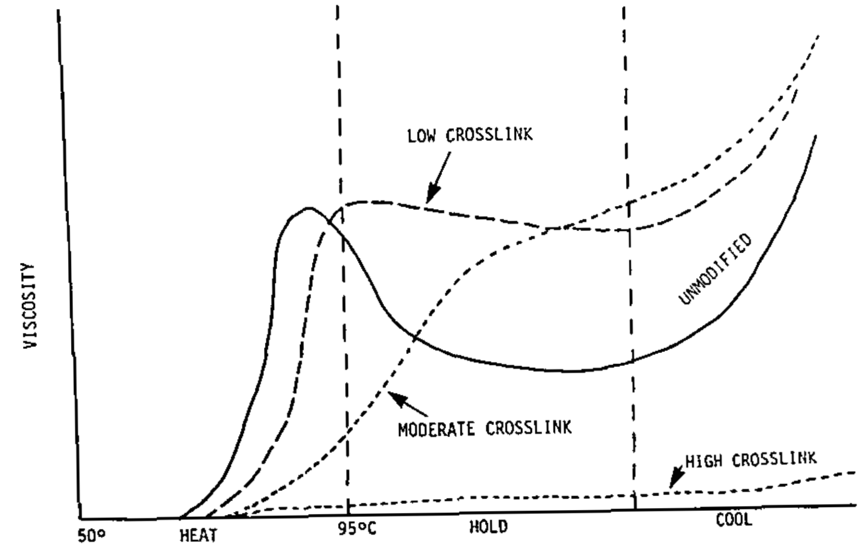


Fig. 9. Amylograph profiles of cross-linked corn starches.

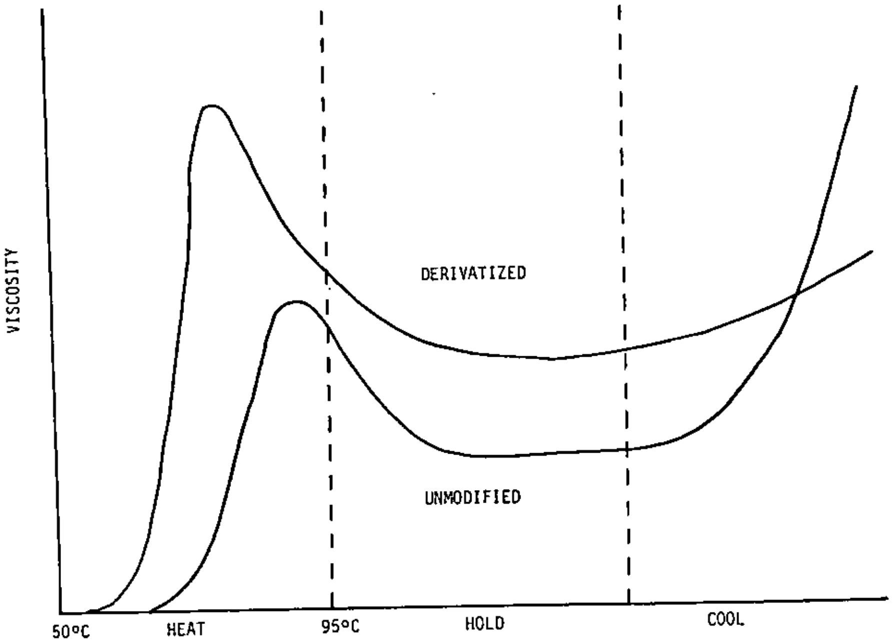


Fig. 10. Amylograph profile, showing the effect of derivatization of corn starch.

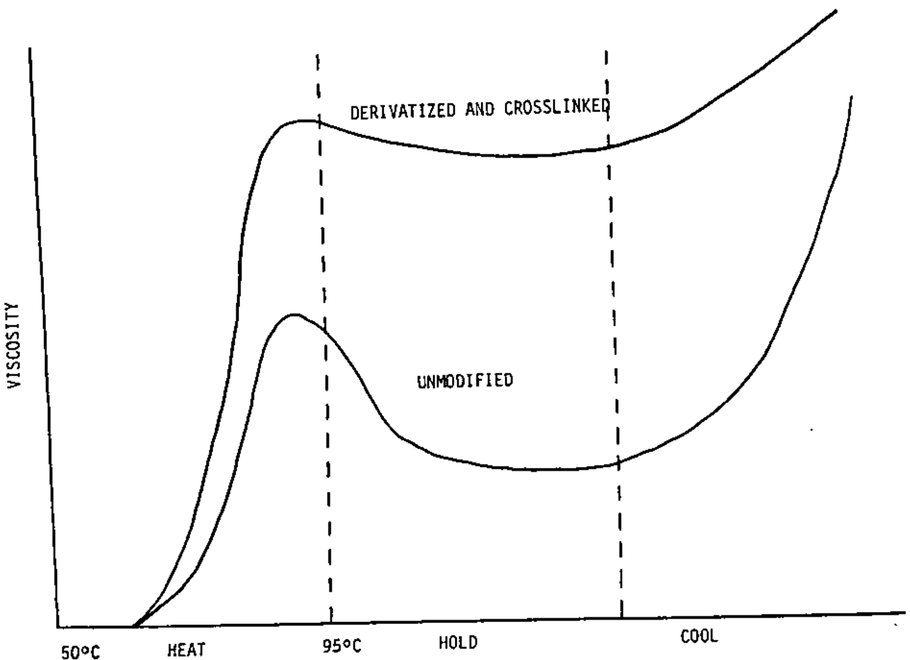


Fig. 11. Amylograph profile, showing the effect of derivatization and cross-linking on viscosity during cooking of corn starch.

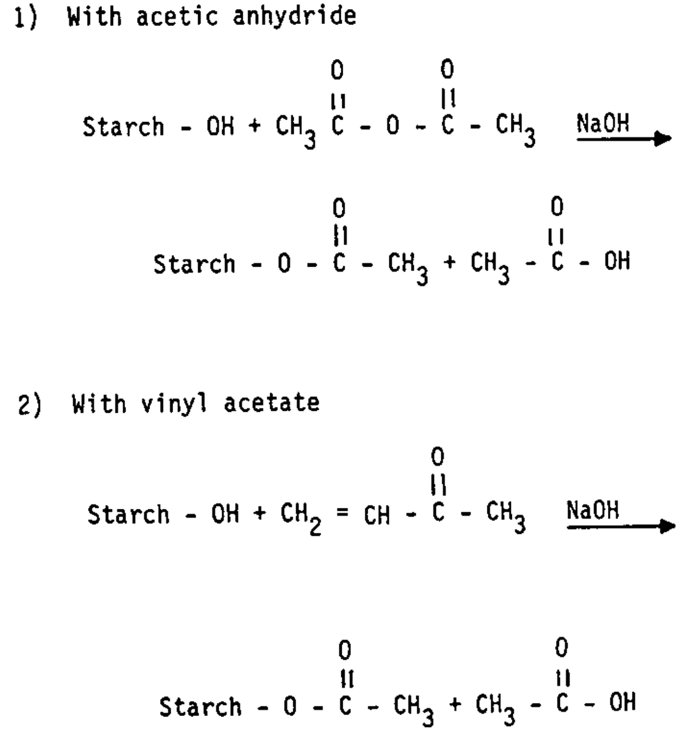
Derivatization retards or inhibits the association of the gelatinized amylose chains in the starches. Improved clarity, reduced gelling, and improved water-holding capacity result (Fig. 10). When substituents such as acetate or hydroxypropyl groups are introduced into the molecule, the tendency toward interbranch associations is reduced or restricted, depending on the level of substitution. Acetylated or propylated cooked corn starch can be kept from gelling. Substituted and cooked waxy corn starch can be kept from losing hydration ability and clarity on storage at low temperatures. Succinylation is used to increase the hydrophilic character through the free carboxy moiety, resulting in improved thickening properties.

In foods, combined cross-linking and substitution are used to give thickeners that have the desired processing characteristics and texture and the desired rheological properties during storage and shipment (Fig. 11) (Moore el al, 1984).

The derivatization of starch with acetate, succinate, octenyl succinate, phosphate, or hydroxypropyl groups is cleared for use by the U.S. Food and Drug Administration under 21 CFR 172.892 (d), (e), and (f).

STARCH ESTERS

The principal starch esters are acetates, phosphates, and octenyl succinates (Fleche, 1985). The low-DS acetylated starches are made by treatment of an aqueous starch dispersion with acetic anhydride at pH 7–12 (Fig. 12). Sodium



1) With acetic anhydride

$$\text{Starch} - \text{OH} + \text{CH}_3\overset{\text{O}}{\overset{\|}{\text{C}}} - \text{O} - \overset{\text{O}}{\overset{\|}{\text{C}}} - \text{CH}_3 \xrightarrow{\text{NaOH}}$$

$$\text{Starch} - \text{O} - \overset{\text{O}}{\overset{\|}{\text{C}}} - \text{CH}_3 + \text{CH}_3 - \overset{\text{O}}{\overset{\|}{\text{C}}} - \text{OH}$$

2) With vinyl acetate

$$\text{Starch} - \text{OH} + \text{CH}_2 = \text{CH} - \overset{\text{O}}{\overset{\|}{\text{C}}} - \text{CH}_3 \xrightarrow{\text{NaOH}}$$

$$\text{Starch} - \text{O} - \overset{\text{O}}{\overset{\|}{\text{C}}} - \text{CH}_3 + \text{CH}_3 - \overset{\text{O}}{\overset{\|}{\text{C}}} - \text{OH}$$

Fig. 12. Chemical reactions of acetylation of starch with acetic anhydride and vinyl acetate.

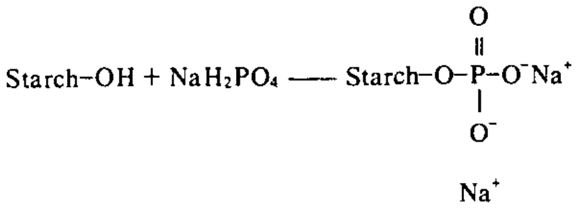
hydroxide is the preferred alkali, with the optimum pH from 8.0–8.4, but it is temperature dependent. Reactions of 70% efficiencies can be obtained. Alkaline-catalyzed transesterification with vinyl acetate in aqueous medium is also used to acetylate starch.

Acetylated starch having about 1.8% acetyl has a gelatinization temperature 5–7° C lower and a higher hot-peak viscosity at about 10° C lower than those of untreated corn starch. The acetylated starches are more readily dispersed on cooking. On cooling, the corn starch acetates do not reach as high a cold-paste viscosity. This is probably due to acetate interference within the amylose portion. Acetylation has been applied commercially to regular corn, waxy corn, and high-amylose variants. Levels of 0.5–2.5% acetyl groups are utilized.

Acetylation has been applied to impart the thickening needed in food starch applications (Wurzburg, 1978). Generally combined with cross-linking, food starches are prepared that withstand retort processing, high shear, and refrigeration, as well as freeze-thaw conditions, and may be used in low-pH foods. Viscosity stability and clarity are obtained with notable low-temperature storage stability. Cross-linking provides textural properties and resistance to breakdown.

Common food uses of acetylated starches are in fruit pies, gravies, salad dressings, and filled cakes. They can also be used as a filling aid in canning, where viscosity breakdown is desired after heat treatment (Moore et al, 1984; Orthoefer, 1984). Nonfood uses of acetylated starches include warp sizing for textiles, surface sizing for paper, and gummed tape adhesives (Sanford and Baird, 1983; Bramel, 1986). These applications take advantage of the convenient preparation and application of acetylated starches, as well as the film-forming, adhesion, and flexibility properties.

The phosphate monoesters of starch are prepared by roasting blends of starch and orthophosphates at pH 5–6.5 for 0.5–6 hr, at 120–160° C.



$$\text{Starch–OH} + NaH_2PO_4 \longrightarrow \text{Starch–O–}\overset{\displaystyle O}{\overset{\|}{P}}\text{–}O^-Na^+ \quad \text{with } O^- \ Na^+ \text{ on P}$$

Tetrasodium pyrophosphate and tripolyphosphates have also been used. The production of cross-linked starch during phosphating is prevented by washing at pH less than 5.0.

Phosphated starches possess good clarity, high viscosity, long cohesive textures, and stability to retrogradation. The primary use for the phosphated derivatives is in the paper industry as wet-end additives (Mentzer, 1984). When combined with cationic derivatives, the phosphated starches improve drainage, increase retention of paper furnish, and improve the strength of the finished sheet. When combined with clays, they have outstanding dispersive properties. Other uses of starch phosphates include textile sizing, thickeners for textile printing, adhesives in corrugating, and flocculants. In foods, the starch phosphates are useful as emulsifiers. Only monosodium orthophosphate and sodium tripolyphosphate are permitted for food use. Residual phosphate may not exceed 0.4% as phosphorus.

The corn starches substituted with octenyl succinate are produced as emulsifying starches, most commonly on a waxy starch base (Moore et al, 1984). Principal uses are for flavor encapsulation, as cloud agents for beverages, and as salad dressing stabilizers.

HYDROXYALKYL STARCHES

The hydroxyalkyl starches possess dispersion stability similar to that of the acetylated starches (Wurzburg, 1978). Substitution with alkylene oxide is usually performed on a 35–45% starch suspension in water under strongly alkaline conditions at temperatures up to 50° C (Fig. 13). The starch reaction tanks are blanketed with inert gas due to the explosivity of the oxide-air mixtures.

Because of the alkalinity required to obtain reaction efficiency and the lowering of the gelatinization temperature with the introduction of hydroxyalkyl groups, salts such as sodium sulfate or sodium chloride are added to minimize the swelling tendency of the starch (Rutenberg and Solarek, 1984). After reaction, the starch is neutralized, filtered, washed, and dried.

Highly substituted starches are produced by "dry reacting" the starch with gaseous alkylene oxide. The alkali and salt are added to the dry powder and the gas is introduced. Ungelatinized hydroxypropylated corn starches that swell in cold water can also be prepared using phosphate salts or carboxylic acid salts as catalysts in place of the alkali.

Common degrees of substitution of 0.1–0.3 are prepared. During substitution, the 2-hydroxyl position of the glucose is favored. At low substitution levels with ethylene oxide, monosubstitution dominates. At high substitution levels, polysubstitution on hydroxyethyl substituents occurs.

The properties of the low-DS, hydroxyethyl, and hydoxypropyl starches are similar to those of the low-DS starch acetates (Wurzburg, 1978). Granule swelling on cooking increases; clarity and cohesiveness increase; and tendency to "gel" on cooling and aging is reduced.

As with the acetates, low-temperature stability, solubility, clarity, and freeze-thaw stability occur. Starch ethers, unlike the esters, are pH-stable and can be used under strongly alkaline conditions. The ether-substituted starches also may be further modified by acid conversion, oxidation, or dextrinization.

The higher the degree of substitution, the lower the gelatinization temperature

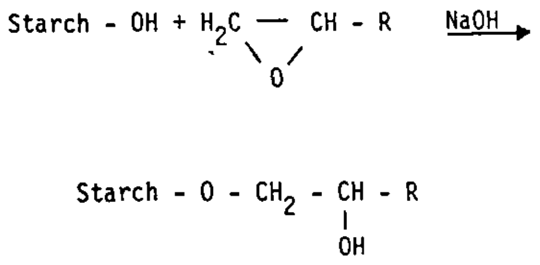


Fig. 13. Reaction of alkylene oxide with starch, forming starch hydroxyalkyl ether.

(Fleche, 1985). Lowering of the gelatinization temperature is used to monitor the progress of the reaction.

The hydroxyethyl starches are prepared for nonfood uses primarily for surface sizing and paper coatings (Bramel, 1986). In surface sizing, they give strength and stiffness to the paper, whereas in coatings, they may be used alone or in combination with other pigment binders. Viscosity stability is a major attribute of the ethylated starches, along with film-forming. The water-holding capacity is useful in preparing adhesives for bag pastes, case sealing, and label and envelope adhesives. A variety of viscosity grades of ethylated corn starches are commercially available.

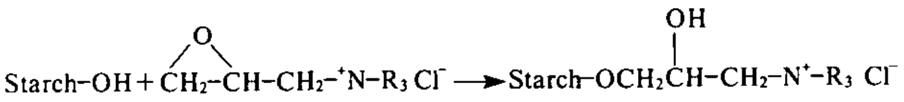
The hydroxypropyl substituted corn starches are sold primarily to the food industry. Normally cross-linked, they provide the desired viscosity, texture, and stability for processing and storage. Common uses are similar to those of the acetylated starches, including use in gravies, sauces, pie fillings, puddings, and salad dressings. Industrial uses include adhesives and wall board binders.

CATIONIC STARCHES

Cationic starches are used extensively in the paper industry, primarily as wet-end additives during formation of the paper (Fleche, 1985; Bramel, 1986). Retention and drainage of the pulp and strength of the finished sheet are benefits seen. These starches are also used in paper sizing, textile sizing, and coatings, as binders in laundry starches, and as flocculants. Total usage is estimated at near 90,000 t.

The most important cationic derivatives are those containing tertiary amino or quarternary ammonium groups (Rutenberg and Solarek, 1984). Derivatives of 0.1–0.4 DS are prepared. Examples of each are:

Quarternary:



Tertiary:

$$\begin{gathered}\text{Starch–OH} + \text{Cl–CH}_2\text{–CH}_2\text{–N–R}_2\\ \downarrow\\ \text{Starch–O–CH}_2\text{–CH}_2\text{–N–R}_2\\ \downarrow\\ [\text{Starch–O–CH}_2\text{–CH}_2\text{–N–R}_2]^{+}\ \text{Cl}^{-}\end{gathered}$$

Under alkaline conditions, the tertiary derivative is a free base. Neutralization converts the free base to the cationic tertiary ammonium salt.

As noted previously, cationization may be combined with phosphating of the starch. These dually derivatized starches, or amphoteric starches, are reported to be useful in papermaking and in pigment retention. Cationic starches are prepared on base starches from common and waxy corn. The starches may be acid-thinned or bleached during derivatization to meet a particular viscosity or functional requirement.

