Principles of Cereal Science and Technology Third Edition

Innehållsförteckning

CHAPTER 1: Structure of Cereals

Every cereal scientist should understand the structure of the industrially important cereal grains, as they are of utmost importance for many aspects of cereal technology, e.g., for milling of common wheat or durum wheat, for processing of maize (corn) or rice, or for barley malting. Insight into the three-dimensional architecture of cereal tissues and the compartmentalization of the various cereal constituents is, in these contexts, of prime importance. In this chapter, we deal with the structures of the most important cereals used for food and/or feed purposes (i.e., wheat, maize, and rice), as well as with those of barley, rye, triticale, oats, sorghum, and pearl millet.

In general, members of the grass family (Gramineae), which include the cereal grains, produce dry, one-seeded fruits. This type of fruit is commonly called a "kernel" or "grain." However, strictly speaking, it is a caryopsis. The wheat caryopsis (or for that matter, the grain, see Fig. 1.1) consists of a fruit coat (or pericarp) and a seed. The fruit coat adheres tightly to the seed coat, which surrounds the remainder of the seed. The seed itself consists of the embryo (or germ), the endosperm, the nucellar epidermis, and the seed coat. The nucellar epidermis and the seed coat enclose the endosperm.

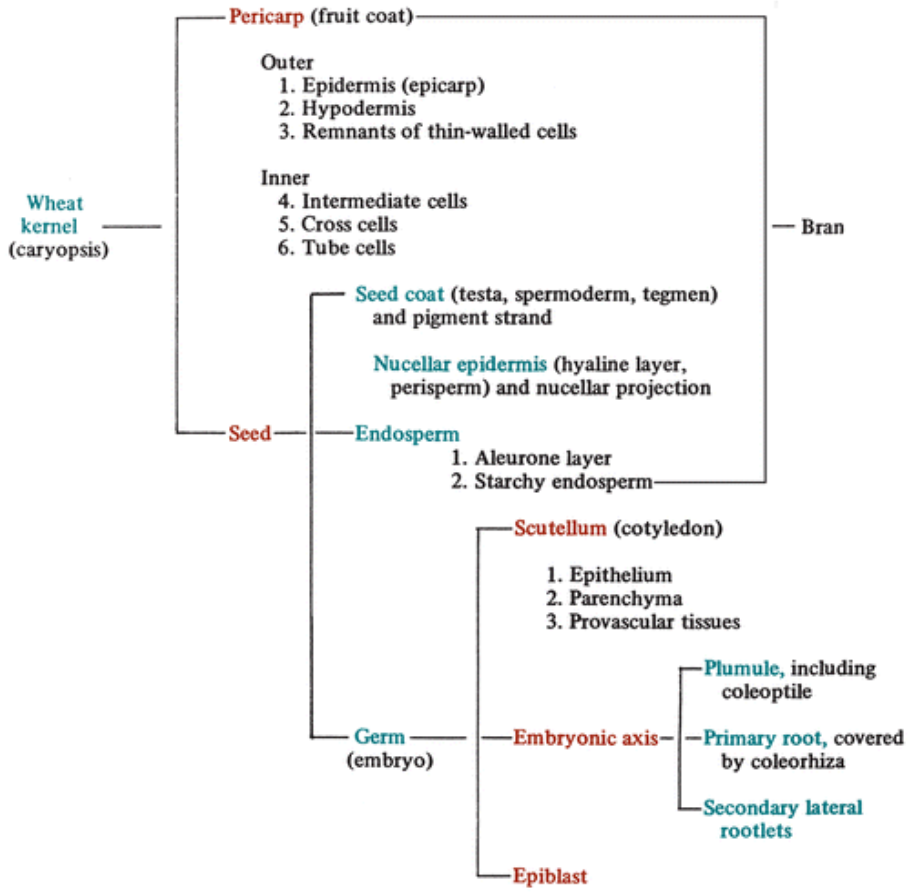


Fig. 1.1. Parts of a wheat kernel. (Reprinted from MacMasters et al 1971)