E. Other Derivatives

Starch has important possibilities as a base for other derivatives (Sanford and Baird, 1983). Some of these are manufactured on a limited scale, whereas others show future potential. The starch xanthates are prepared under strongly alkaline conditions with carbon disulfide. Recent interest has centered on their use as encapsulants for pesticides. Dialdehyde starches have been proposed for use in paper as a wet-strength additive, in water-resistant adhesives, and in leather tanning. These are prepared by periodic acid oxidation of the 2,3-glycol structure specifically to aldehydes. The high process cost has limited their development.

F. Starch as a Source of Chemicals

Starch is a prime candidate for use as a raw material because it is readily available at low cost and can be converted into a variety of useful products by chemical and biochemical means (Rutenberg and Solarek, 1984; Swinkels, 1985). Fermentation of starch to ethanol theoretically produces 567.9 g of ethanol per kilogram of starch. Gasoline blends (90:10) have received continued commercial interest (Chapter 19).

Conversion of starch to glucose and then to cyclic and acyclic polyols, aldehydes, ketones, acids, esters, and ethers has been investigated (Fleche, 1985). Sorbitol, the hexahydroxyl derivative of glucose, is the most widely produced and utilized derivative. Methyl glucoside (methyl α-D-glucopyranoside), prepared by reacting glucose with methanol, has shown promise for making polyesters for rigid polyurethane foam production. Higher-alkyl glucosides are sold commercially as nonionic surfactants. Oil-modified urethane coatings and alkyds also have been investigated.

Starch has been proposed for use in plastics because it is a renewable resource and is biodegradable. Starch-polyvinyl chloride, starch-polyethylene, starch-polyvinyl alcohol, and others have received attention.

Graft polymerization of starch has also been investigated. The graft polymers produced have utilized the generation of a free radical on the starch backbone, using cerium catalysis and then allowing the free radical to react with a polymerizable vinyl or acrylic monomer. Styrene, isoprene, acrylonitrile, and alkyl acrylates and methacrylates have been studied (Weaver et al, 1976).

VII. CORN STARCH UTILIZATION

Corn starch utilization is split, with about 35% going to foods and the remainder to nonfood applications (Whistler, 1984). The brewing industry accounts for about 20% of the edible use, with similar quantities in chemicals, drugs, and pharmaceuticals. The next largest uses are in canning (7.5%) and confectionery (6.5%). The baking industry uses approximately 6%. Condiments, prepared mixes, and miscellaneous uses account for the remainder.

Nonfood use is primarily in the paper industries, which account for 86% of the total. Adhesives, textiles, and other miscellaneous uses such as laundry starch account for the remaining 14%. Laminating and corrugating uses make up the single largest use, 26% of the total. Consumption in other paper applications such as wet-end addition, size press, calendering, and coatings make up 68%. Building products account for the remaining 6%.

A. In Foods

In foods, corn starches are used in the granular form or as dry powders, as swollen granules, and in molecular dispersions (Table I). As dry powders, the starches are treated to provide anticaking, dusting, or molding properties. Various treatments, such as redrying or addition of flow agents and oils, impart the desired compaction or flow characteristics (Orthoefer, 1984).

When using starches as swollen granules, one must pay attention to the processing conditions of time, temperature, pH, and shear. In the selection of a particular starch, one must consider the method of preparation, the desired function of the starch, the method of preparation of the fininshed food, the storage condition, the eating quality, and the desired appearance.

Overall, the type of modification as well as the base starch must be balanced with the product and the processing equipment. Adjustment of modification to obtain fully swollen granules is generally desired. In some instances, a highly delayed gelatinization through cross-linking may be desired for efficient heat penetration during retort processing of foods. Substitution to obtain instability such as for filling aids for canning is also utilized.

Many of the differences in native starch gel characteristics carry through the starch modification process. Some examples are: 1) high clarity from substituted, cross-linked waxy starch, 2) a slightly gelled texture from a substituted cross-linked starch from common corn, and 3) a film-forming starch from an acid-thinned high-amylose corn starch. Interfacing the base starch with the use, type and degree of substitution or modification, amount of cross-linking, and use of cook-up or pregelled starch is a complex process.

B. In Paper

Approximately 90% of the starch used in paper is derived from corn. Starch addition results in improvements in the physical properties of paper and reduced production costs; however, native starches produce thick and unstable cooked pastes that have only limited use in papermaking applications (Mentzer, 1984). Therefore, starch is modified to make it a more functional and versatile papermaking additive (Casey, 1983). For food packaging, "Industrial Starch Modified" is classified by the U.S. Food and Drug Administration under 21 CFR 178.3520.

TABLE I
Food Uses of Corn Starch

Physical Form of Starch	Application
Granules	Anticaking agent
	Dusting
	Diluent
	Molding
Swollen granules	Viscosity
	Texture
	Solids suspension
	Processing aid
	Binder
Molecular dispersion	Film-forming
	Colloid protection
	Encapsulation

Starches may be modified in the paper mill as well as by the starch producer. Modifications performed in the mill may consist of cationization, enzyme thinning, high-temperature conversion, and chemical-thermal conversion techniques. Conversion with enzymes requires special equipment capable of handling the extremely high initial viscosity of the starch paste before thinning. The uniformity of the conversion is dependent on close control of pH, time, temperature, and concentration of enzyme promoters such as calcium salts.

Modification of starches at high temperatures utilizes jet cookers. Limited thinning occurs due to shear and heat when the starch is cooked at about 160°C. Chemical modifiers are added before cooking. Ammonium persulfate at a concentration of 0.05–0.2% based on starch weight is the preferred additive, with hold times of 4–5 min at about 150°C. Other additives used have been hydrogen peroxide, sodium hypochlorite, alum, and citric acid.

Control of pH and storage temperatures is required to maintain the viscosity of the cooked starch. Avoiding the 67–87°C temperature range prevents amylose crystallization, and storage below 54°C prevents irreversible retrogradation.

Differences exist between starches converted at the paper mill and premodified starches. Low-molecular-weight starch components and sugars in premodified starches are removed by washing before drying (Bramel, 1986). These low-molecular-weight products have poor film-forming and binding properties compared to those of starch. The high-temperature conversion used in the mill gives more thoroughly dispersed starches, which are more likely to fractionate and retrograde upon cooling. With ammonium persulfate or other oxidizing chemicals used in the conversion, some carboxyl formation occurs during mill conversion. Enzyme-modified starches are less harshly treated.

Special converting corn starches are marketed by corn starch producers for conversion at the paper mill. Unmodified common corn starch with additives may be buffered to adjust pH; salts may be added for enzyme activity and antifoams added to control foaming. Other starches may be supplied that are slightly bleached and lightly acid-thinned. These provide both convenience and improved uniformity during paper mill conversion. Some starches are lightly modified to have lower peak paste viscosities, contain less protein, and have a reduced tendency to fractionate.

The commercially modified starches consist of acid-thinned, oxidized, acetylated, and hydroxyethylated types. The acid-thinned starches are used for paper sizing, calendering, and coating applications (Bramel, 1986). Acid-thinned products, although the least costly of the premodified starches, are not widely used because of their low film strength and greater tendency to retrograde.

Oxidized starches with thin to thick viscosities and carboxyl contents up to 1% are produced for sizing and coating applications. The oxidized starches exhibit excellent film-forming and binding properties plus resistance to retrogradation and congealing. The use of oxidized products in paper is declining because of their dispersing effect on fillers and fines, which also have an anionic character. This dispersing effect is seen in the wet end of the paper machine, where repulped paper containing oxidized starch lowers retention and efficiency.

Acetylated starches, sometimes referred to as gums, are used in coatings and surface sizes because of their excellent film-forming and reduced gelling tendencies. The instability of the acetate substitution somewhat limits their use, since free acid is generated during cooking and during storage, resulting in equipment corrosion and, of course, loss of acetate functionality.

Hydroxyethylated starches are produced at different levels of substitution and varying viscosities. The hydroxyethyl substitution is pH-stable as opposed to the less stable ester linkage. The films are strong, flexible, and clear. The cooked pastes are noncongealing and viscosity-stable, with desirable water-holding and rheological characteristics. Good compatibility with latex coatings is observed.

The diverse functional characteristics of starches produced for the paper industry ensure that starch will maintain its position relative to competitive products such as petroleum-based substitutes.

C. Future for Starch Utilization

The utilization of corn starch in foods and industrial markets has been challenged by substitute as well as competitive products. The use of more desirable native starches in foods has been met with processing and modification of either waxy or common corn starches. However, in nonfood utilization, the challenge is more severe. Hot-melt and pressure-sensitive adhesives have taken much of the former dextrin market. Latexes of various types have displaced starches in paper coatings and other applications.

New starch derivatives continue to be explored. Attempts are being made to penetrate markets that require functional properties outside those required by the traditional starch markets. Starch will likely maintain its position with continued technical improvement.

The possibilities of starch as an agricultural raw material are attractive. Much research attention, both academic and industrial, has focused on corn starch as a source of chemicals. The abundance, availability, and low price of corn starch make it an attractive commodity.

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CHAPTER 17

CORN SWEETENERS

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I. INTRODUCTION

Corn sweeteners are defined as those nutritive sweeteners manufactured from corn starch. Included in this category are crystalline monohydrate and anhydrous dextrose (D-glucose, corn sugar), high-fructose corn syrup (HFCS) (isosyrup, isoglucose), regular corn syrups (glucose syrup, starch syrup), and maltodextrins (hydrolyzed cereal solids). A variety of enzymatic and acid-catalyzed processes are used for the manufacture of corn sweeteners. For instance, dextrose is prepared by enzymatic hydrolysis of starch and purified by crystallization. HFCS is produced by partial enzymatic isomerization of dextrose hydrolysate, followed, in some cases, by enrichment to a higher fructose level by chromatographic separation. Regular corn syrups and maltodextrins are manufactured by partial hydrolysis of corn starch, using acid, acid-enzyme, or enzymatic techniques. Corn sweeteners are refined and sold in dry or syrup form for a wide range of uses depending on individual functional properties. U.S. manufacturers of corn sweeteners are listed in Table I, along with the estimated capacity of each as a percentage of the total industry.

Sweeteners are produced commercially throughout the world from other starch sources such as wheat, rice, potato, sweet potato, and tapioca. However, within the United States, corn starch is used exclusively as the raw material for production of starch-based sweeteners. This is due to the favorable cost, availability, and storage properties of corn, as well as the benefit of revenues generated from coproducts such as starch, oil, and animal feed. Typically, about 11–13% of the U.S. corn utilization has been used in wet-milling operations (Table II; see also Chapter 7). The one exception was in 1983. Of the total purified starch recovered from corn, about 75% is used for sweetener production. Consequently, corn sweeteners are major commodity products throughout the world and are used extensively in various food applications. Utilization has increased rapidly during the last 25 years, reaching 51% of the per capita consumption of corn sweeteners and sucrose in 1985 (Table III).

II. HISTORY

The study of starch-based sweeteners began in the early 19th century when a search was initiated for a sucrose replacement. During a French-English war, a British blockade of European ports caused a cane sugar shortage that led to studies on alternate sweeteners. J. L. Proust was awarded a prize by Napoleon for his work on preparing dextrose from grapes (Wichelhaus, 1913); however, Kirchoff's work in 1811 (Kirchoff, 1811) provided the basis for an eventual corn sweetener industry. While searching for a gum arabic substitute as a binder for clay, Kirchoff discovered that a sweet material was formed when a suspension of potato starch was heated in the presence of sulfuric acid. Samples were made of dry and evaporated syrups, as well as dextrose crystals separated from the syrup. For this discovery, Kirchoff was decorated by the Russian emperor and given a lifetime pension. In 1815, de Saussere reported that acid conversion of starch to sugar proceeded by hydrolysis rather than dehydration and that starch sugar was the same as grape sugar.

U.S. manufacture of dextrose by hydrolysis of potato starch began commercially in 1842, and corn sugar was first manufactured in a Buffalo, New York, plant in 1866. By 1876, 47 U.S. factories were in production and the corn sweetener industry was firmly established.

Research efforts were soon directed toward producing new and more sophisticated products. A major breakthrough occurred with the development of a process for manufacturing pure crystalline dextrose. Early efforts between 1880 and 1920 were of limited success and required repeated crystallization or crystallization from nonaqueous solvents. Large commercial quantities were not manufactured, but sufficient material was prepared to establish the therapeutic value of crystalline dextrose (Porst, 1921). In 1921, however, a commercially viable process was developed for crystallizing dextrose using carefully controlled conditions of concentration, agitation, temperature, and seed crystals (Newkirk, 1923).

Until the 1930s, acid was used exclusively for converting starch to syrups and sugar. Products and applications were often limited, however, due to the formation of off-flavors and color as a result of the nonspecific nature of acid hydrolysis. In the late 1930s, research in the area of fungal-derived enzymes led to an acid-enzyme process (Dale and Langlois, 1940) for the production of a sweeter, less viscous syrup that found application in many areas. This improvement, along with reduced regulatory constraints on corn syrup use, resulted in an increase in corn syrup and corn sugar consumption by 86 and 68%, respectively, between 1940 and 1942 (Jones and Thomason, 1951).

TABLE I
Estimated 1984 U.S. Corn Sweetener Manufacturing Capacity

Company	Location	Estimated Capacity (% of total industry)[a]
ADM Foods	Cedar Rapids, IA	31
A.E. Staley Manufacturing Co.	Decatur, IL	24
Cargill, Inc.	Minneapolis, MN	17
CPC International, Inc.	Englewood Cliffs, NJ	12
American Maize Products Co.	Stamford, CT	7
Coors	Johnstown, CA	<5
Grain Processing Corporation	Muscatine, IA	<5
Hubinger	Keokuk, IA	<5
Minnesota Corn Processors	Marshall, MN	<5
Penick and Ford	Cedar Rapids, IA	<5

[a] Data from Greditor (1983).

The success of the acid-enzyme process inspired further research efforts to improve dextrose production using enzymes. By the 1960s, commercial processes were developed that used a fungal enzyme (glucoamylase) to convert partially acid-hydrolyzed starch slurries to higher dextrose levels than those attained with acid hydrolysis alone. By the 1970s, bacterial enzymes (α-amylases) were commercialized that were effective for replacing the acid hydrolysis step. Thus, a total enzyme process for dextrose production was achieved that provided an increase in dextrose yield.

The introduction of enzymatic processes had taken the corn sweetener industry a long way from Kirchoff's discovery in 1811; however, one goal not attained was the commercial production of a corn sweetener at least as sweet as sucrose. Such a sugar, fructose, occurs naturally in many fruits and vegetables and is about 1.8 times as sweet as sucrose. Fructose was first isolated in 1847 (Doty, 1980) and was prepared by alkaline isomerization of dextrose in 1895 (Lobry DeBruyn and Van Eckenstein, 1895). Many attempts were made to

TABLE II
Utilization of Corn in Wet Milling[a]

		Corn Used in Wet Milling		
Crop Year[b]	Corn Disappearance[c] (bu × 10^6)	Sweeteners (bu × 10^6)	Total (bu × 10^6)	Total Usage as Percent of Disappearance
1980/81	7,223.4	350	515	7.1
1981/82	6,980.2	375	595	8.5
1982/83	7,290.1	400	665	9.1
1983/84	6,573.9	445	740	11.2
1984/85	7,003.4	500	795	11.4
1985/86[d]	6,845.0	520	840	12.3

[a] Source: USDA (1986).
[b] Oct. 1 to Sept. 30.
[c] To convert to metric tons multiply by 0.0254. Values include exports.
[d] Projected.

TABLE III
Per Capita Consumption of Corn Sweeteners and Sucrose

Year	Sucrose (kg)	Corn Sweeteners (kg)	Total (kg)	Corn Sweeteners (% of total)
1900[a]	29.5	...	29.5	...
1925[a]	46.4	...	46.4	...
1960[a]	44.4	5.2	49.6	10.5
1975[b]	40.5	12.5	53.0	23.6
1980[b]	37.9	18.2	56.1	32.4
1985[b]	28.7	29.5	58.2	50.7

[a] Data from Kean (1978).
[b] Data from Anonymous (1986).

develop a commercial process for producing a fructose syrup by alkaline isomerization. In 1943, a syrup containing 20% fructose was produced commercially (Cantor and Hobbs, 1944) for use as a moisturizing agent in tobacco; however, a food product was not manufactured due to problems of color, off-flavor, degradation products, and low fructose yield.

Studies in the early 1950s indicated that enzymes previously thought only to catalyze the isomerization of xylose could also convert dextrose to fructose. This observation was reported in 1957 (Marshall and Kooi, 1957) and patented in 1960 (Marshall, 1960), although the patent was later invalidated due to misidentification of the enzyme source. Interest in a commercial enzymatic process for isomerization of dextrose decreased in the United States, but research continued in Japan and eventually led to the discovery of enzymes that produced high yields of fructose. Commercial production of HFCS began in Japan in 1966 (Takasaki, 1966), and a U.S. patent was issued in 1971 (Takasaki and Tanabe, 1971) that consolidated several Japanese applications. Japanese technology was licensed for use in the United States, and a limited amount of 15% fructose syrup was produced in 1967 (Mermelstein, 1975), followed by a 42% fructose product the next year. Initially, HFCS products were produced in a batchwise system using soluble enzyme. However, concentrated effort within the corn refining industry resulted in a continuous system using bound enzyme technology in 1972 (Lloyd et al, 1972; Thompson et al, 1974); other industrial processes were developed shortly thereafter.

In the years immediately following the development of HFCS, sucrose prices increased dramatically due to increased demand and reduced inventory. As a consequence, the less costly HFCS became increasingly popular as a sugar substitute, and sales increased significantly. U.S. shipments of HFCS in metric tons (71 wt % basis) amounted to 21 in 1967, 102 in 1970, 679 in 1975, and 1,553 in 1978 (Peckham, 1979). The development of commercial processes for HFCS production occurred at the right time to take advantage of high sucrose prices, and, therefore, HFCS has continued as a viable alternative sweetener to sucrose in many applications.

III. CHEMISTRY

A. Starch Hydrolysis

Starch used to produce corn sweeteners is generally prepared from U.S. grade No. 2 corn by the wet-milling process. The starch is about 99% pure and contains, on a dry basis (db), 0.25–0.35% protein, 0.5–0.6% lipid, and less than 0.1% minerals.

Corn starch granules are composed of two distinct fractions, i.e., amylose, a linear polymer of 1,4-linked α-D-glucopyranosyl units, and amylopectin, a branched polymer containing short 1,4-linked glucose chains connected by 1,6 branch points. Typically, the amylose fraction represents 25–30% of the starch granule and exhibits a molecular weight of about 250,000, whereas the much larger amylopectin fraction represents 70–75% of the granule and has a molecular weight of 50–500 million (Zobel, 1984).

Corn sweeteners are produced by the hydrolytic action of enzymes or acid on the α-1,4, and α-1,6 glucosidic linkages. Saccharides of various molecular

weights are liberated and, depending on the extent and type of hydrolysis, sweeteners of different functional properties are produced. The number of dextrose units in a saccharide is referred to as degree of polymerization (DP), where DP-1 is dextrose, DP-2 is a disaccharide such as maltose or isomaltose, DP-3 is a trisaccharide such as maltotriose or panose, and DP-4$^+$ is a tetra- or higher saccharide. Degree of hydrolysis is expressed in terms of dextrose equivalent (DE), a measurement of the reducing content of a starch hydrolysate calculated as dextrose on a dry basis. Since starch contains only one reducing group per molecule, it exhibits essentially zero DE. Complete hydrolysis to dextrose yields a 100-DE product, and partial hydrolysis produces a product of intermediate DE. DE is determined by reacting reducing sugars with an alkaline solution of a copper salt. The amount of copper reduced is proportional to the amount of reducing sugars present (AACC, 1983). Alternatively, given the composition of a starch hydrolysate by a procedure such as high performance liquid chromatography (Brobst and Scobell, 1981; Bernetti, 1982), DE is calculated by summing the DE contribution of each saccharide, where DP-1 = 100 DE, DP-2 = 62 DE, DP-3 = 40 DE, and DP-4$^+$ = about 18 DE. Since the composition of the DP-4$^+$ fraction varies depending on the hydrolysis technique, the DE contributed by this fraction must be determined for each type of product. An approximate relation between DP and DE can be expressed as follows:

$$\mathrm{DP} = [(20{,}000/\mathrm{DE}) - 18]/162\,.$$

Each hydrolytic scission is accompanied by the addition of one molecule of water. The weight gain due to water addition is referred to as chemical gain; therefore, complete hydrolysis of starch to dextrose yields a dry substance increase by a factor of (162 + 18)/162 or 1.11. Partial hydrolysis yields a lower chemical gain factor. The relationship between DE and chemical gain factor can be described as follows:

$$\text{Chemical gain factor} = (0.00111)(\mathrm{DE}) + 0.9973\,.$$

B. Acid Hydrolysis

Acid hydrolysis of starch proceeds randomly, cleaving both α-1,4 and α-1,6 linkages and releasing increasing amounts of low-DP material with time. At a given DE level, the same saccharide composition is obtained regardless of the hydrolysis conditions used. Typical compositions at varied DE levels are shown in Table IV.

Since acid is not a specific catalyst for hydrolysis only, other reactions occur as hydrolysis proceeds. For instance, dehydration of dextrose yields hydroxymethylfurfural. In turn, this compound may decompose to levulinic and formic acids or polymerize to compounds believed to be intermediates to color formation (Singh et al, 1948). In addition, acid-catalyzed recombination of saccharides forms gentiobiose and branched polymers of higher molecular weight. Other reactions occur that produce off-flavor and color components that are often difficult to remove from the finished product. Consequently, syrups produced by acid hydrolysis are limited to about 42 DE to avoid problems associated with side reactions.

C. Enzyme Hydrolysis

Enzymatic hydrolysis of starch is much more specific than acid hydrolysis. This specificity minimizes off-flavors, color, and degradation product formation, resulting in higher product yields and reduced refining costs. Enzymes used in corn sweetener production include bacterial and fungal α-amylases, glucoamylase, β-amylase, and pullulanase.

α-AMYLASES

Bacterial α-amylases are produced from *Bacillus* organisms in aerated, submerged-culture fermentation media specifically formulated to maximize enzyme production. α-Amylases are classified as endoenzymes, since hydrolysis proceeds randomly within the molecule, cleaving α-1,4 linkages only and releasing shorter fragments or saccharides retaining the α configuration. The action pattern of bacterial α-amylases varies, depending on the source of the enzyme. For example, *B. subtilis* amylases produce significant quantities of maltose, maltotriose, and maltohexose (Allen and Spradlin, 1974), whereas *B. licheniformis* amylase releases a significant amount of maltopentaose (Saito, 1973). α-Amylases from fungal sources such as *Aspergillus oryzae* are also endoenzymes and exhibit specificity for α-1,4 linkages. Unlike bacterial α-amylases, however, fungal α-amylases are considerably less thermostable and produce maltose as the main product. Consequently, these enzymes are used to make syrups with a high maltose content.

Typical use conditions for α-amylases depend on the particular enzyme and process. Enzymes from *B. licheniformis* or *B. stearothermophilus* are the most thermostable of the bacteria-derived α-amylases and can be used at 105–110° C for a short time. *B. subtilis* α-amylases are less stable and are generally used at temperatures of 85–90° C. Fungal α-amylases are much less stable than bacterial enzymes and are used in reactions conducted at 55–60° C. The best pH range for starch hydrolysis is 5.5–7.0 for bacterial α-amylases and 5.0–5.5 for fungal α-amylases.

TABLE IV
Composition of Acid-Converted Corn Starch

	Saccharide (%, db)							
DE[a]	DP[b]-1	DP-2	DP-3	DP-4	DP-5	DP-6	DP-7	DP-8+
20	6	6	5	5	5	4	4	65
25	8	8	7	7	6	5	4	55
30	11	9	9	8	7	6	5	45
35	13	11	10	9	8	6	5	38
40	18	13	11	10	8	6	6	28
45	22	15	12	10	8	6	5	22
50	25	17	13	10	8	6	5	16
55	32	18	13	9	7	5	4	12
60	36	20	13	9	6	4	4	8
65	42	21	13	8	5	3	3	5

[a] Dextrose equivalent.
[b] Degree of polymerization.

GLUCOAMYLASE

Glucoamylase (also called amyloglucosidase or γ-amylase) is produced from strains of *A. niger* in submerged fermentation (Armbruster, 1961). The fermentation broth contains two distinct glucoamylase isozymes (Svensson et al, 1982), α-amylase, possibly transglucosidase, and other enzymes such as protease and cellulase. The presence of the α-amylase is important, since it assists saccharification by hydrolyzing large starch fragments to provide additional substrate for the action of glucoamylase (Kooi and Armbruster, 1967). Transglucosidase, however, reduces dextrose yield by catalyzing the formation of isomaltose. Consequently, the removal of this enzyme from the fermentation broth is accomplished by adsorption on a clay mineral or by other techniques (Kerr, 1961, 1962; Hurst and Turner, 1962; Kooi et al, 1962; Kathrein, 1963). Complete elimination of transglucosidase is also possible, since transglucosidase-free mutants have been isolated (Norman, 1979).

Glucoamylase exhibits exoamylytic activity and releases dextrose stepwise from the nonreducing end of the substrate by cleaving both α-1,4 and α-1,6 linkages. Rates of hydrolysis are dependent on the type of linkages present and substrate size (Abdullah et al, 1963). Typically, in commercial processes, glucoamylase produces a dextrose hydrolysate containing about 96% dextrose (db). The enzyme also catalyzes the reverse reaction (reversion) of dextrose to disaccharides. At a normal commercial solids level of 30 wt %, a hydrolysate containing 87% dextrose, 11% isomaltose, and 2% maltose (db) would be produced (Subramanian, 1980) if the reaction reached equilibrium. Equilibrium dextrose level, a function of total dry solids, increases from 87% at 30 wt % solids to 92 and 96% at 20 and 10 wt % solids, respectively (Subramanian, 1980). The kinetics of hydrolysis and reversion reactions catalyzed by glucoamylase have been investigated by Shiraishi et al (1985) and Beschkov et al (1984).

Glucoamylase exhibits good stability over a wide pH range; however, in commercial processes, a pH of 4.0–4.5 is generally used. Recommended temperatures are about 58–62° C, since a higher temperature reduces enzyme stability and a lower temperature increases the possibility of microbial contamination.

β-AMYLASE

Barley β-amylase is a maltogenic enzyme used for syrup production. The enzyme, an exoamylase, releases maltose in the β configuration sequentially from the nonreducing end of a molecule. Unlike that of the α-amylases, the action of β-amylase is terminated near an α-1,6 linkage and, in the absence of endoamylase activity, yields a highly branched β-limit dextrin. The presence of α-amylase endoamylytic activity in malt, however, provides additional substrate for β-amylase activity. Reaction conditions are generally 55–60° C, pH 5.0–5.5.

PULLULANASE

Pullulanase, a debranching enzyme, is specific for hydrolyzing α-1,6 bonds in starch. When used in combination with glucoamylase, an increased rate of dextrose production is achieved, resulting in higher dextrose yields. The combined action of pullulanase and a maltogenic enzyme also yields higher maltose levels.

D. Isomerization

Glucose isomerase (D-xylose ketol-isomerase, xylose isomerase) catalyzes the isomerization of dextrose to D-fructose and of D-xylose to D-xylulose and is important in the corn sweetener industry because of its use in producing HFCS. The enzyme is produced in aerated, submerged fermentation from a wide variety of bacterial organisms (Chen, 1980a, 1980b). Xylose is frequently used as an inducer; however, constitutive mutants have been developed (Armbruster et al, 1974; Outtrup, 1976). Since the enzyme is produced intracellularly, mechanical disruption or treatment of the cells with surfactants or lysozyme is required to produce a soluble enzyme. The enzyme exhibits activity at a temperature as high as 90°C, although stability is low and commercial operations are conducted at about 60°C. Typically, optimum pH is in the range of 7.5–8.5, although 70% of the activity is retained at pH 7 (Zittan et al, 1975). Magnesium is added as a cofactor to maintain isomerase stability and prevent inhibition by trace levels of calcium.

IV. MANUFACTURING PROCESSES

A. Dextrose

Dextrose (D-glucose) has been produced commercially from starch by a wide variety of acid, acid-enzyme, and enzyme-catalyzed processes. Presently, most production schemes use a thermostable α-amylase for thinning (liquefying) starch to 10–15 DE, followed by saccharification with glucoamylase to about 95–96% dextrose (db). The hydrolysate is clarified and refined and then is further processed to crystalline dextrose, liquid dextrose, high-dextrose corn syrup, or to HFCS feed (Fig. 1).

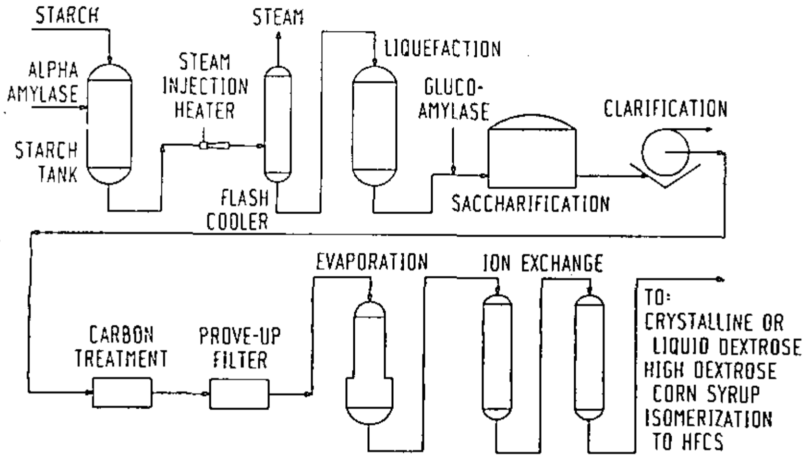

Fig. 1. Dextrose production.

STARCH HYDROLYSIS

Until about 1960, commercial dextrose processes were conducted by straight acid hydrolysis. The process consisted of acidifying a 15–25 wt % starch suspension with HCl to 0.03–0.04*N* and heating at *140–160°C for 5–10 min or* until a maximum dextrose level was reached. However, due to acid-catalyzed formation of degradation products, a dextrose level of only about 86% (db) was achievable (Kooi and Armbruster, 1967).

The development of glucoamylase for saccharification provided a major improvement in dextrose production technology by allowing a reduction in the extent of acid hydrolysis. Liquefaction was conducted batchwise in corrosion-free equipment by adjusting a 30–35 wt % starch suspension to pH 1.8–2.0 with HCl or H_2SO_4 and thinning at 120–140°C until a 10–20 DE hydrolysate was obtained. The hydrolysate was then saccharified with glucoamylase. Control of DE is important in this type of process, since the level of acid-reversion products increases with increasing DE, resulting in reduced dextrose yield during subsequent saccharification. Conversely, if DE is too low, i.e., less than 10, starch retrogradation occurs and filtration problems may develop. Typically, an acid-enzyme process yields a dextrose level of 92–94% (db) (Woolhouse, 1976).

Total enzyme processes were developed in the 1960s, when thermostable α-amylases derived from *B. subtilis* became commercially available. The lower temperature and neutral pH used for liquefaction were effective in minimizing side reactions and increasing the dextrose yield to 95–97% (db) (Kooi and Armbruster, 1967; MacAllister, 1979). The *B. subtilis* enzyme is sufficiently stable to be used at 85–95°C for a short time (Reichelt, 1983), and processes were designed to take advantage of this property. A typical process is conducted by thinning a 30–40 wt % starch suspension with α-amylase at pH 6.0–6.5, 85–90°C, for 1 hr in the presence of 200–400 ppm calcium (db) added for enzyme stabilization. The reaction is continued by using a 5–10-min heat treatment at 120–140°C to dissociate insoluble complexes of fatty acid and amylose that are present in starch or formed during processing and are resistant to the action of enzyme (Hebeda and Leach, 1974). A heat treatment is needed, since a temperature of 100°C or higher is required to dissociate the complex, as evidenced by differential scanning calorimetry studies (Kugimiya et al, 1980; Bulpin et al, 1982). Since the high reaction temperature completely inactivates *B. subtilis* α-amylase, a second enzyme addition at a reduced temperature is required to continue the hydrolysis before the complex reforms. The second stage of the reaction is conducted at 85°C for about 1 hr to produce a 10–15-DE hydrolysate for saccharification. This process is effective in preventing the occurrence of insoluble starch particles in the final hydrolysate and, therefore, maximizing filtration rates during processing.

The next improvement in enzymatic dextrose process technology was achieved when enzymes became available that exhibited increased thermostability and retained activity above 100°C. α-Amylases derived from *B. licheniformis* (Chiang et al, 1979; Rosendal et al, 1979) or *B. stearothermophilus* (Anonymous, 1984a) are effective at a sufficiently high temperature to eliminate the need for a heat treatment step. A typical process (Slott and Madsen, 1975) is conducted by thinning a 30–40 wt % starch slurry containing 100–200 ppm calcium (db) with α-amylase through a steam injection heater at 103–107°C, pH 6.0–6.5. The instantaneous heating gelatinizes the starch rapidly and completely and dissociates the amylose-lipid complex. The temperature is maintained for 5–10 min in a holding tube; batch or continuous reaction then follows for 1–2 hr at about 95°C to yield a 10–15-DE hydrolysate. This type of liquefaction process, currently in widespread use throughout the wet-milling industry, produces an efficiently thinned low-DE hydrolysate for subsequent saccharification.

α-Amylase stability during liquefaction is a function of the combined effects of temperature, pH, dry substance, time, and calcium. Knowledge of these variables allows calculation of residual activity (Rosendal et al, 1979). For instance, at 105°C and otherwise typical liquefaction conditions, only about 20% of the α-amylase activity is lost. Since operation above 100°C is effective in achieving complete starch gelatinization and rapid dissociation of the amylose-lipid complex, the residual activity is sufficient to hydrolyze amylose rapidly and prevent reassociation of the complex; therefore, a second enzyme addition or heat treatment is not required. An additional advantage of the highly thermostable α-amylase is a low level of contaminating protease. As a result, protein solubilization is minimized during processing, allowing the use of reduced-purity starch containing protein levels that are higher than normal (Reichelt, 1983).

Other specialized processes that have been suggested as alternatives to conventional starch liquefaction techniques include the Kroyer process for hydrolyzing impure starches such as corn grits (Holt et al, 1975), low-temperature granular starch processes (Hebeda et al, 1975), and a dual-addition thermostable enzyme process for thinning wheat starch (Reichelt, 1983).

Regardless of the manner in which starch is thinned, saccharification is conducted with glucoamylase to produce a dextrose hydrolysate. Saccharification is conducted by batch or continuous operation in reactors that are often as large as several hundred thousand liters. Thinned starch is diluted to 28–30 wt % solids and is cooled to about 60°C; the pH is adjusted to 4.0–4.5, and sufficient glucoamylase is added to achieve a maximum dextrose level in 24–96 hr. Temperature control is important, since a higher temperature reduces enzyme stability and a lower temperature increases the risk of microbial contamination. At a typical final solids level of 30 wt %, a dextrose level of 96% (db) is achieved. Decreasing the solids level to 10–12 wt % is effective in increasing maximum dextrose level to 98–99% (McMullen and Andino, 1977). However, the increased dextrose level is attained at the expense of increased evaporation cost and risk of microbial contamination. Conversely, at a higher solids of 40 wt %, dextrose is reduced to 94% (Norman, 1981). Typical dextrose hydrolysate compositions attained at varied solids levels are shown in Table V. At maximum dextrose, DP-2 consists of roughly equal amounts of maltose and isomaltose with a trace of maltulose. At this point, the maltose level is at equilibrium. Isomaltose, however, is still substantially below the equilibrium level, and extending the reaction time reduces the dextrose level due to continual accumulation of isomaltose via the reversion reaction. Consequently, accurate control of glucoamylase dosage and reaction time is required to avoid loss in dextrose yield during saccharification. Typical saccharification curves (Fig. 2) show the effects of dosage and time.

An additional source of dextrose yield loss is the formation of maltulose (4-*O*-α-D-glucanopyranosyl D-fructose). Precursors to this disaccharide are formed when end dextrose units of oligosaccharides are isomerized to fructose by alkaline isomerization during the liquefaction step (Norman, 1979). During saccharification, the last α-1,4 linkage of the oligosaccharide is resistant to hydrolysis because of the terminal fructose and, therefore, maltulose accumulates in the hydrolysate, with an equivalent loss in dextrose. This reaction is minimized by controlling thinning pH below 6.3.