In general, all cereal grains have these same parts in approximately the same relationship to each other. Their caryopses develop within floral envelopes, which are actually modified leaves. These are called the "chaffy parts" or "glumes." In rice and most cultivars of barley and oats, the floral envelopes cover the caryopsis so closely and completely that they remain attached to the caryopsis when the grain is threshed and constitute the hull of those grains. In wheat, rye, maize, grain sorghum, and pearl millet, the grain and hull separate readily during threshing, and the grains are said to be "naked" (i.e., to have an uncovered caryopsis).

The chemical constituents of cereal grains are often separated from each other by cell walls or other barriers. Such compartmentalization, along with the relatively low water activity, is largely responsible for the stability of the grain during storage. The grains themselves often contain both degrading enzymes and the substrates of these enzymes. Certainly, if the two come in contact and a proper water activity threshold is passed (such as in germination), degradation processes can easily start. However, if enzyme and substrate are protected from coming in contact with each other, the system is stable.

Wheat is grown on more land than is any other food crop. The reasons for this are probably twofold. First, the wheat plant is quite hardy and can grow under a wide variety of environmental and soil conditions. Second, significant parts of the world population like wheat-based products.

TERMINOLOGY

In the following discussion, we use the term *wheat* for both *Triticum aestivum* L. and*T. durum* Desf., also referred to as *T. turgidum* L. subsp. *durum* (Desf.). The species*T. aestivum* is a hexaploid cereal (i.e., it contains three genomes, A, B, and D), while*T. durum* is tetraploid and contains only the A and B genomes.

In North American terminology, the *T. aestivum* wheats are divided into soft and hard wheats (Fig. 1.2). The terms *hard* and *soft* refer to the force required to crush the kernels. Generally, the North American soft cultivars, which are easy to crush, are used for cookies (biscuits), while the hard cultivars, which are more difficult to crush, are used in breadmaking. In contrast, in some European countries, the term *soft*(e.g., French: *tendre;* Dutch: *zacht*) wheat is used for both non-breadmaking and breadmaking *T. aestivum* wheats, while the term *hard* (French: *dur;* Dutch: *hard*) wheat refers to *T. durum,* the normal raw material for pasta production. To avoid confusion, this book uses the North American terminology. In this section, all of these wheats are discussed as a group, and possible reasons for the obvious differences in hardness are commented on.