Maximum dextrose level can be increased by using a specialized glucoamylase preparation (Tamura et al, 1981b) or by using a debranching enzyme in combination with glucoamylase to increase rate of dextrose formation relative to isomaltose formation. Increased dextrose yields of 2% or more have been obtained with pullulanase (Hurst, 1975) or isoamylase (Norman, 1982). However, in both cases, enzyme instability under normal saccharification conditions limits commercial utilization. A thermostable, acidophilic debranching enzyme from *B. acidopullulyticus* (Nielsen et al, 1982) has been used at pH 4.5, 60°C in the presence of glucoamylase to increase dextrose levels. Other reported advantages include reduced glucoamylase requirement, higher solids operation, and reduced reaction time.

Commercial dextrose processes use soluble glucoamylase, although the use of immobilized glucoamylase has been studied extensively. Many different supports have been evaluated for binding glucoamylase, and the immobilized enzyme has been studied in continuous operation by many investigators, including Bachler et al (1970), Smiley (1971), Gruesbeck and Rase (1972), Park and Lima (1973), and Lee et al (1975). Its commercial utilization, however, has been prevented by several factors, including 1) the need for clarified feed, 2) a relatively short enzyme life, and 3) 1.0–2.5% lower dextrose yield (Daniels, 1980; Rugh et al, 1979) due to diffusion problems and increased reversion. Specific problem areas have been addressed and potential solutions suggested. For instance, dextrose yield can be increased by using a partially saccharified feed (Hebeda et al, 1979). Use of a nonporous carrier reduces reversion by minimizing diffusion (Wasserman et al, 1982), and use of a more stable glucoamylase (Tamura et al, 1981a) increases enzyme half-life. In addition, purification of glucoamylase is effective in providing a bound enzyme preparation of increased potency, resulting in reduced residence time requirement (Lobarzewski and Paszczynski, 1983).

REFINING

Refining of dextrose hydrolysate is required to remove insolubles contributed by the starch, as well as ash, color, and protein solubilized during processing.

TABLE V
Dextrose Hydrolysate Composition as a Function of Solids

Final Hydrolysate Solids (wt %)	Saccharide (%, db)			
	DP-1	DP-2	DP-3	DP-4+
10	98.8	0.6	0.2	0.4
15	98.2	1.1	0.2	0.5
20	97.5	1.6	0.3	0.6
25	96.9	2.1	0.3	0.7
30	96.1	2.7	0.3	0.9
34	95.5	3.1	0.4	1.0

Clarification to remove traces of insoluble fat, protein, and starch is accomplished by centrifugation or precoat filtration using a diatomite filter aid (Basso, 1982). The hydrolysate is then treated with powdered or granular carbon (van Asbeck et al, 1981) and ion-exchange resins to remove residual trace impurities such as color, color precursors, proteinaceous material, and inorganics. The decolorized liquor is evaporated to 50–55 wt % solids and may be refined additionally before being processed to crystalline monohydrate or anhydrous dextrose, liquid dextrose, or high-dextrose corn syrup.

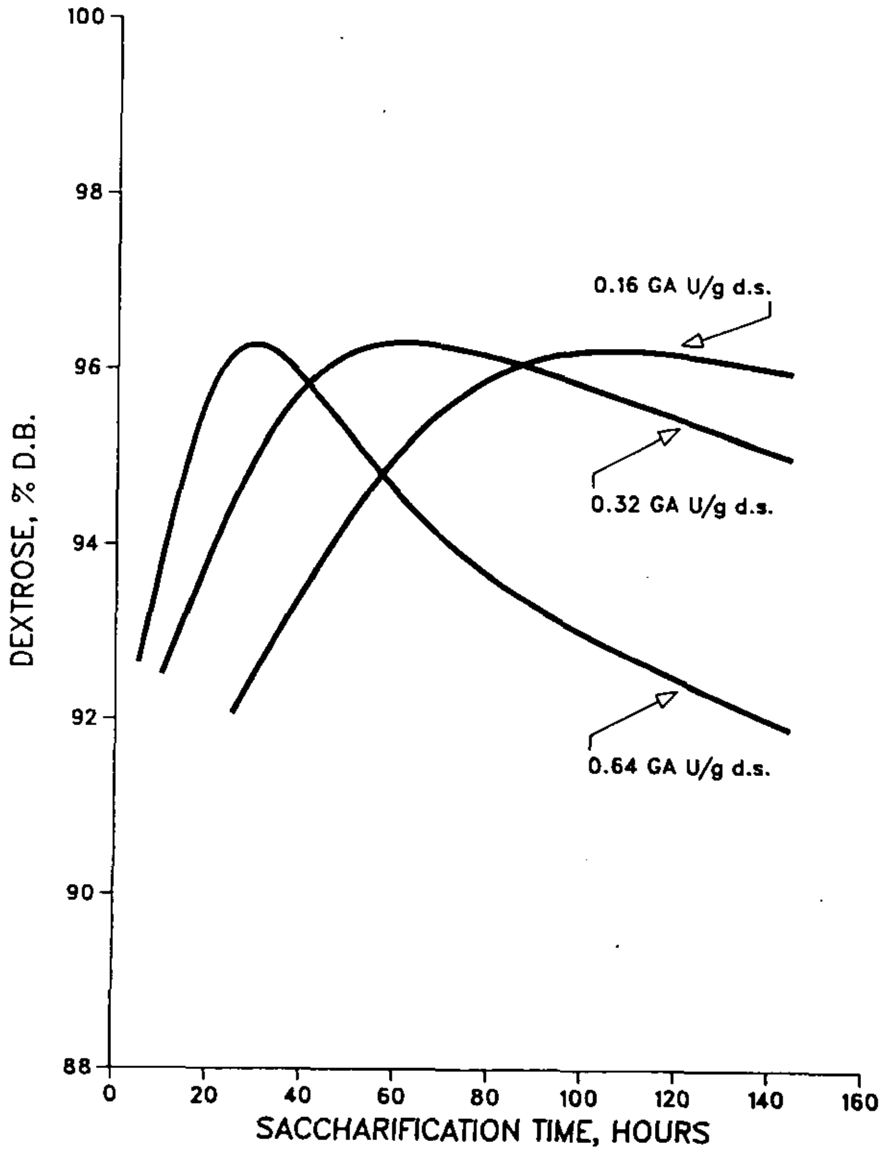

Fig. 2. Effect of glucoamylase (GA) dosage on dextrose production.

CRYSTALLINE DEXTROSE

Crystalline dextrose monohydrate is produced by evaporating the refined dextrose hydrolysate to 70–78 wt % solids, cooling to about 46° C, and mixing with seed crystals from the prior batch in a crystallizer. The mass is agitated and cooled slowly to 20–30° C over a period of three to five days, during which about 60% of the dextrose is crystallized as the monohydrate. The magma is centrifuged to remove the mother liquor (greens); the crystals are washed with a spray of cold water and dried in a rotary dryer to about 8.5% moisture, a level slightly below the theoretical value of 9.1% for one molecule of water of crystallization per dextrose molecule. By reducing moisture to this level, the caking tendency of dextrose crystals is minimized. The mother liquor may be partially recycled to the initial crystallization step or concentrated and crystallized to obtain a second crop of crystals and corresponding second greens. The second greens contain about 60% dextrose (db), and a total dextrose crystal yield of 87.5% is obtained based on a hydrolysate dextrose level of 95% (MacAllister, 1979). USP grade dextrose, which is used for special therapeutic purposes, is obtained by dissolving the centrifuge cake and recrystallizing to achieve a very high degree of purity.

Anhydrous α-dextrose is manufactured by crystallizing dissolved dextrose monohydrate at a temperature of 60–65° C in a vacuum pan. Evaporative crystallization is required to prevent color formation at high temperature and hydrate formation at low temperature. Crystals are separated, washed, and dried.

LIQUID DEXTROSE

Liquid dextrose is prepared by dissolving crystalline dextrose to 71 wt % solids. A high-dextrose corn syrup is made by refining a dextrose hydrolysate containing 95–96% dextrose and concentrating it to 70–75 wt % solids. This particular product is technically a corn syrup, since dextrose is defined as a material that exhibits a DE of 99.5 or higher.

SHIPPING

Crystalline dextrose is shipped in 45.4-kg bags or in bulk. Liquid products are transported in insulated tank cars or trailers at approximately 50° C to prevent crystallization.

PRICE

The price of crystalline dextrose monohydrate since 1970 is shown in Table VI. Dextrose price is affected by a variety of factors, including sucrose pricing, corn and production costs, process capacity, and demand. However, the price of dextrose is generally controlled to the largest extent by the price of sucrose. In 1985, the average crystalline dextrose price on a dry weight basis was about the same as the price of refined sucrose, and 126, 114, and 214% of the prices of 42% HFCS, 55% HFCS, and corn syrup, respectively. The high price of dextrose relative to that of HFCS is due in part to limited production facilities and to the high cost of crystallizers. Mid-1984 prices for crystalline anhydrous dextrose and USP anhydrous dextrose were $0.91/kg ($0.41/lb) and $1.03/kg ($0.47/lb), respectively.

B. High-Fructose Corn Syrup

Corn syrups containing 42% (db) fructose (levulose) are manufactured from refined dextrose hydrolysate by converting a portion of the dextrose to fructose with immobilized glucose isomerase. Chromatographic separation techniques are used to produce a 90% fructose product that is blended with 42% HFCS, to yield a 55% HFCS product (Fig. 3).

IMMOBILIZED ISOMERASE

In the early stages of HFCS development, it became evident that batchwise isomerization with soluble enzyme was economically prohibitive due to high enzyme cost. In addition, the long reaction time required to minimize enzyme consumption was responsible for the production of undesirable by-products, such as mannose, psicose, color, and off-flavors, resulting in high refining costs. Consequently, to reduce reaction time, and at the same time reduce enzyme cost, a process was needed that would allow enzyme reuse. Many different types of enzymes and immobilization systems were studied, and several reached the point of commercial utilization.

Glucose isomerases used in commercial operation have been developed from a variety of bacterial sources including *Actinoplanes missouriensis* (Shieh et al, 1974), *Aerobacter levanicum* (Shieh and Donnelly, 1974), *Arthrobacter* (Lee et al, 1972), *B. coagulans* (Outtrup, 1976), *Flavobacterium arborescens* (Anon., 1983a), *Streptomyces griseofuscus* (Anonymous, 1984b), *S. olivaceus* (Brownewell, 1971), *S. olivochromogenes* (Armbruster et al, 1976), and *S. rubiginosus* (Anonymous, 1984c). Techniques for immobilizing enzymes include treating whole cells to maintain enzyme activity and structural integrity or separating the enzyme from the cells and attaching the soluble enzyme to a solid support. Examples of processes for producing commercial whole-cell products include cross-linking cells with gluteraldehyde (Zienty, 1973); flocculating whole-cell aggregates with a polyelectrolyte, polyacid, or mineral hydrocolloid (Lee and Long, 1974); or rupturing cells by homogenization and reacting with gluteraldehyde (Amotz et al, 1976). Cell-free products are produced by adsorption of soluble enzyme onto ion-exchange cellulose (Sutthoff et al, 1978) or adsorption within pores of alumina or other inorganic materials (Messing, 1974; Eaton and Messing, 1976). Soluble enzyme may also be adsorbed onto an inorganic carrier followed by cross-linking with a bifunctional reagent (Levy and Fusee, 1979; Rohrbach, 1981).

TABLE VI

Price ($/kg) of Corn Sweeteners in the United States[a]

Year	Dextrose[b]	HFCS-42[c]	HFCS-55[d]	Corn Syrup[e]
1970	0.21	0.36	···	0.15
1975	0.43	0.37	···	0.31
1980	0.59	0.38	···	0.26
1981	0.60	0.34	0.40	0.28
1982	0.55	0.26	0.32	0.25
1983	0.53	0.29	0.37	0.23
1984	0.54	0.32	0.40	0.23
1985	0.49	0.30	0.36	0.20
1986[f]	0.48	0.32	0.36	0.18

[a] Based on 1970–1975 data (Anonymous, 1976) and 1980–1986 data (Anonymous, 1986).

[b] Monohydrate basis, in 45.4-kg bags.

[c] 42% fructose, 71 wt % solids, in tank cars.

[d] 55% fructose, 77 wt % solids, in tank cars.

[e] 80.3 wt % solids, in tank cars.

[f] July price.

HFCS-42

Regardless of the type of enzyme or immobilization technique used, process conditions for HFCS production are generally very similar. A high-quality HFCS feed stream is prepared from a 93–96% dextrose hydrolysate by clarification, carbon and ion exchange refining, and evaporation to 40–50 wt % solids. Clarification is generally conducted using traditional rotary-drum precoat filtration. Flocculation and continuous removal of insolubles has also been reported (Anonymous, 1983b). A high-quality feed is important to prevent accumulation of insolubles within the enzyme bed, resulting in a reduced flow rate.

Magnesium as $MgSO_4$ is added to the feed to activate and stabilize isomerase and also counteract the inhibitory effect of residual calcium. A magnesium level of 0.0004*M* is sufficient to overcome a maximum calcium level of 1 ppm; however, up to 15 ppm calcium can be tolerated if magnesium is added at a magnesium-calcium molar ratio of at least 20 (Anonymous, 1981). Addition of sulfite or bisulfite salts to the feed is also effective in increasing enzyme stability and reducing color formation (Cotter et al, 1976). Cobalt, another known activator of isomerase, was used in initial batch processes in which pH was maintained at a low level to minimize side reactions (Carasik and Carroll, 1983).

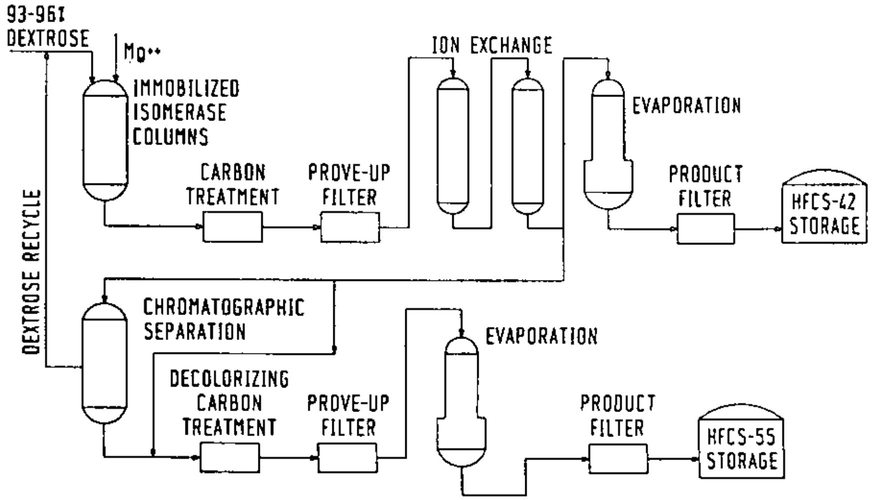

Fig. 3. High-fructose corn syrup production.

At the higher pH levels used in continuous systems, however, cobalt is not needed. An additional potential problem is the presence of dissolved oxygen in the dextrose feed. Therefore, deaeration may be necessary to prevent formation of by-products and inactivation of isomerase.

Reaction temperature and pH depend on the specific enzyme preparation used; however, conditions recommended by the enzyme suppliers are within the ranges of 55–61° C and 7.5–8.2 pH. Isomerase activity decreases below pH 7, and the enzyme is inactivated below pH 5 and above pH 9 (Anonymous, 1981). In general, the pH level should be controlled as low as possible to minimize side reactions while still maintaining optimal activity.

The isomerization reaction is conducted by passing feed through a fixed bed of immobilized isomerase at a controlled rate sufficient to yield 42–45% (db) fructose. An equilibrium fructose level of 51% (db) can be achieved at 60° C by increasing the reaction time significantly; however, this approach is not commercially viable. Minimizing nondextrose saccharides and, therefore, maximizing dextrose in feed is advantageous, since the reaction time required to attain the target fructose level is reduced. Isomerase performance is not affected by the presence of maltose or isomaltose (Hultin, 1983) or other nondextrose saccharides normally present. An exception may be reduced isomerase efficiency due to the presence of maltulose or other components formed under conditions that produce maltulose (Hurst and Lloyd, 1983).

During the isomerization process, enzyme activity decreases due to a combination of thermal inactivation and other factors such as the presence of feed impurities. Therefore, residence time is increased by reducing the flow rate through the column to maintain the desired fructose level. Enzyme half-life is normally several weeks. The enzyme is generally used for two to three months through several half-lives until its residual activity is reduced to 10% of the initial level (Carasik and Carroll, 1983).

Refining. The isomerized product is refined to an acceptable final quality by adjusting the pH to 4–5 and treating it with carbon to remove undesirable color and flavor. Additional refining by ion-exchange is conducted with a strong-acid cation resin in the hydrogen form followed by a weak-base anion resin in the free base form to remove salts and residual color. The product is then evaporated to 71% solids at a low temperature.

Shipping. The product is transported in tank cars or by rail. Storage at 30–32° C is required to prevent crystallization. If crystallization does occur, heating to 38° C is necessary to dissolve the crystals before unloading.

HFCS 55 and 90

HFCS containing 42% fructose was the first corn sweetener produced that provided a sweetness approaching that of sucrose. In certain applications such as soft drinks, however, a sweetener exhibiting sweetness equivalent to sucrose was desired. Several techniques have been studied for increasing the fructose level. These include the use of a chemically stabilized isomerase at a higher isomerization temperature (Lloyd, 1983), complexation of fructose with borate compounds, or removal of dextrose by crystallization. Current commercial processes use a chromatographic separation technique to produce products enriched in fructose. Products of this type were first introduced commercially in limited quantities in 1976.

Enrichment. Enrichment is accomplished by passing 42% HFCS through a column of adsorbent containing calcium or other cations (Long, 1978) or a nonresin, nonswelling mineral adsorbent (Broughton et al, 1977). Fructose is bound to the adsorbent and is retained to a greater extent than dextrose or oligosaccharides. In batch operations, elution with water produces a high-dextrose fraction, followed by a mixture of dextrose and fructose and, finally, by a relatively pure fructose fraction. Batch operations are not efficient; therefore, to increase production rate and reduce water consumption, continuous systems were developed (Keller et al, 1981; Teague and Arnold, 1983). Continuous operations utilize, in principle, a simulated moving-bed process in which feed and desorbent enter the column at different points, while fructose (extract) and the nonfructose fraction (raffinate) are withdrawn. Points of entry and withdrawal change in periodic fashion in correspondence with respective material flows through the column. In this way, separation of fructose and dextrose is maximized and costs are minimized. In a typical operation, a 42% fructose feed at 50 wt % solids is passed through a column to yield a product stream containing, on a dry basis, 94% fructose and 5% dextrose, and a raffinate containing 86% dextrose and 6% fructose. Fructose extraction efficiency is 91.5% (Teague and Arnold, 1983). The enriched HFCS is blended with 42% HFCS to provide a product containing 55% fructose. Raffinate at about 20 wt % solids is recycled to isomerization or blended into saccharification tanks to convert a portion of the oligosaccharides to dextrose before isomerization. Alternatively, raffinate can be saccharified using immobilized glucoamylase (Rugh et al, 1979). Reportedly, this technique is being used in commercial operations (Anonymous, 1984d).

Shipping. The 55% HFCS product is evaporated to 77 wt % solids for shipment. Crystallization is not a problem because of the high fructose level and reduced dextrose content. The 90% HFCS product can be evaporated to 80 wt % solids for shipment as a noncrystallizable syrup.

CRYSTALLINE FRUCTOSE

Pure crystalline fructose has been produced commercially by a variety of processes (Hamilton et al, 1974; MacAllister, 1980). For instance, pure fructose has been made by oxidation of glucose with glucose oxidase, followed by precipitation of sodium gluconate and crystallization of fructose from methanol (Holstein and Holsing, 1962). A more direct approach for producing commercial quantities of crystalline fructose involves the use of a sulfonated-polystyrene resin in the calcium form to separate fructose from invert followed by crystallization (Bollenback, 1983). Because of the difficulty involved in crystallizing fructose, alcohol was used as a solvent in many processes to decrease fructose solubility (Lauer et al, 1971; Nitsch, 1974). Fructose, however, can be crystallized from aqueous solution by using a high level of seed crystals (Kusch et al, 1970). Most recently, HFCS has been used as raw material for commercial production of crystalline fructose. This process involves production of 42% HFCS, chromatographic separation to obtain a fraction containing 97% fructose, evaporation to 70%, and crystallization of about 50% of the fructose in 80–100 hr (Morris, 1981).

A different approach to production of pure fructose has been suggested that involves enzymatic conversion of dextrose to D-glucosone followed by hydrogenation to fructose and recovery by crystallization (Neidleman et al, 1981). Alternates to crystallization include spray drying (Lundquist et al, 1976) or preparation of a noncrystallized dry product by adding anhydrous fructose to a highly concentrated fructose solution, kneading, and drying (Yamauchi, 1975).

Crystalline fructose is packed in multiwalled bags containing a foil liner. The product can be stored for at least 12 months without significant moisture pickup if storage conditions are at 60% rh and 25° C or less (Osberger, 1979).

PRICE

The price of HFCS (Table VI) is controlled by many of the same factors affecting dextrose pricing; however, sucrose price is probably the most important factor. Traditionally, HFCS is priced 10–20% below sucrose. In 1985, the price discounts of 42% and 55% HFCS to sugar were 23.4 and 13.6%, respectively (Anonymous, 1986). The price differential between 42% and 55% HFCS has increased from 8.5% in 1981 to 20.0% in 1985, representing the increased demand for 55% HFCS as a replacement for sucrose in soft drinks.

In mid-1984, the prices of 90% HFCS and crystalline fructose were $1.47/kg ($0.67/lb) and $2.27/kg ($1.03/lb), respectively, at commercial solids. A new product that contains a blend of crystalline fructose and sugar and that reportedly is 10–80% sweeter than sugar alone is expected to be in production in 1987 at a price of $0.77–$1.32/kg ($0.35–$0.60/lb) (Anonymous, 1986).

C. Corn Syrups

Regular corn syrups are, by definition, those products that range from 20 to 99.4 DE. Products with lower DE are classified as maltodextrins and those with higher DE are categorized as dextrose. HFCS is considered a special type of corn syrup and is not defined on a DE basis.

Corn syrups are produced by straight acid or acid-enzyme hydrolysis, although enzyme-enzyme processes can be used for some syrups. Typical commercial corn syrups are straight acid products of 26–42 DE, high-conversion acid-enzyme syrups of 64–70 DE, and high-maltose syrups. These syrups are often referred to as "glucose syrups," even though the actual D-glucose level may be very low.

ACID SYRUPS

Acid hydrolysis of starch is conducted by batch or continuous processes using a 35–40 wt % starch slurry adjusted to 0.015–0.2*N* with hydrochloric acid (Fig. 4). The slurry is held at 140–160° C for 15–20 min or until the desired DE is reached. Batch processes are conducted in manganese bronze convertors as large as 10,000 L, using direct steam injection to heat the water in the reactor to boiling. Starch slurry containing acid is added; the reactor is pressurized; and the reaction is allowed to proceed until the desired DE is attained. At the end of the reaction, pressure is used to discharge the hydrolysate to a neutralizer tank, where the pH is adjusted to 4.5–5.0 with sodium carbonate. Continuous convertors use indirect heating and, because of improved process control, yield a more uniform product than batch operation does. The composition of acid corn syrups is shown in Table IV. Commercial acid corn syrups do not generally exceed 42 DE since, at higher DE levels, color and flavor components formed during extended acid hydrolysis are difficult to remove by traditional refining techniques.

HIGH-CONVERSION SYRUPS

High-conversion syrups are prepared commercially from acid substrates of 38–42 DE, although enzymatically liquefied starch can also be used. Saccharification is conducted with a combination of glucoamylase and fungal α-amylase at 55–60° C, pH 4.8–5.2 for 24–48 hr. A typical syrup at 63 DE contains, on a dry basis, 36% dextrose, 30% maltose, and 13% DP-3. The ratio of dextrose to maltose and levels of each can be altered by changing the ratio and amount of enzymes used for saccharification. A heat treatment step to inactivate enzymes and stop the reaction at the proper time is recommended; however, the heat treatment step can be eliminated by careful control of dosage and time (Reichelt, 1983).

HIGH-MALTOSE SYRUPS

High-maltose syrups are prepared from acid- or enzyme-thinned substrates by saccharifying with a maltose-producing enzyme such as a fungal α-amylase derived from *A. oryzae* or barley β-amylase extracted from germinated barley. Reaction conditions are about 55° C, pH 5, and 35–45 wt % solids. A hydrolysate containing 50–55% (db) maltose is obtained in a typical operation. A higher maltose level, i.e., 60–80% (db), is achieved by the addition of pullulanase to the saccharification step. The debranching enzyme hydrolyzes α-1,6 linkages and provides additional substrate for the maltogenic enzyme. Typical maltose syrup compositions are given in Table VII.

A maltogenic exo-α-amylase from *B. stearothermophilus* has been reported to be effective in producing a high-maltose syrup (Outtrup and Norman, 1984). Improved yields have been obtained by recombinant DNA techniques, and the enzyme can produce 60–70% maltose alone or 80% maltose in combination with

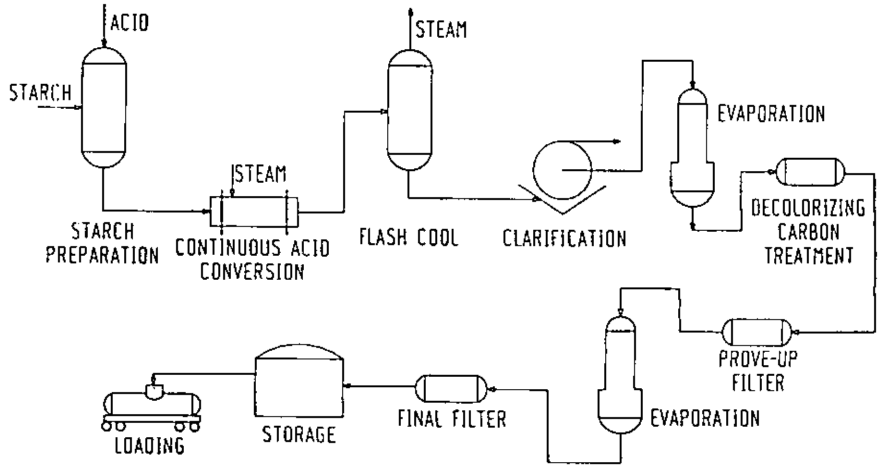

Fig. 4. Corn syrup production.

a debranching enzyme. Other bacterial enzymes from sources such as *B. cereus* (Takasaki, 1978) and *B. megaterium* (Armbruster and Jacaway, 1970) have been shown to be maltose producers. These enzymes, however, are not used commercially.

SPECIALTY SYRUPS

Many enzymes produce specialty corn syrups exhibiting unique saccharide distributions. For instance, a maltotetraose syrup is produced with a *Pseudomonas stutzeri* enzyme (Abdullah, 1972), and a maltohexose syrup is made using an enzyme from *Ae. aerogenes* (Kainuma et al, 1975). In addition, *B. licheniformis* α-amylase produces a maltopentose syrup (Saito, 1973), and a maltose-maltotriose syrup is made with a porcine α-amylase (Allen and Spradlin, 1974). None of these syrups have been produced commercially.

SYRUP PRODUCTION WITH IMMOBILIZED ENZYMES

The use of immobilized enzyme systems for corn syrup production does not have the disadvantages associated with its use for dextrose production. Therefore, in certain applications, bound enzymes provide a viable alternative to soluble enzymes. Systems have been studied for producing high-conversion syrups using immobilized glucoamylase alone (Rugh et al, 1979) or a combination of immobilized fungal α-amylase and glucoamylase (Bohnenkamp and Reilly, 1980; Hausser et al, 1983). In addition, high-maltose syrups can be produced using immobilized β-amylase (Maeda et al, 1978) or a combination of immobilized β-amylase and pullulanase (Ohba and Ueda, 1980).

REFINING

Corn syrup hydrolysate is clarified by centrifugation and/or filtration, evaporated to 60 wt % solids, carbon treated to remove color and acid degradation products (Heros and Bailey, 1977), and concentrated to 75–86 wt % solids. Sulfur dioxide is added during evaporation to some grades of syrup to reduce color development. As an alternative to evaporation, some types of corn syrup, especially those of low DE, are spray dried or roll dried and referred to as corn syrup solids.

SHIPPING

Corn syrup is transported in rail cars and tank trucks equipped with coils that can be heated with steam or hot water to reduce viscosity and aid in unloading. Corn syrup solids are shipped in moisture-proof bags.

TABLE VII
Maltose Syrup Composition[a]

Enzyme	Saccharide (%, db)			
	Dextrose	Maltose	DP-3	DP-4+
Fungal α-amylase	4	52	23	21
Malt β-amylase	2	54	19	25
Malt β + pullulanase	1	76	16	7

[a] Data from Heady and Armbruster (1971).

PRICE

Typical corn syrup prices are shown in Table VI. The price has been relatively constant since 1972, when competitive factors forced prices to a very low level of $0.124/kg ($0.056/lb) (Keim, 1979).

D. Maltodextrins

Maltodextrins are starch hydrolysis products of less than 20 DE. Commercial products are manufactured by hydrolysis of regular corn starch or waxy maize starch by straight acid, acid-enzyme, or enzyme-enzyme techniques. Acid processes are similar to those described for corn syrup. Acid-enzyme processes are conducted by thinning starch to a low DE with acid (Armbruster and Harjes, 1971; Morehouse et al, 1972), followed by neutralization to pH 6–7 and hydrolysis with bacterial α-amylase at 80–85° C for 1–3 hr to the desired DE. A typical total enzyme process uses bacterial α-amylase hydrolysis at 85–92° C, pH 6–8, 30 wt % solids for about 1 hr, followed by additional conversion at 80° C to the desired DE (Armbruster and Kooi, 1974). A heat treatment at 120° C is used to inactivate the enzyme before final processing. Another type of enzymatic approach uses a two-stage process (Armbruster, 1974). Starch is hydrolyzed at pH 7.5–8, 90–92° C for 1 hr with α-amylase to 2–15 DE, followed by a high-temperature heat treatment at 120–150° C for several minutes. Additional enzyme is added and the reaction continued at 80–85° C to the desired DE. The heat treatment is effective in improving the filtration rate and reducing the level of insoluble starch. Typical maltodextrin compositions attained by this procedure are shown in Table VIII. Higher-temperature processes using thermostable α-amylases above 93° C have also been proposed for producing maltodextrins of 10–13 DE (Coker and Venkatasubramanian, 1984).

Maltodextrins prepared from cornstarch are susceptible to haze formation during storage due to association and precipitation of linear amylose fragments. However, when waxy starch is used for maltodextrin production, increased stability is achieved, since the branched polysaccharides do not retrograde as readily as the linear saccharides derived from regular starch. However, even maltodextrins prepared with waxy starch at less than 15 DE develop haze when stored for more than about three days at 70 wt % solids (Harjes et al, 1976). Several techniques have been developed to achieve increased stability. For instance, using as substrate a starch dextrin having a degree of branching of at

TABLE VIII
Maltodextrin Composition (%, db)[a]

DP	Product			
	5 DE	10 DE	15 DE	20 DE
1	<1	<1	<1	1
2	1	3	6	8
3	2	4	7	9
4	2	4	5	7
5	2	4	5	8
6	3	7	11	14
7+	90	78	66	53

[a] Data from Armbruster (1974).

least 7% improves product stability (Harjes et al, 1976). In addition, maltodextrins stable at 70–80 wt % solids can be made from oxidized starch by thinning to 7 DE with acid or enzyme and then converting with α-amylase to the desired DE (Harjes and Wermers, 1976). Stable products are also made by simultaneously liquefying and oxidizing starch to about 4 DE with an oxidizing agent at elevated temperature and then hydrolyzing it with α-amylase (Horn and Kimball, 1976). The hazing tendency may also be reduced through derivatization by introducing nonionic, cationic, or anionic groups (Hull, 1972). Another method for production of nonhazing syrups is to hydrolyze starch to 20–40 DE and then remove low-molecular-weight material by reverse osmosis (Meyer, 1973) or molecular exclusion (Deaton, 1973) to provide stable products of 5–18 DE.

Maltodextrins are refined in the same manner as other corn sweeteners, using clarification, carbon treatment, and ion exchange. The final products are spray dried to a moisture level of 3–5% or evaporated to 75 wt % solids.

V. PROPERTIES

A. Dextrose

Dextrose crystallizes as α-D-glucose, α-D-glucose hydrate, or β-D-glucose, depending on temperature. The physical properties of each form are given in Table IX. In solution, dextrose mutarotates to an equilibrium level of about 62% β- and 38% α-dextrose. At equilibrium, the solubility of dextrose is 51.2 g/100 ml. However, initial solubility characteristics vary depending on the particular crystalline form of dextrose used. For instance, the hydrated form of dextrose dissolves rapidly at 25° C to its solubility level of 30.2%. As mutarotation to the more soluble β-form occurs, solubility increases to a level of 51.2%. Anhydrous dextrose dissolves past the limit of dextrose hydrate solubility, at which point dextrose hydrate then crystallizes from solution and solubility follows the pattern for dextrose hydrate. In solution, both α- and β-dextrose exist primarily in the pyranose form and in equilibrium with a small amount of the open-chain aldehyde form. This open-chain form is responsible for the reducing properties of dextrose.

TABLE IX
Physical Properties of D-Glucose[a]

Property	α-D-Glucose	α-D-Glucose Hydrate	β-D-Glucose
Molecular formula	$C_6H_{12}O_6$	$C_6H_{12}O_6 \cdot H_2O$	$C_6H_{12}O_6$
Melting point, °C	146	83	150
Solubility (at 25° C), g/100 g of solution	62→30.2 – 51.2[b]	30.2→51.2[b,c]	72→51.2[b]
$[\alpha]_D^{20}$[d]	112.2→52.7[b]	112.2→52.7[b,c]	18.7→52.7[b]
Heat of solution (at 25° C), J/g[e]	−59.4	−105.4	−25.9

[a] Source: Hebeda (1983); used by permission of John Wiley & Sons, Inc.

[b] Equilibrium value.

[c] Anhydrous basis.

[d] Specific rotation.

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

In acidic solution, dextrose yields condensation products such as isomaltose and gentiobiose. In addition, dextrose may undergo a dehydration reaction to 5-hydroxymethylfurfural, a water-soluble, high-boiling, unstable compound that can decompose to levulenic and formic acids or polymerize to dark-colored compounds. In alkaline solution, dextrose is isomerized to fructose and mannose. Other decomposition products such as saccharic acids are also formed.

Oxidation reactions yield gluconic acid with dilute alkali and saccharic, tartaric, and oxalic acids with nitric acid. Heating dextrose with methanol in the presence of anhydrous hydrogen chloride yields α-methyl-D-glucoside and a small amount of β-D-glucoside. Similarly, reactions also occur with higher alcohols, although reaction products are more difficult to crystallize. Reaction of dextrose with acid anhydrides in the presence of basic catalysts gives a mixture of esters. Catalytic hydrogenation of dextrose yields sorbitol, and hydrogenolysis produces mixtures of glycols and other degradation products. Reaction of dextrose with a reactive nitrogen, as found in amino acids or proteins, yields a variety of pigments of varied molecular weight via the Maillard reaction. The type of pigments produced is dependent on reaction conditions such as pH, temperature, type of nitrogen, and concentration of reactants.

Important functional properties of dextrose include sweetness, fermentability, and osmotic pressure. In dry and liquid forms, dextrose is about 76 and 65–70%, respectively, as sweet as sucrose (Hanover, 1982). However, perceived sweetness is controlled by many factors such as solids concentration, temperature, and the presence of other ingredients. For instance, synergistic effects in some formulations of dextrose-sucrose blends yield perceived sweetness levels that are equal to or greater than that of sucrose alone. In applications where fermentability is desired, dextrose is an excellent carbohydrate source and is fermented rapidly by yeast and other organisms. Dextrose also produces a greater osmotic effect than sucrose on an equal weight basis and offers advantages where this property is important.