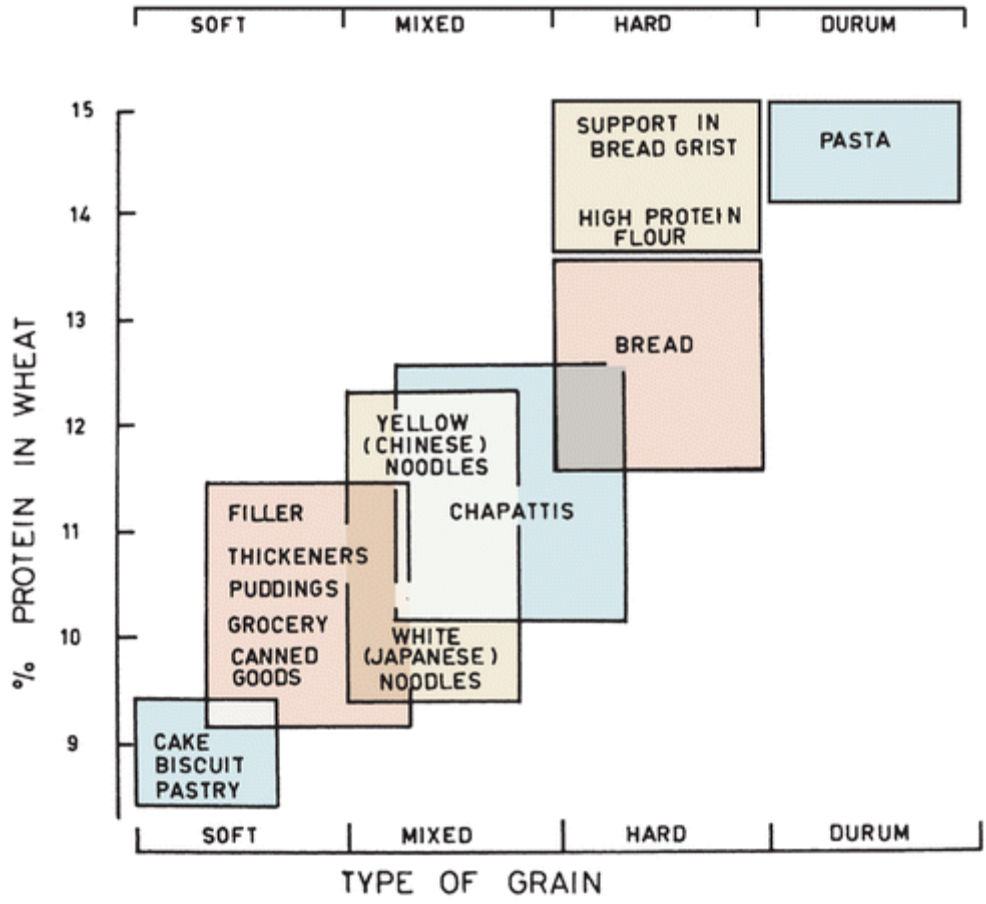


Fig. 1.2. Wheat types and the types of products made from them. Note that the figure is valid for applications of North American wheats and that the terminology of *soft, hard,* and *durum* wheats is that used in North America. In Europe and other areas, wheats of softness comparable to that of the North American soft wheats are not available. (Reprinted, with permission, from Moss 1973)

THE WHEAT KERNEL

Figure 1.3 shows a caryopsis, or kernel, of wheat diagrammatically in both longitudinal and cross sections. The kernels of North American wheats average about 8 mm in length and weigh about 35 mg. European wheats weigh an average of about 55 mg. Their sizes vary widely depending upon the cultivar and their location in the wheat head or spike. Wheat kernels are rounded on the dorsal side (the same side as the germ) and have a longitudinal crease over the length of the ventral side (opposite the germ). The crease, which runs nearly the entire length of the kernel, extends nearly to its center. The two cheeks may touch and thus mask the depth of the crease. The crease not only makes it difficult for the miller to separate the bran from the endosperm with a good yield but also forms a hiding place for microorganisms and dust.