B. High-Fructose Corn Syrup

Pure fructose is a ketohexose monosaccharide that has a melting point of 102–104° C and crystallizes as β-D-fructopyranose. In solution at 36° C, fructose mutarotates to an equilibrium mixture containing 57% β-fructopyranose, 31% β-fructofuranose, 9% α-fructofuranose, and 3% α-fructopyranose (Doddrell and Allerhand, 1971). The solubility of fructose at equilibrium is 80 wt % at 25° C. Fructose reacts in the same manner as other carbohydrates to form esters, ethers, and acetals. Condensation products such as difructose dianhydride are formed in aqueous solution (Binkley et al, 1971). Fructose in solution is most stable at pH 3–4; however, degradative reactions at high and low pH occur more readily than with dextrose (MacAllister and Wardrip, 1978).

Crystalline fructose exhibits a sweetness of 1.8 times that of sucrose and 2.4 times that of crystalline dextrose (Hanover, 1982); however, in solution, the less-sweet forms of fructose reduce apparent overall sweetness. The sweetness of fructose is greatest at cold temperatures, increasing by a factor of 1.8 when temperature is reduced from 60 to 5° C (Freed, 1970). This effect is apparently due to a reduced rate of mutarotation to the less-sweet forms at the lower temperature. Sweetness perception is greatest at neutral or slightly acid pH or when the fructose is in dilute solution (Olefsky and Crapo, 1980) or in the presence of organic acids (Hanover, 1982).

The most important property of HFCS is sweetness. HFCS products are less sweet than pure fructose, due to the presence of dextrose and higher saccharides. However, even though oligosaccharides reduce overall sweetness, taste is not affected (MacAllister and Wardrip, 1978). HFCS is considerably sweeter than regular corn syrups, but as is the case with pure fructose or dextrose, the intensity of sweetness is due to several factors such as temperature, pH, and concentration. HFCS containing 55% fructose exhibits about the same sweetness as sucrose, whereas, 42 and 90% HFCS are 9% less sweet and 6% sweeter than sucrose, respectively (Hanover, 1982).

Other important functional properties of HFCS include high solubility, which prevents crystallization during shipment; humectancy (ability to retain moisture), which gives increased shelf life of bakery products; decomposition during baking, which supplies color and flavor; and high osmotic pressure. Due to the low molecular weight of HFCS, viscosity is relatively low even at high concentration. At a normal commercial solids level of 71 wt %, viscosity ranges from 52 cp at 43°C to 360 cp at 16°C (MacAllister and Wardrip, 1978).

C. Corn Syrup

Important functional properties of corn syrups include fermentability, viscosity, humectancy-hygroscopicity, sweetness, colligative properties, and participation in the browning reaction.

The fermentability of corn syrups is dependent on the specific process and organism used, but in general, dextrose, maltose, and maltotriose are considered fermentable by yeast in brewing and baking. Since the levels of mono-, di-, and trisaccharides increase as syrup DE is increased, fermentability also increases with increasing DE.

The viscosity of corn syrups increases as DE decreases and is an important functional property in many food applications, affecting both organoleptic properties and product stability. Typical viscosity data for acid and acid-enzyme syrups are given in Table X.

The hygroscopicity of corn syrup is related to dextrose level, and rate of moisture absorption increases with increasing DE. Humectancy is also important; moisture retention increases with increasing DE, causing difficulties in drying high-DE syrups.

TABLE X
Viscosity (1,000 cp) of Corn Syrups

	Dextrose Equivalent and Corresponding Solids[a]			
Temperature (°C)	43 80.3	43 82.9	64 81.7	63 83.8
27	56	285	22	79
38	15	56	6	18
49	5	15	2	5

[a] % wt basis.

The sweetness of corn syrups depends on the level of simple sugars, i.e., dextrose and maltose, and therefore increases with increasing DE. Syrups of 63 and 42 DE are 45 and 30% as sweet as sucrose and 67 and 45% as sweet as dextrose, respectively (Hanover, 1982).

Other important properties of corn syrup include contribution to browning via the Maillard reaction, flavor enhancement, freezing point depression, and osmotic pressure, all of which increase with increasing DE. Properties such as body contribution, cohesiveness, foam stabilization, and prevention of sugar crystallization increase with decreasing DE.

D. Maltodextrin

Maltodextrin is the least hygroscopic of corn sweeteners due to a low DE, i.e., a low monosaccharide content. At the same time, maltodextrins exhibit high viscosity and contribute mouthfeel and body due to the presence of higher-molecular-weight saccharides. Sweetness is not a consideration; maltodextrins are essentially tasteless. In general, maltodextrin properties are similar to those of very low-DE corn syrups.

VI. APPLICATIONS

Corn sweeteners are used in a variety of food and nonfood applications to provide a wide range of nutritive, physical, and chemical properties. Sales of dextrose, HFCS, and corn syrup to major food industries are given in Table XI.

A. Dextrose

Dextrose is used alone or in combination with other sweeteners in the beverage, confectionery, baking, and other industries. For instance, in many applications where sweetness is desired, dextrose is used in conjunction with sucrose (Godzicki, 1975), since the combination may be as sweet as pure sucrose at an equivalent concentration (Nieman, 1960). Dextrose can also be used in combination with aspartame to yield a synergistic effect relative to sweetness (Homler, 1984).

In the beverage industry, dextrose is used to supply sweetness, body, and osmotic pressure. In beverage powders, dextrose enhances flavor and reduces excessive sweetness. Dextrose is used in light beer production as a completely fermentable adjunct to reduce the residual carbohydrate level and therefore the caloric content (Hebeda and Styrlund, 1986). Dextrose is also used in wine manufacture as an additive to grape and other juices low in fermentable sugars. In the confectionery industry, dextrose supplies sweetness, softness, and crystallization control. In confections such as chewing gum and candies, it is used for coating, strength, hardness, color, and gloss. In baking applications, it reacts with protein to provide color and flavor in crusts and strength in bread for improved slicing and handling. In cookies, dextrose gives a tenderizing effect and crust coloration. The use of dextrose in cakes and cake mixes results in improved physical characteristics such as texture and color. Dextrose is also used in prepared mixes for biscuits, pancakes, waffles, doughnuts, and icings. In canning, dextrose is used in sauces, soups, gravies, fruits, and juices to provide flavor, body, and sweetness, as well as to improve texture and aesthetic quality. In dairy applications, it is used in ice cream and frozen desserts to provide sweetness and control crystallization for a smooth, creamy texture. Other food applications include use in such diversified products as peanut butter, meat, pickles, and condiments.

In pharmaceutical applications, dextrose is used for intravenous and subcutaneous injections and for tableting.

Dextrose or high-dextrose corn syrups are used in the fermentation industry as a raw material for biochemical synthesis of products such as citric acid, antibiotics, vitamins, amino acids, and enzymes. Ethanol produced by yeast fermentation of unrefined dextrose hydrolysate is used in gasoline as an octane enhancer or additive (Keim, 1983). Production of other chemicals by fermentation of dextrose has been suggested as a potential alternative to petrochemicals (Ng et al, 1983).

In chemical processes, dextrose is used for production of sorbitol (Morris, 1983) and methyl glucoside (Tokay, 1983), as well as gluconic acid, gluconates, and heptonates. Acid-catalyzed polymerization of dextrose in the presence of a polyol is used to manufacture polydextrose, a cross-linked polymer used as a water-soluble, low-calorie, bulking agent (Torres and Thomas, 1981). Polydextrose has been proposed as a replacement for sugar in various confections, baked goods, and other products to provide low-calorie foods containing reduced sugar and fat levels.

TABLE XI
Distribution (1,000 t) by Industry of Dextrose, High-Fructose Corn Syrup (HFCS), and Corn Syrup in the United States[a,b]

Product and Year	Baking	Beverage	Canning	Confectionery	Dairy	Total
Dextrose						
1965	178	8	21	37	6	468
1970	174	8	23	52	7	547
1975	157	18	15	62	7	561
1980	51	66	4	55	2	513
1982	50	77	6	51	2	481
1983	56	82	5	63	2	488
1984	54	86	4	66	1	465
HFCS						
1970	18	39	9	0.5	5	99
1975	129	279	64	4	36	715
1980	365	1,093	235	15	140	2,659
1982	390	2,086	277	27	189	3,968
1983	385	2,621	272	31	201	4,603
1984	392	3,698	264	34	229	5,479
Corn syrup						
1965	209	36	104	410	159	1,211
1970	222	93	98	439	213	1,449
1975	315	205	174	416	278	2,278
1980	196	384	126	446	241	2,201
1982	161	359	143	458	268	2,295
1983	148	370	124	467	267	2,299
1984	110	376	139	464	276	2,305

[a] *Source: Hebeda (1983); used by permission of John Wiley & Sons, Inc.*
[b] Commercial basis.

Dextrose may also be used in adhesives to provide flow control, in library paste to increase open time, in wallboard as a humectant to prevent brittle edges, in concrete as a setting retardant, in resin manufacture as a modifier and plasticizer, as a reducing agent in metal treatment, and as a diluent for standardizing dyes.

B. High-Fructose Corn Syrup

HFCS sales in the United States have increased dramatically in recent years. For instance, between 1970 and 1984, HFCS sales increased from 5 to 69% of total corn sweetener sales. Much of this increase was due to the increased use of 55% HFCS. Between 1980 and 1985, sales of 55% HFCS increased from 33 to 65% of total HFCS sales (Vuilleumier, 1985). The rapid increase of HFCS use has been primarily due to the acceptance of HFCS as a replacement for sucrose in soft drinks. In 1985, about 96% of the sweetener used by the beverage industry was HFCS (Vuilleumier, 1985).

The first substitution of HFCS for sucrose in soft drinks took place in 1974, when high sucrose prices led to the approval of a 25% replacement of sucrose with 42% HFCS in several different products. With the development of a 55% HFCS product, increased substitution levels of as much as 100% were approved for some products in 1978 and 1979. The next major increase in HFCS usage occurred in 1983, due to the improved product consistency requested by soft drink producers. Quality improvements were initiated in 1982 through a cooperative effort among HFCS producers (Morris, 1984), and improved standards were achieved through better control of processing and refining to maintain consistency in ash, color, pH, solids, and saccharide composition. Currently, the approved HFCS substitution level is 100% in most major soft drinks.

The second largest use for HFCS is in the baking industry, where 42% HFCS is used to replace all or a portion of sucrose and still achieve the same product characteristics. In canning, HFCS is used as the predominant sweetener in combination with sucrose and high-conversion syrup. In dairy applications, blends of HFCS and corn syrup function as a bodying agent and also improve texture and mouthfeel. In confectionery, HFCS supplies sweetness, grain control, and humectancy.

HFCS containing 90% fructose can be used in reduced-calorie products to lower the caloric level by 30–50% in a wide range of foods, including dairy products, frozen and canned fruit, soft drinks, confections, salad dressings, baked goods, dry cereals, and table top sweeteners (Young and Long, 1982).

Crystalline fructose is essentially pure and is therefore used in low-calorie and specialty foods. Examples are frozen desserts, yogurt, puddings, dry beverage powders, ice cream, candy, baked goods, and table top sweeteners.

C. Corn Syrup

Corn syrup is often used in combination with sucrose, dextrose, or HFCS (Godzicki, 1975). Its application is based on specific functional properties, and the type of syrup used depends on the properties desired in the final product.

The primary use of corn syrup is in the confectionery industry in virtually all types of products from hard candies to marshmallows to provide viscosity, mouthfeel, sweetness, texture, grain inhibition, hygroscopicity, and resistance to discoloration.

In the beverage industry, corn syrups are used as a source of fermentables in beer and malt liquor production (Hebeda and Styrlund, 1986) and also to enhance flavor and provide body. High-conversion or high-maltose syrups are used as replacements for dry cereal adjuncts to achieve a fermentable level that approximates that produced during mashing. Corn syrups are generally not used in manufacture of carbonated beverages, although Maeda and Tsao (1979) report that the mild sweetness of high-maltose syrup has found application in soft drinks in Japan.

In the dairy industry, corn syrups provide texture, smoothness, and grain control; modify melt-down and shrinkage; and function as bodying agents. Generally 36–42 DE acid-converted syrups are used in ice cream, sherbet, iced milk, and other frozen desserts.

In baking, high-conversion or high-maltose syrups are used as a source of fermentables. Syrups are used in yeast-raised products and in cakes for viscosity and rheological properties and for maintaining moisture balance and improved shelf life. In cookies, syrups are used as a tenderizing ingredient and provide crust color and moisture retention.

The major application for syrups in canning is in canned fruit to prevent crystallization of sucrose and provide body and accentuate fruit flavor while improving color and texture. Generally, high-conversion syrups are used.

Other food applications are in icings and fillings to improve sheen and appearance; in chewing gum for sweetness and for softening the gum base; in meat products to supply flavor, humectancy, body, and viscosity; and in pickles for viscosity and mouthfeel.

Hydrogenation of corn syrup is used to produce a nonreducing sweetener that can replace regular corn syrups in various confections (Rockstrom, 1980).

In nonfood applications, corn syrup may be used in adhesives to improve stability, as a setting retardant in concrete, as a humectant in air fresheners, for evaporation control in colognes and perfumes, as a carrier and sweetener in medicinal syrups and lozenges, and as a humectant in tobacco.

D. Maltodextrins

Maltodextrins are used in applications where nonsweet, nonhygroscopic, water-holding properties are desired. For instance, maltodextrin is used as a bodying agent or bulking agent in puddings, soups, frozen desserts, and dry mixes. It is also used as a spray-drying adjunct for coffee and tea extracts, a dispersing agent in synthetic coffee whitener, and as a moisture-holding agent in breads, pastries, and meats. Maltodextrin can be used as a partial or total replacement for sweeteners in gum confection (Godzicki and Kimball, 1971; Horn and Kimball, 1971) or to replace a portion of the protein whipping agent in aerated confections (Horn et al, 1971). In addition, maltodextrin can improve hygroscopicity characteristics in hard candy (Horn and Godzicki, 1974). Nonhygroscopic, water-soluble fondants are prepared using a combination of a

dry sugar and maltodextrin (Sands and Marino, 1975a, 1975b). Maltodextrin used in combination with dextrose is effective in preparing a direct-compression vehicle for tableting for use in pharmaceutical applications (Kanig, 1975; Nelson et al, 1977).

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CHAPTER 18

CORN OIL: COMPOSITION, PROCESSING, AND UTILIZATION

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I. INTRODUCTION

Among the edible vegetable oils in the marketplace, corn oil is a minor oil, since it constituted only about 9.0% of the 1984/85 U.S. vegetable oil production. The U.S. oil market is dominated by soybean oil, which amounted to 78.4% of the 1984/85 production. The other edible vegetable oils produced in the United States are cottonseed, sunflower, and peanut, with 8.0, 3.3, and 1.3% of the market, respectively. Worldwide, the major oils produced include rape, olive, cocoa, palm and palm kernel, peanut, and sunflower. Nevertheless, corn oil is an important food oil because it has a positive image with both the user and the consumer (Erickson and Falb, 1979). Its high polyunsaturated fatty acid content, which has been widely publicized, has important nutritional and health benefits. The oxidative stability of corn oil during use and its lack of precipitation under refrigeration have contributed to its market demand (Reiners, 1978). All but a minor fraction (<5%) is used in foods; the largest single use is bottled oil, followed by margarine and industrial snack-frying operations.

II. PRODUCTION AND MARKETS

Corn oil production in the United States doubled from 1976 to 1986, based on the USDA (1986) projection of 1.349 billion pounds (612×10^3 t) produced in 1986. This has been due largely to expansion of the corn wet-milling industry, which has increased its capacity by 8–10% a year for the last 10 years. Of the 1.195 billion pounds (542×10^3 t) produced in 1984/85, over 90% was produced as a by-product of corn wet milling, with the remainder from dry milling (CRA, 1986; USDA, 1986). Twenty-eight major corn refining plants in the United States produce isolated corn germ, and all either process germ into oil or meal, or sell germ on an oil basis for processing. In the wet-milling industry, 14 of 16 plants produce crude corn oil and eight produce refined corn oil. Twelve

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degerminating-type corn dry mills operate in the United States, and all produce corn oil (Chapter 11). The largest worldwide producers of corn oil after the United States include Brazil, China, Rumania, the USSR, Yugoslavia, and South Africa (Anonymous, 1985). The United States is the major exporter of corn oil. U.S. exports reached 300 million pounds (136×10^3 t) in 1984/85 (USDA, 1986), with the principal growth markets being in Asia and the Middle East. The European Economic Community is the largest importer of corn oil.

The limited production of corn oil, compared to that of soybean and other major oils, and the high market demand lead to the ready sale of all corn oil that is produced. Corn oil production has increased markedly in recent years due to increased volumes of corn being used in sweetener and starch production (USDC, 1985b). The supply of corn oil is largely dependent on the demand for the major products of corn wet milling: starches and sweeteners (CRA, 1986). The U.S. starch industry markets have been shown to grow with population and increases in the gross national product (USDC, 1985a). The market for sweeteners is nearly mature, with significant increases in capacity projected only for the next few years. Much of the increase in capacity is now in place or under construction. In addition to the starch and sweetener push on corn processing, fuel alcohol has gained attention (CRA, 1986).

III. COMPOSITION AND CHARACTERISTICS OF CORN OIL

Refined corn oil is composed of triglycerides (99%) (Sonntag, 1979a). Its chemical structure is discussed in Chapter 10. It has an average molecular weight of 326 and is a liquid at room temperature. The fatty acids are composed of hydrocarbon chains ranging from 16 to 20 carbons each, with 18 carbons being the most common. Each chain may have up to three double bonds. The typical fatty acid composition of refined corn oil is given in Table I. Because of its relatively low linolenic acid content, corn oil is inherently more stable than several other vegetable oils (Sonntag, 1979b; Erickson and List, 1985). The component lipids and their chemical characteristics have been thoroughly described in Chapter 10. This chapter emphasizes chemical characteristics of most importance to refining and utilization. Figure 1 shows four of the chemical reactions that occur in the refining process.