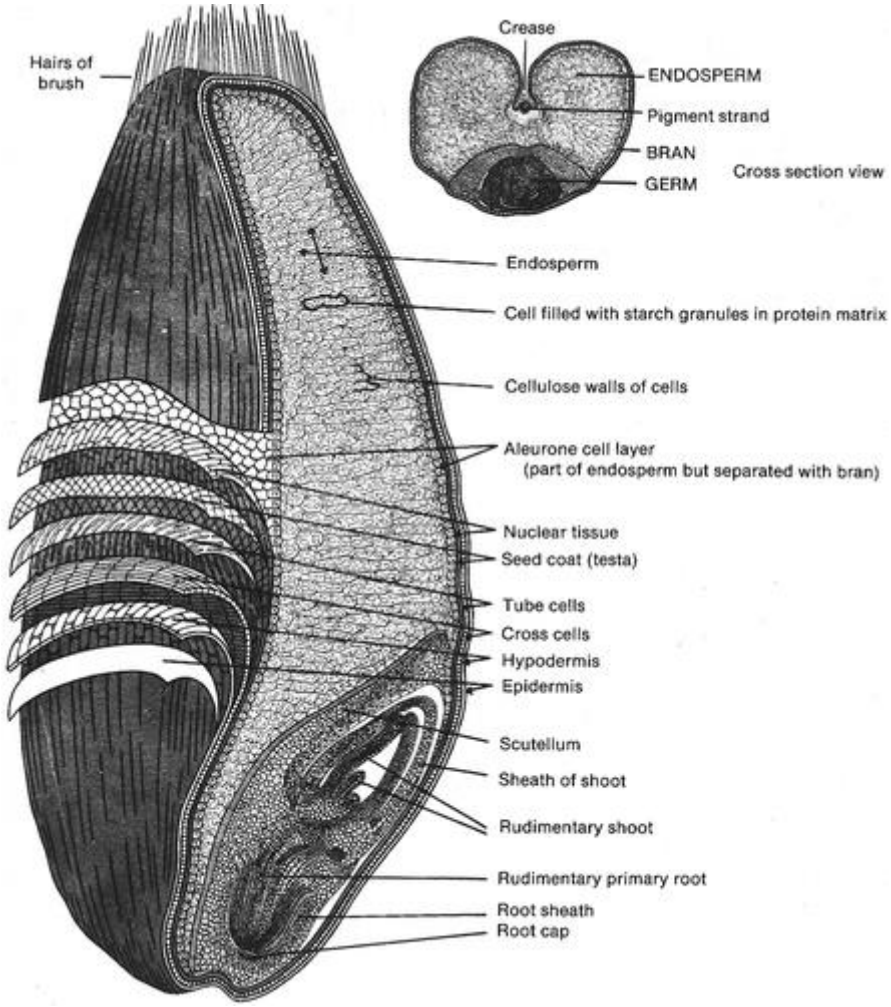


Fig. 1.3. Longitudinal and cross sections of a wheat kernel. (Courtesy Wheat Flour Institute, Washington, D.C.)

Wheat kernels vary widely in endosperm texture (i.e., hardness) and color. The variation in texture, which appears to be related to binding forces in the endosperm, is discussed later in this chapter. The color of the seed, usually white or red, is related to pigment in the seed coat. Purple and even black seeds are known but are not common. The type and presence of the pigments is under genetic control and thus can be manipulated by the plant breeder.

Pericarp

The pericarp surrounds the entire seed and is itself composed of several layers (Fig. 1.4). The total pericarp makes up about 5% of the kernel and consists of about 6% protein, 2% ash, 20% cellulose, and 0.5% fat, with the remainder being nonstarch polysaccharide. The outer pericarp is what millers call the "beeswing." The innermost portion of the outer pericarp consists of the remnants of thin-walled cells. Because of their lack of continuous cellular structure, they form a natural plane of cleavage. Thus, the beeswing is often lost before milling.

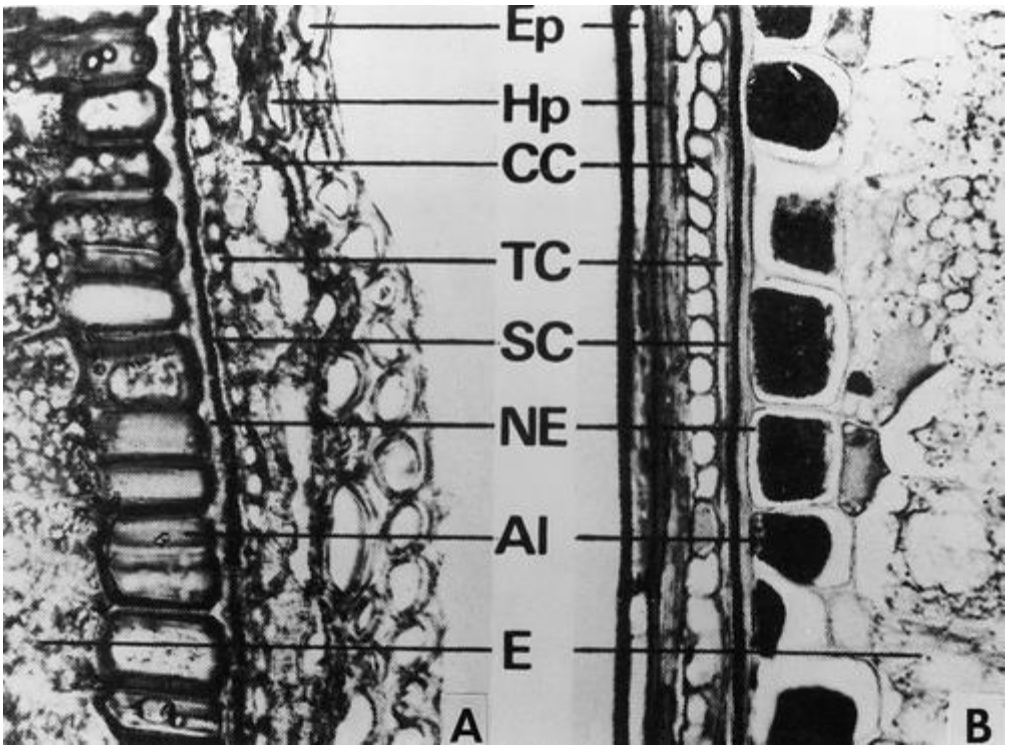


Fig. 1.4. Cross section **(A)** and longitudinal section **(B)** through the pericarp and adjacent tissues of a wheat kernel. Epidermis (Ep), hypodermis (Hp), cross cell (CC), tube cell (TC), seed coat (SC), nucellar epidermis (NE), aleurone layer (Al), and starchy endosperm (E). (Reprinted from MacMasters et al 1971)

The inner pericarp is composed of intermediate cells, cross cells, and tube cells. Neither the intermediate nor tube cells completely cover the kernel. The cross cells are long and cylindrical (about 125 × 20 μm); their long axis is perpendicular to the long axis of the kernel. The cross cells are tightly packed, with little or no intercellular space. The tube cells are of the same general size and shape as the cross cells but have their long axis parallel to the long axis of the kernel. They are not packed tightly and thus have many intercellular spaces.

Seed Coat and Nucellar Epidermis

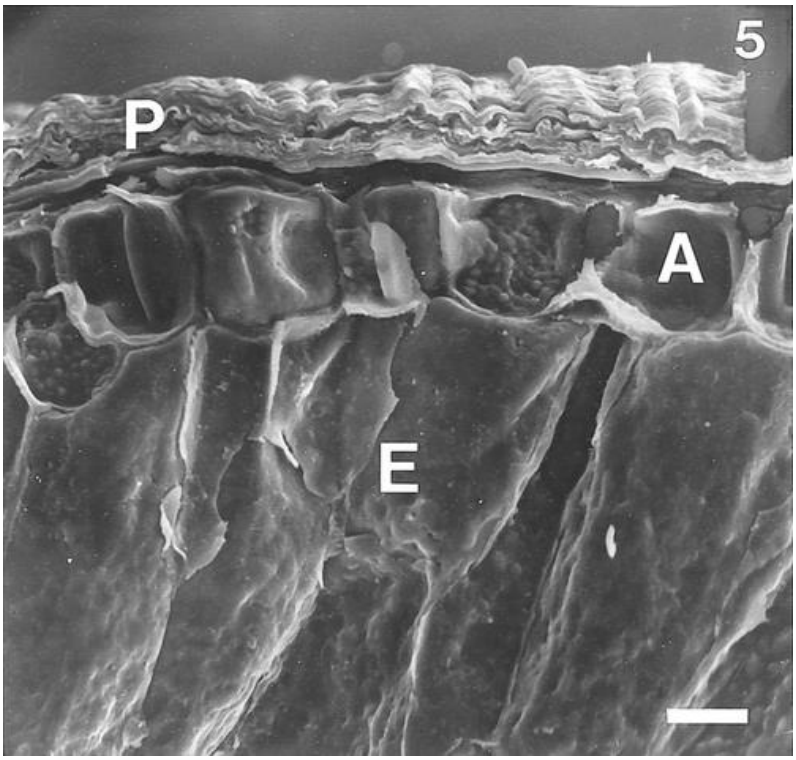
The seed coat is firmly joined to the tube cells on their distal (outer) side and to the nucellar epidermis on its proximal (inner) side. It consists of three layers: a thick outer cuticle, a layer that contains pigment (for colored wheats), and a thin inner cuticle. The seed coat of white wheat has two compressed cell layers of cellulose containing little or no pigment. The thickness of the seed coat varies from 5 to 8 μm. The nucellar epidermis, or hyaline layer, is about 7 μm thick and tightly bound to both the seed coat and the aleurone layer.