One property of unsaturated fatty acid components of corn and other vegetable oils is the addition of hydrogen to the double bonds. Hydrogenation is performed to give fats the desired physical properties, including melting point, plasticity, and oxidative stability (Allen, 1982). Complete hydrogenation yields products that are extremely hard, with melting points above 60°C. In partial hydrogenation, saturation is selective, with the most unsaturated fatty acids being hydrogenated. Positional and geometric isomerization also occurs. Hydrogenation is manipulated by control of hydrogen gas pressure, rate of agitation, temperature, and catalyst type (Allen, 1982). Corn oil presents no unusual problems in hydrogenation, and various products, particularly frying and margarine oils, are readily made.

TABLE I

Fatty Acid Composition of Corn Oil[a]

Common Acid Name	R Chain Length:No. of Double Bonds	Percent of Total Fatty Acids
Palmitic	$C_{16:0}$	11.0 ± 0.5
Palmitoleic	$C_{16:1}$	0.1 ± 0.1
Stearic	$C_{18:0}$	1.8 ± 0.3
Oleic	$C_{18:1}$	25.3 ± 0.6
Linoleic	$C_{18:2}$	60.1 ± 1.0
Linolenic	$C_{18:3}$	1.1 ± 0.3
Arachidic	$C_{20:0}$	0.2 ± 0.2
Essential fatty acids		61.2 ± 0.9

[a] Average for oil from U.S. Midwest, 1977–1985. (Personal communication, J. M. Hasman, Best Foods, Union, NJ)

Linoleic acid is selectively hydrogenated to form oleic acid, which is hydrogenated in turn to form higher levels of stearic acid. The greater amounts of stearic acid ($C_{18:0}$) and oleic acid ($C_{18:1}$) add to the oil's stability and increase the melting point, giving it higher solids at a given temperature or plasticity.

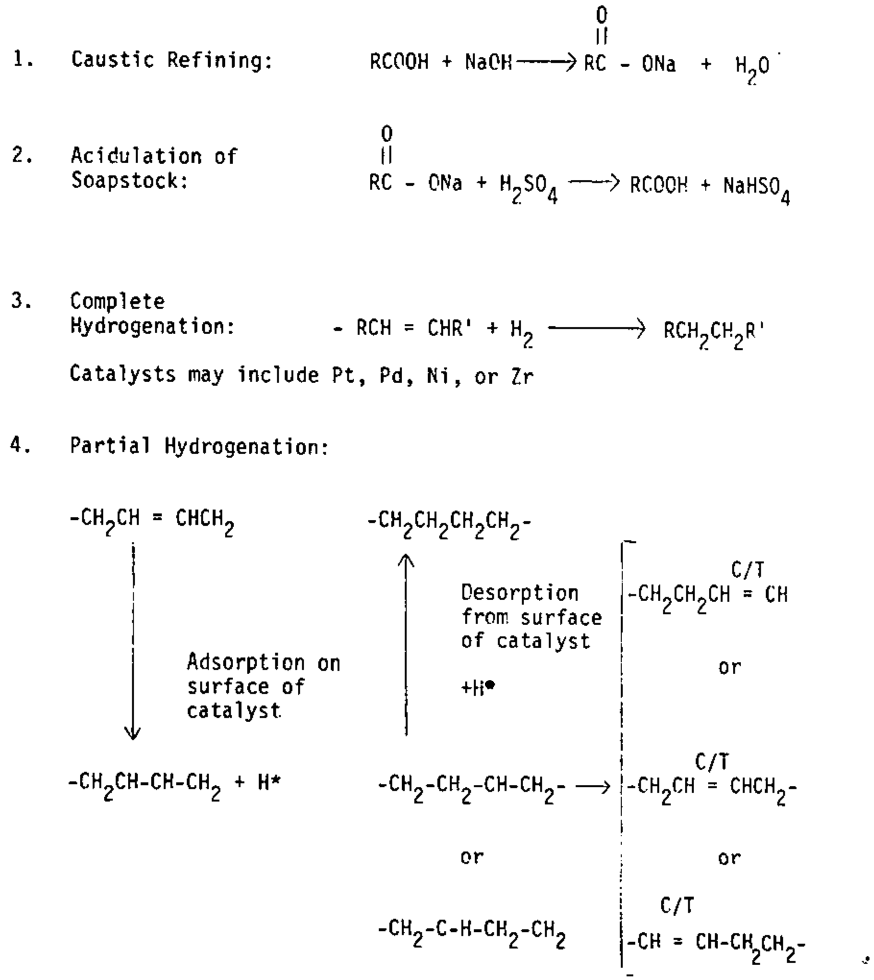

Fig. 1. Chemical reactions of corn oil refining. (Adapted from Albright, 1970)

Autoxidation of the unsaturated fatty acids leads to oxidative rancidity, which produces off-flavors and off-odors in vegetable oils. Autoxidation, or free-radical oxidation, can occur at cool temperatures, even 0° C, but is accelerated at elevated temperatures. It is accelerated in the presence of added or naturally occurring free radical promoters, such as iron, copper, benzoyl peroxide, and also light. The degradative reactions are inhibited by the presence of compounds that react with free radicals. Common synthetic antioxidants added to corn oil are *tert*-butylhydroquinone (TBHQ), butylated hydroxytoluene (BHT), and butylated hydroxyanisole (BHA). Antioxidants generally act as proton donors or free radical accepters, reacting principally with the free hydroperoxy radical R00* (Perkins, 1984).

Thermal oxidation reactions occur at temperatures above 150° C, as in pan frying or deep fat frying. Six-membered ring structures and large polymers (30,000 mol wt) can be formed (Perkins, 1984). Thermal polymerization occurs at high temperatures (250° C) in the absence of oxygen, also forming polymerized compounds, but at this temperature the oil would probably become inedible.

IV. RECOVERY OF CRUDE OIL

Corn itself contains approximately 4.5% oil, about 85% of which is located in the germ. Corn germ isolated by the dry-milling process contains 25–30% oil, and germ recovered by the wet-milling process contains 45–50% oil.

In wet milling, after separation and washing of the germ to remove free starch, the germ is dried. Oil is recovered from the dried germ, usually by a combination of mechanical expression and solvent extraction. In mechanical expression, continuous screw expellers, under high pressure and moderate heat, press the oil from the germ. As much as 94% of the oil can be removed by expelling. Usually only about 80% is recovered with screw expellers. After the expellers, the germ cake may be flaked and the remaining oil extracted using hexane as the solvent. The solvent-oil solution is filtered and the solvent stripped in an evaporator or stripping column. Solvent in the germ flake is removed by heating and steam stripping. The solvent from both the oil and germ is condensed for recycling. The corn oil recovered by mechanical pressing is combined with the solvent-extracted crude oil.

In dry milling, germ is a by-product of the primary products, cornmeal and grits. Small mills include germ as a component of hominy feed, but the larger mills recover the oil by screw pressing, alone or followed by solvent extraction. Dry-milled crude corn oil has less color and lower refining losses than oil derived from wet-milling.

V. CORN OIL PROCESSING

A. Crude Corn Oil

Crude corn oil consists of a mixture of triglycerides, free fatty acids (FFAs), phospholipids, sterols, tocopherols, waxes, and pigments (Table II, see also Chapter 10). Nearly all the oil is used in foods, which requires removal of most extraneous components (refining) to obtain the quality necessary for food applications. During refining of the oil, substances that detract from the quality are removed or reduced in concentration. These include FFAs, phospholipids, color bodies, odors, flavors, pesticides, aflatoxin, metals, oxidative by-products, and milling residues.

The steps involved in refining the oil are: 1) degumming—removal of most of the phospholipids; 2) alkali wash—removal of FFAs, phospholipids, and color; 3) bleaching—pigment and phospholipid removal; 4) winterization—wax removal; and 5) deodorization—improvement of flavor and odor and reduction in FFA content.

Hydrogenation of the oil also may be a part of the corn oil refining process. The process flow for refining of crude oil to refined corn oil is detailed in Fig. 2.

B. Crude Oil Filtration and Degumming

The process of crude oil filtration and degumming removes solids and gums (hydrated phospholipids) from crude corn oil in preparation for caustic or physical refining. Lecithin, a coproduct of corn oil degumming, may also be recovered. Crude oil is transferred from a crude storage tank to a scale for metering the correct amount of ingredients. The oil is heated to 71–82° C and slurried with diatomaceous earth (filter aid) before the filtration. Residual fiber, dirt, metal fragments, etc., are removed. The filtered oil is mixed with approximately 1–3% soft water (depending upon the phosphatide level of the crude oil) and is allowed to hydrate in an agitated tank. The wet oil is then passed through a degumming centrifuge that separates the dense wet gums from the oil. The degummed oil is vacuum-dried and either cooled to about 38° C for storage or sent directly to refining.

While in storage, the degummed oil is kept agitated to prevent separation of residual phosphatides (Norris, 1982). Phosphoric acid may be added to degummed oil before storage to improve refining yield. This acid aids in the hydration of nonhydratable gums and improves the efficiency of primary separation (Taylor, 1975). The phosphoric reaction requires approximately 12 hr. Some refiners eliminate the degumming step and rely entirely on caustic refining for phosphorus removal.

TABLE II
Average Composition of Crude and Refined Corn Oil Components[a]

	Crude Oil Components (%)	Refined Oil Components (%)
Triglycerides	95.6	98.8
Free fatty acids	1.7	0.03
Waxes	0.05	0.0
Phospholipids	1.5	0.0
Cholesterol	0.0	0.0
Phytosterols	1.2	1.1
Tocopherols	0.06	0.05

[a] Data from Reiners (1978).

C. Caustic Refining

Caustic refining is the treatment of degummed oil with a dilute sodium hydroxide solution to remove residual gums and FFAs, color, etc. (Carr, 1976). The caustic reacts preferentially with FFAs, forming water-soluble soaps. Residual phosphatides remaining after degumming also react with caustic to form oil-insoluble hydrates. Total removal of impurities is impractical. Removal of impurities must be balanced to minimize the loss of triglycerides and ensure adequate oil quality. The major triglyceride loss occurs during alkali refining.

Before being injected into the degummed oil, caustic is diluted with soft water to approximately 17–18° Be' NaOH. The amount of caustic solution added to the oil is termed the "treat." The correct treat will produce an adequately refined oil with the highest refining efficiency (minimum loss of neutral oil). The treat is based on the percent of FFAs in the degummed oil. A 0.13% excess treat (above the quantity of NaOH required to neutralize the FFAs) is commonly used for unreacted phosphatides (Mounts and Anderson, 1983). The excess treat is determined by experience and is adjusted according to laboratory results.

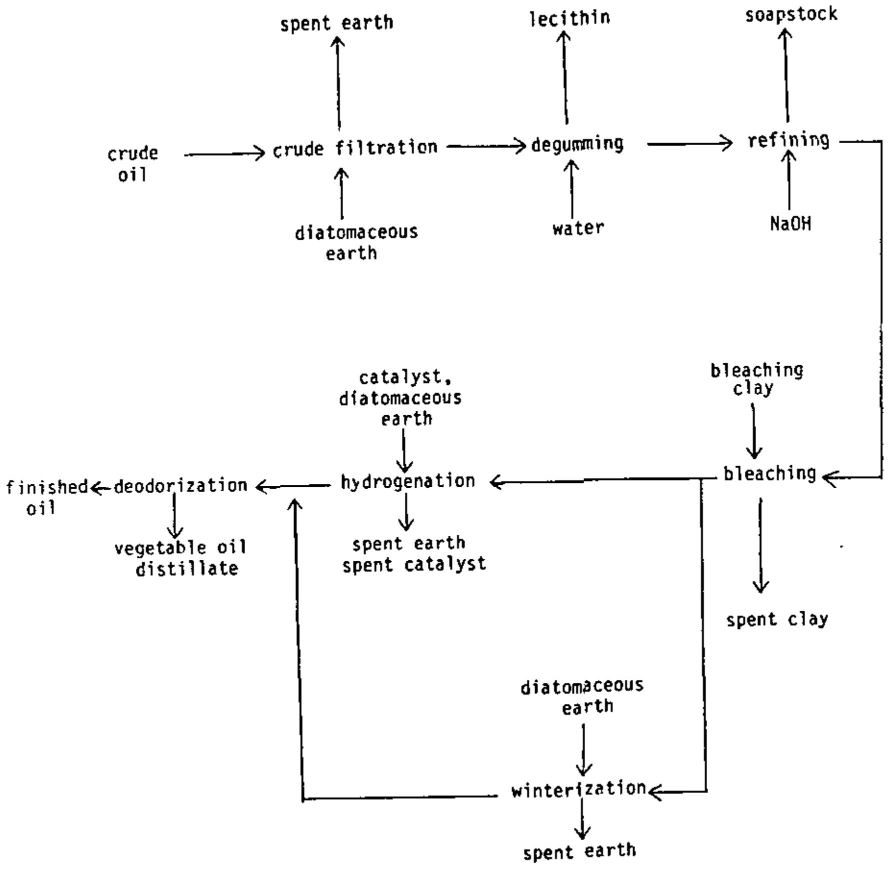

Fig. 2. Processing diagram for corn oil caustic refining. (Adapted from CRA, 1986)

After the caustic is injected, it is mixed for 3–5 min to ensure thorough contact with the fatty acids and phosphatides. Thorough mixing without formation of a stable, inseparable emulsion is required. The caustic-treated oil is then heated to create a thermal "shock," which assists in breaking the emulsion of the oil-soapstock-water mixture. The mixture is then fed to a refining centrifuge, where the lower-density oil phase and higher-density soapstock phase are separated into two layers. The main factors influencing the ease of separation include: 1) density difference between the two phases, 2) temperature of the feed stock (higher temperatures give improved separations), 3) viscosities of the two phases, 4) amount of centrifugal force, and 5) residence time in the centrifuge (Norris, 1982).

Most of the soap remaining in the oil following primary centrifugation (typically 200–600 ppm) is removed by a water-washing step. The once-refined corn oil at 82° C is mixed with 93° C soft water at a rate of approximately 15% of the oil flow. The majority of the soap distributes itself with the water. To aid separation, phosphoric acid may be added to the wash water before it is mixed with oil for adequate pH control. Thermal shock created by the greater water temperature than oil temperature also aids separation in water-wash centrifugation. The low-soap, water-washed oil is then either vacuum-dried to remove residual moisture before bleaching and sent to storage or is sent wet from the water-wash separator directly to bleaching.

D. Physical Refining by Steam

An alternative refining method is "physical" or "steam" refining. The phosphatide level must be low before physical refining, to prevent darkening of the oil and development of off-flavor. In addition, nonhydratable phosphatides are not removed by physical refining (Hvolby, 1971). A degumming step and phosphoric acid treatment are required for adequate phosphatide removal before physical refining (Taylor, 1975). The degummed oil is steam-sparged under vacuum, to remove volatile components, primarily the FFAs. Because the oil is very high in FFAs, corrosion-resistant 316 stainless steel is used in equipment fabrication. The FFA level is reduced from approximately 1.0–3.0% in degummed oil to less than 0.05% in finished oil. Additional trays or sections in deodorizers are required to give the oil longer retention time for maximum FFA removal during the steam stripping. Carotenoids are removed in the steam refining step. A typical flow diagram for physical refining of corn oil is shown in Fig 3.

E. Bleaching

The purpose of bleaching is to remove pigments and residual soap in once-refined or caustic-treated oil before hydrogenation and deodorization. Once-refined corn oil (either from storage or directly from the water-wash centrifuge) is slurried with bleaching clay, a natural hydrated aluminum silicate. The hot slurry (105° C) enters a vacuum bleacher, where excess moisture is removed and absorption of the color bodies and soap onto the clay surface occurs. After about 20 min, the dried slurry is pumped from the bleacher to leaf filters precoated with diatomaceous earth to separate the oil from the clay. The spent clay is steamed for oil removal, discharged to a hopper, and transported to bins for landfill disposal (Watson and Meierhoefer, 1976). Residual oil levels in spent clay may range from 30 to 70%, depending upon the extent of steaming (Patterson, 1976).

F. Winterization

Corn oil contains trace quantities of waxes that crystallize at home refrigerator temperatures (<4° C), producing a cloudy appearance. This is prevented by removal of waxes in the "winterization" process. Normally, ammonia or Freon is used in the refrigeration system. After cooling to approximately 4° C, the oil is passed through a filter coated with diatomaceous earth. Older units winterize the corn oil in batches, requiring up to three days per batch, but newer units winterize semicontinuously. Winterization is not necessary for corn oil that is to be hydrogenated.

G. Hydrogenation

In the hydrogenation process, hydrogen is chemically combined with the unsaturated double bonds of the triglycerides. The purpose of hydrogenation is to increase the oil's oxidative stability and to impart physical properties similar to those of butter or margarine. The hydrogenation reaction is done in a pressurized vessel, or converter, in the presence of a catalyst, usually nickel. The reaction with hydrogen gas is exothermic, making it necessary to cool the vessel during the reaction. Reaction pressures of 0.703–4.218 kg/cm^2 (10–60 psig) at 121–128° C are used. When the end point is reached, the oil is passed through a filter precoated with diatomaceous earth for removal of most of the catalyst. A chelating agent such as citric acid is added to the filtered oil to complex the remaining catalyst. Diatomaceous earth is also added. Following mixing, the chelated nickel and earth are filtered from the oil. The oil is then transferred to storage tanks before being blended.

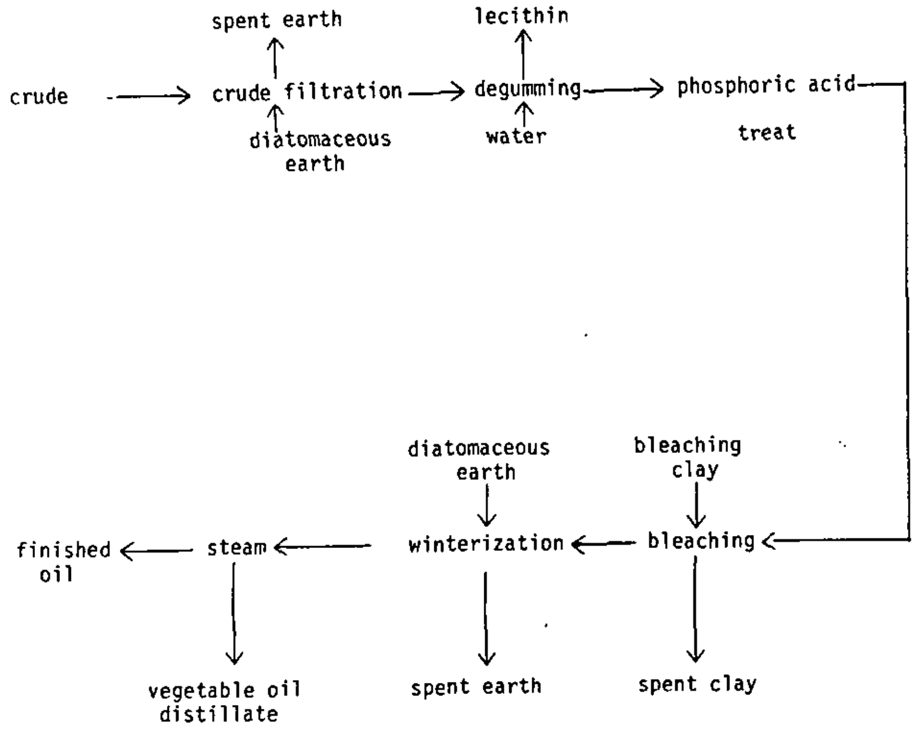

Fig. 3. Processing diagram for corn oil physical refining. (Adapted from Norris, 1982)

H. Blending of Hydrogenated Oil

Certain products, such as margarine oil, require hydrogenated corn oil with very specific properties, including solid fat content, commonly called a solid fat index (SFI) profile, melting point, and fatty acid composition. Since some of these specifications are not easily met by a single set of hydrogenation conditions, blends of two or more hydrogenated stocks with different properties are necessary. In the blending process, the proper quantities of each stock are transferred to agitated mixing tanks. Following thorough agitation, the oil is analyzed for the expected specifications and is finally deodorized.

I. Deodorization

Deodorization removes volatile materials in the oil: tocopherols, sterols, FFAs, herbicides, pesticides, dissolved gases, and moisture, as well as flavor components. Deodorized oil has lighter color, improved oxidative stability, and lower FFA and peroxide values (Reiners and Gooding, 1970). The process is similar for either unhydrogenated or hydrogenated corn oils. The bleached and/or hydrogenated oil is first partially heated and deaerated. Citric acid is added to chelate metals in the oil. The oil is further heated to approximately 232° C as it enters the vacuum vessel (≈2–10 mm of Hg). Steam is sparged through the oil during deodorization.

Corn oil may be deodorized continuously, semicontinuously, or in batches (Gavin, 1977; Norris, 1985). In one type of semicontinuous deodorizer, the oil enters into a large tray at the top of the vacuum vessel. At the end of about 8 min, the oil overflows into a tray below; this is repeated until the oil has passed through four trays. The oil is sparged with steam to provide agitation and to aid distillation of the FFAs. The overall retention time is about 32 min. Another type of deodorizer processes a batch of oil in a series of separate compartments. As the oil exits the deodorizer, it is cooled to approximately 38° C for corn salad oil, or 5° C above the melting point for each hydrogenated oil. Chelating agents such as citric and phosphoric acids and antioxidants such as TBHQ, BHT, and BHA may be added to the oil for improved stability following deodorization.

J. Quality Analyses for Corn Oil

Numerous tests have been developed by the American Oil Chemists Society and others to measure chemical and physical characteristics of corn and other vegetable oils (Sonntag, 1982; AOCS, 1985). Table III compares typical quality control specifications for refined corn oil and crude corn oil. These principal analyses give significant information about the oils and the efficiency of the total refining process. The tests are summarized below.

The FFA test indicates the efficiency of the caustic treatment and the deodorization. The presence of FFAs lowers the smoke point of the oil.

Lovibond color is determined by finding the closest red and yellow color matches between the oil sample and the standards for the test. Typically, the yellow component of finished oil is about 10 times the magnitude of the red component. Factors that contribute to finished oil color include degree of refining, conditions of oil extraction from the germ, whether the germ was dry- or wet-milled, level of hydrogenation, and color components (chlorophyll, carotenoids, etc.) present in the crude oil.

Peroxide value is a measure of the degree of oil oxidation. It is determined by reacting the oil with iodine, followed by titration with sodium thiosulfate in the presence of a starch paste indicator.

Flavor in partially oxidized corn oil is composed primarily of volatile aldehydes, including such compounds as pentanal, hexanal, nonanal, and 2-decenal. Corn oil flavor is evaluated on a scale of 1 to 10, with high scores corresponding to mild or bland flavors. Common flavor descriptors of acceptable corn oil include *bland, nutty, corny*, and *buttery*. Marginal descriptors include *metallic, hydrogenated*, and *grassy*. Descriptors of unacceptable oil include *rancid, burnt, painty*, and *fishy* (Jackson, 1985).

Iodine value is defined as the number of grams of iodine required to react with 100 g of oil. The higher the iodine value, the less saturated the oil is.

The melting point of triglycerides is dependent upon their chain length, degree of saturation, composition, and crystalline structure. All vegetable oils are mixtures of various triglycerides having a melting range. The melting point of a corn oil sample is seldom very sharp and generally has a range over several degrees.

The SFI measures the solid fat content of the oil at 10, 21.1, 26.7, 33.3, and 40°C. SFIs are usually measured dilatometrically. Such information is especially important in applications where plasticity is critical, as in the manufacture of shortenings and margarines.

Smoke, flash, and fire points are reached sequentially when oil is exposed to extremely hot temperatures (204–371°C). For each determination, oil is heated in an open cup with a flame, and the specific temperatures are noted when the sample smokes, flashes, and burns. This information is important in establishing thermal oxidation stability, as for deep-fat frying applications.

TABLE III
Typical Specifications for Crude and Refined Oil[a]

Analytical Constants	Refined Corn Oil Specifications	Refined Corn Oil Typical Values	Crude Corn Oil Specifications
Free fatty acids, %	0.05 max.	0.02–0.03	1.0–1.5
Color			
Lovibond	3.0 red max.	2.0–2.5 red	10–12 red[b]
Gardner	6 max.	3.5	...[c]
Peroxide value, meq/kg	0.5 max.	...	<0.5
Flavor	Bland	Bland	n.a.[d]
Moisture, %	n.a.	n.a.	<0.5
Iodine value[e]	...	122–128	...
Density, g/cm³	...	0.922–0.928	...

[a] Data from CRA (1986).
[b] From 1-in. tube reading.
[c] No value given.
[d] Not applicable.
[e] Grams of iodine absorbed per 100 g of fat.

VI. PROCESSING OF CORN OIL COPRODUCTS

A. Corn Lecithin

Corn oil lecithin, a potentially valuable product, is produced by removing water from the wet gums that result from the degumming process. Thin-film vacuum dryers are used. The lecithin may then be adjusted by addition of peroxide for bleaching and fatty acids or divalent salts for viscosity control to meet customer specifications. Lecithin is used as an emulsifier, antioxidant, nutrient, dispersant, etc. However, many oil refiners add the wet gums to refining soapstock rather than processing them into lecithin.

B. Soapstock

Soapstock is processed to be used in poultry and livestock feeds and in fatty acid distillation. It is usually acidulated to a neutral or slightly acidic pH or converted back to fatty acids with sulfuric acid. After sulfuric acid treatment (acidulation), the FFAs are again insoluble in water and separate into a two-phase oil-water system.

C. Vegetable Oil Distillate

Vegetable oil distillate is the condensed volatiles removed from the oil during deodorization. The distillate, composed mostly of FFAs, also contains tocopherols, carotenoids, herbicides, pesticides, and flavor and odor components. This material is used as a source of tocopherols for Vitamin E.

VII. HANDLING

A. Storage

Corn oil is held in bulk storage tanks between refining steps, during blending, and before loadout. Correct storage conditions include the absence of air, light, moisture, and heavy metals (Leo, 1985). For corn salad oil, the storage temperature should not exceed 38°C. For hydrogenated oil products, the storage temperature is kept about 5°C above the melting point. To avoid stratification, the tanks are usually equipped with agitators or recirculation facilities. The presence of air is avoided by use of nitrogen in the headspace of airtight tanks. Light exposure is not of concern if covered metal tanks are used. Moisture buildup may be a problem in cold weather, due to condensation accumulating on the top interior surface. Heavy metals, including iron and especially copper, cause the oil to quickly deteriorate, particularly in the presence of heat, moisture, and air. Ideally, stainless steel or plastic should be used to minimize the oil's exposure to active metals.

B. Loadout and Shipping

Finished corn oil, unfinished intermediate products, and coproducts are normally loaded out in tank trucks and rail cars (Erickson and List, 1985). Some products are packed in drums, pails, and glass and plastic containers. The same handling conditions apply to loadout as to storage. Air exposure is minimized by not allowing oil to splash as it enters the tank. The oil is sparged with nitrogen to remove air from the oil and to provide an airless headspace above the oil. Exposure to light is not a concern with metal rail cars and trucks. However, light may be a problem when the oil is bottled in clear glass. Most corn salad oils are presently bottled in clear glass or plastic, which may have a negative impact on shelf life unless the oil is properly stored. Most tank trucks are made of stainless steel.

C. Prevention of Oxidation

The shelf life of corn oil can be extended by the use of antioxidants, chelating agents, and "brush" (slight) hydrogenation (Erickson and List, 1985). Common antioxidants include BHA, BHT, TBHQ, propyl gallate, and tocopherol. Chelating agents include citric, phosphoric, and ascorbic acids. Antioxidants inhibit the autoxidative pathway, and chelating agents act as metal scavengers. Although the use of chelating agents and antioxidants can extend shelf life, their use cannot compensate for poor storage or handling conditions. Lightly hydrogenating the oil reduces the most highly unsaturated fatty acids, which aids in preventing oxidation.

VIII. NUTRITION

Before about 1940, the primary consumer cooking fats were lard and butter. Mazola corn oil had been introduced in 1911 by Corn Products Refining Company with the goal of establishing the brand name and building market share (Anonymous, 1985). By 1940, the essential role of fat in the diet was recognized, and the "health" image of Mazola Corn Oil's essential fatty acid content was being promoted. During the 1950s, corn oil was advertised as a substitute for saturated fats to reduce serum cholesterol (CRA, 1986). Promotion of corn oil subsequently emphasized the role of fat-modified diets on various heart disease risk factors. Consumer awareness of corn oil was noted in a study conducted by the American Soybean Association in 1978 (Erikson and Falb, 1979). Corn oil was ranked above both soybean and sunflower oils. The image created for corn oil carried through to the margarine industry.

Fat is, of course, an essential component of the diet, serving both physiological and biochemical functions (Harwood, 1978). In foods, it serves as an energy source, carrier of fat-soluble vitamins, and a source of polyunsaturated fatty acids (linoleic and linolenic acids). Corn oil is rich in polyunsaturated fatty acids. The typical linoleic acid content for U.S. production is 60.1%.

The role of essential fatty acids was demonstrated in 1929 for rats and in 1958 for human infants. The essential fatty acids linoleic and arachidonic are involved in fat transport and in the prevention of dermatitis (Alfin-Slater et al, 1980). The linoleic requirement is in the range of 1–3% of the dietary calories. Even a moderate dietary intake of 5–15 g of corn oil per day meets the essential fatty acid requirement of most people. The role of corn oil in lowering serum cholesterol was noted in about 1950 (Rathman, 1957). The favorable altering of serum lipid composition was later found. Combined, these changes were assumed to furnish protection against coronary heart disease.

Around 1980, the lowering of blood pressure by a change to a diet high in polyunsaturates and low in saturated fatty acids was observed (Vergroesen and Fleischman, 1978; Fleischman et al, 1979). The possible mechanism is through prostaglandins, a group of hormonelike lipid-derived substances. This is not well understood, however.

Corn oil is a source of various tocopherols that remain with the oil through the refining process. The tocopherols contribute to the stability of the oil, and several isomers possess vitamin E activity (see Chapter 10). The human requirement for vitamin E is proportionate to body size and polyunsaturated fat intake (Garrison, 1985). Corn oil can supply about 15% of the U.S. recommended daily allowance of vitamin E for an adult consuming 1 tablespoon (120 calories) per day.

IX. USES AND APPLICATIONS

Corn oil is considered a premium vegetable oil because of its flavor, color stability, and clarity at refrigerator temperatures. The nutritional benefits, primarily related to its polyunsaturated fatty acid and vitamin E contents, have made it a premium oil to the consumer (CRA, 1986). The two current major uses of corn oil are frying or salad applications and margarine formulations (Mounts and Anderson, 1983). About 50% of the refined oil is used for frying and salad oil, and 30–35% is used in margarine production. Currently, 100% corn oil margarines represent over 10% of the total margarine production (USDA, 1984). In the first two months of 1986, 28.4 million pounds of corn oil were used for margarine manufacture. This is approximately 170 million pounds per year (NAMM, 1986).

A. Margarines

A variety of margarine types are marketed in the United States. These include stick types, soft (tub) types, diet, imitation, liquid margarine, and vegetable oil spread. In most margarine formulations, liquid oil is blended with a partially hydrogenated component to give a fat having a sufficient solids content below the melting point to give the margarine its characteristic semisolid form. Both soft (tub) margarines and stick (hard) margarines are prepared commercially. In some instances, the liquid corn oil is blended with partially hydrogenated soybean or cottonseed oils. Regular margarines contain 80% fat and about 16–18% aqueous phase (Brekke, 1980). The aqueous phase may include an edible protein such as nonfat dry milk plus 2–3% salt, emulsifiers such as lecithin or monodiglycerides, preservatives, flavoring, and coloring. The coloring is primarily β-carotene. Fortification with 15,000 USP units of vitamin A is required. Vitamin D fortification, 2,000 USP units, is sometimes used (Crysam, 1979).

Other types of margarinelike spreads produced are 60% fat spreads and imitation margarines with 40% fat. The decreased-fat blends contain proportionately larger amounts of water. These have been developed to meet the consumer demands for lower calories or less fat. Butter blends containing corn oil have recently been introduced (Mounts and Anderson, 1983). The corn oil content varies but generally is in the 40% range. Table IV lists the typical fatty acid compositions of corn oil margarine and stick and soft margarines.

The basic steps in formulating a margarine are: blending the oil components, formulating the aqueous phase, preparing the emulsion, solidifying the emulsion, packaging, and tempering.

Formulation of the fat, cooling and working of the cooled emulsion, and tempering may be used to control the margarine's consistency. Mechanical working increases the plasticity of the emulsion, producing a spreadable product at refrigerator temperatures (Brekke, 1980).

In the preparation of margarine, the oil and aqueous phases are prepared separately and then blended in the proper proportions. The emulsion is then solidified, using tubular, scraped-surface heat exchangers. The emulsion temperature is decreased rapidly to 7–10° C. For stick margarines, the emulsion from the scraped-surface units is pumped to a stationary location to permit crystal growth, providing time for the product to become sufficiently firm for extruding, shaping, and wrapping (Chrysam, 1979). SFI data are used to control the process.

Soft tub margarines, containing as much as 80% liquid oil, are produced by mixing the chilled mass in large, agitated crystallizers. Working the chilled emulsion limits crystal growth and produces a flowable product. The product can be filled into tubs using liquid fillers. Tempering of the filled tubs at 5–10° C permits the development of a crystal structure that provides a desirable stabilized plasticlike product.

TABLE IV

Fatty Acid Composition for Typical Margarine Corn Oil and Stick and Soft Margarines[a]

	Percent of Total Fatty Acids in		
Fatty Acid	**Margarine Corn Oil**	**Stick Margarine**	**Soft Margarine**
$C_{16:0}$	10.9	8.7	8.7
$C_{18:0}$	5.9	4.7	3.1
$C_{18:1}$	47.5	38.0	31.7
$C_{18:2}$	33.9	27.1	33.7
$C_{18:3}$	0.8	0.6	0.7
$C_{20:0}$	0.3	0.2	0.2

[a] Source: A. E. Staley Manufacturing Company.

B. Frying or Salad Oils

The oils used for salads must not solidify, cloud, or deposit a crystalline fraction at refrigerator temperatures (Brekke, 1980). Properly winterized corn oil easily passes a 5.5-hr winter test, as specified by the American Oil Chemist Society (AOCS, 1985).

When the oil is used in prepared salad dressings, the presence of a crystalline fraction may cause the breaking of the emulsion. The undesirable cloudy appearance of nonwinterized bottled oils is avoided by using winterized oils in salad dressings intended for the consumer market.

Fats in deep-frying applications aid in heat transfer and, because of absorption by the food, contribute to its nutritive value and flavor. Frying oils should have a bland or very weak flavor, a smoke point minimum of 204° C, and adequate resistance to deterioration during use. Acceptable flavor is attained by proper deodorization of the oil. Reduction in FFAs to 0.05% or less provides the increased smoke point. Silicone compounds (e.g., dimethyl polysiloxane) are added as antifoam compounds, resulting in increased fryer stability (Brekke, 1980).

In addition to deep frying, corn oil is used for pan or grill frying (Brekke, 1980; Crysam, 1979; Mounts and Anderson, 1983). Commercial pan-frying oils commonly contain lecithin as an antistick compound. The consumer's choice of oil for pan or grill frying is often based on price alone (Mounts and Anderson, 1983).

C. Other Uses

Many other uses exist for vegetable oils. Some of these include shortenings of various types (ranging from plastic to pourable products) for baked foods, icings and cream fillers, imitation dairy products, and confectionery coatings. Soybean oil is the principal oil used. Most of the soybean oil is modified through hydrogenation to give it the physical characteristics that meet the demands of each application.

Corn oil, although having a slightly lower iodine value and lower degree of unsaturation than soybean oil, can be manipulated in a similar way through hydrogenation. In most instances, the type or degree of hydrogenation is not presently known. Adjustment to fit intended applications is possible.

X. TRENDS

Use of corn oil to meet the needs of the marketplace will depend primarily on price and availability. Much of the future growth will probably depend on tax and trade policy. Should significant increases in alcohol production by wet milling occur, additional corn oil will probably be available. The recent trend has been to process whole corn for ethanol production. Corn oil's market position may change if corn wet-milling capacity is greatly increased or if sources of oils high in linoleic acid, particularly sunflower and safflower oils, are developed.

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