Endosperm

The endosperm consists of the outer aleurone layer and the starchy endosperm.

The Aleurone Layer. This layer, which is generally one cell layer thick, completely surrounds the kernel, covering both the starchy endosperm and the germ. From a botanical standpoint, it is the outermost layer of the endosperm. Milling removes the aleurone, the nucellar epidermis, the seed coat, and the pericarp together to form what the miller calls "bran."

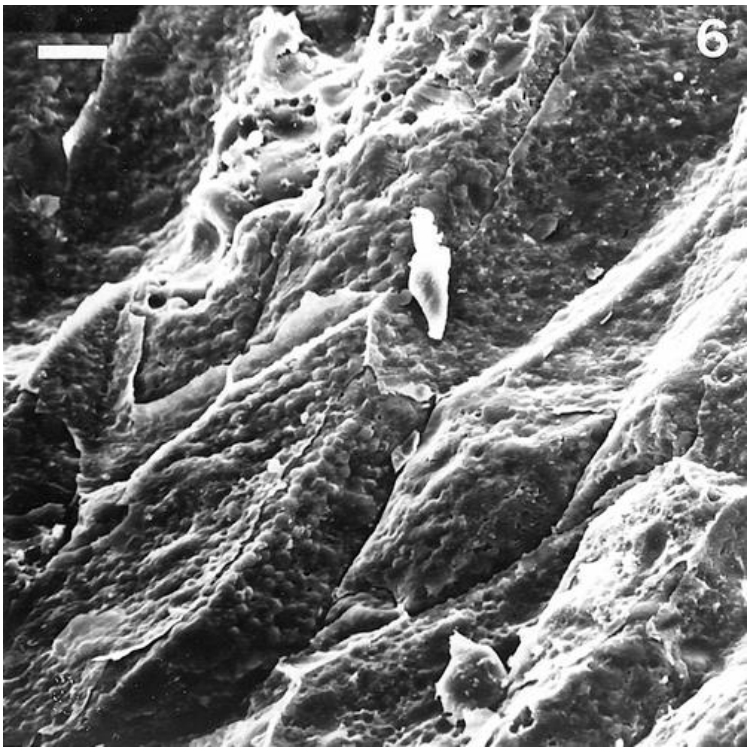
The aleurone cells covering the starchy endosperm are thick-walled, essentially cuboidal, and free of starch at maturity (Fig. 1.5). The average cell is about 50 μm across. Aleurone cell walls are 3–4 μm thick and have been reported to be largely cellulosic in composition. The aleurone cells contain a large nucleus and a large number of aleurone granules (Fig. 1.5). The structure and composition of the aleurone granules are complex. The aleurone layer is relatively high in enzyme activity and in ash, protein, total phosphorus, phytate phosphorus, and lipid contents. In addition, the vitamins niacin, thiamin, and riboflavin have higher concentrations in the aleurone than in the other parts of the bran. Over the embryo, the aleurone cells are thin-walled and may not contain aleurone granules. Their thickness is about 13 μm, or less than one-third the thickness found for the aleurone cells surrounding the starchy endosperm.



Figs. 1.5. and 1.6. Scanning electron micrographs of a cross section of a hard winter wheat kernel. (Reprinted, with permission, from Hoseney and Seib 1973)

1.5. Pericarp (P), aleurone layer (A), and endosperm (E). Bar is 20 µm.

1.6. Endosperm cells.



The Starchy Endosperm. When reduced to appropriate particle size, the contents and cell walls of the endosperm produce either flour, farina, or semolina. Flour is generally a product reduced to pass a 132-µm sieve, while farina and semolina are products of larger size that are milled from *T. aestivum* and *T. durum,* respectively.

The starchy endosperm is composed of three types of cells that vary in size, shape, and location within the kernel. They are referred to as "peripheral," "prismatic," and "central." The peripheral starchy endosperm cells are the first row of cells inside the aleurone layer; they are usually small and are equal in diameter in all directions or slightly elongated (Fig. 1.5). Next are several rows of elongated prismatic starchy endosperm cells (Fig. 1.6). They extend inward to about the center of the cheeks and are about 150 × 50 × 50 μm in size. Then come the central starchy endosperm cells. They are more irregular in size and shape than the other cells are.

The wheat endosperm cell walls are mainly composed of arabinoxylans (in older literature referred to as "pentosans"). They contain minor levels of β-glucans and other hemicelluloses, but not cellulose. The thickness of the cell walls varies with location in the kernel, being thicker near the aleurone.

The cells are packed with starch granules embedded in a protein matrix. The protein is mostly, but not entirely, gluten, the storage protein of wheat. During maturation, gluten is synthesized and deposited as protein bodies. However, as the grain matures, the protein bodies are compressed together into a matrix that appears mud- or claylike, and the bodies are no longer discernible. The starch granules occur as large, lenticular (lens-shaped) granules of up to 40 μm across the flattened side and as small, spherical granules 2–8 μm in diameter. In actuality, one can find granules of all sizes between these extremes, but these two size-shape combinations are preponderant. Close examination also shows a large number of very small starch granules (<1 μm in diameter). Although these small granules are numerous, they account for only a very small percentage of the mass of starch.

Germ, or Embryo

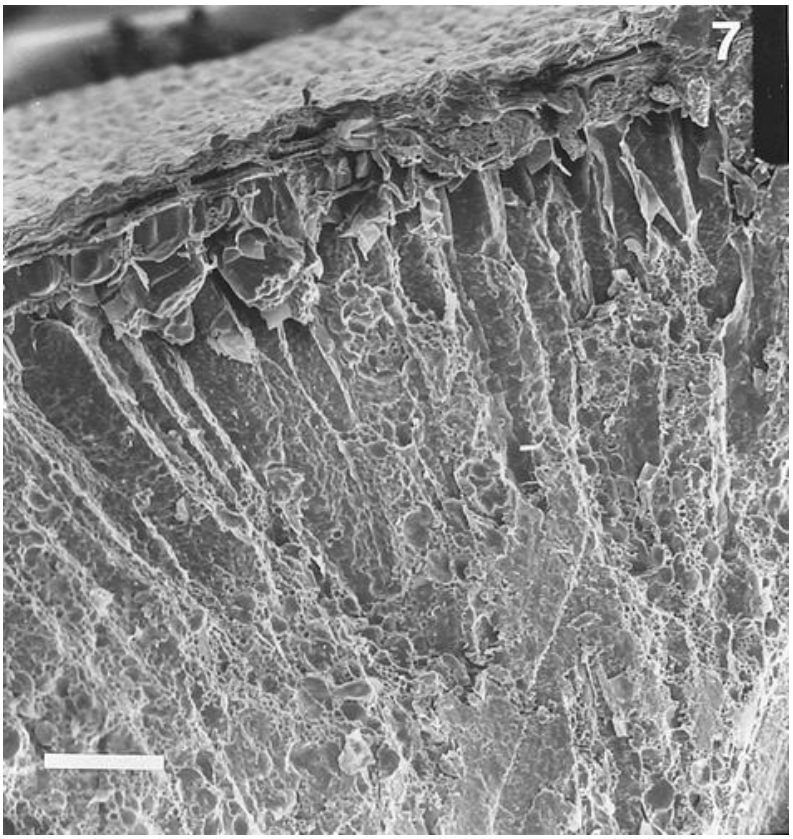
The wheat germ makes up 2.5–3.5% of the kernel. As detailed in Fig. 1.3, it consists of two major parts, the embryonic axis (rudimentary root and shoot) and the scutellum, which functions as a storage organ. The germ is relatively high in protein (25%), sugar (18%), oil (16% of the embryonic axis and 32% of the scutellum), and ash (5%). It contains no starch but is rather high in B vitamins and contains many enzymes. The germ is quite high in vitamin E (total tocopherol), with levels of up to 500 ppm. The sugars are mainly sucrose and raffinose.

WHEAT ENDOSPERM TEXTURE AND APPEARANCE

Wheat Endosperm Texture

The reasons for differences in wheat endosperm hardness are not clearly understood. However, major differences in the hardness (texture) found in soft, hard, and durum wheats seem to be attributable to the presence, absence, or sequence polymorphism of the proteins puroindolin a and puroindolin b. One theory is that these proteins control the interaction of gluten with the surface of starch granules and that this interaction controls the hardness.

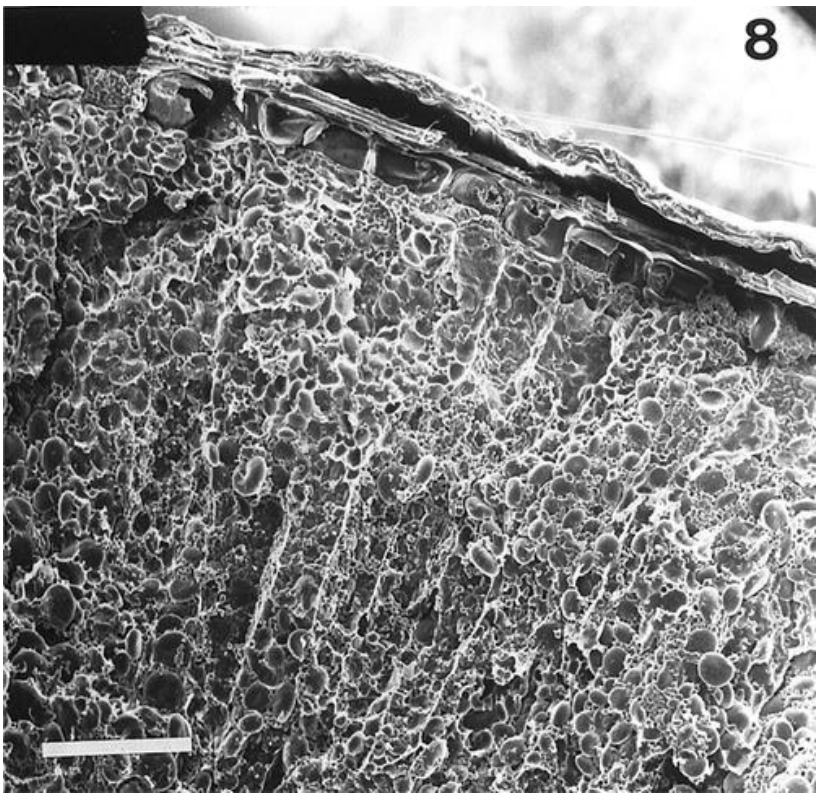
Cell wall thickness varies among cultivars and between hard and soft *T. aestivum* wheat types (Figs. 1.7 and 1.8). This difference between hard and soft wheats may be the result of selection. Hard wheats (bread wheats) have been selected for high water absorption and hence for thick endosperm cell walls, as the arabinoxylan component in cell walls absorbs high levels of water. In contrast, high levels of water absorption are not desired in soft wheat flour; thus, soft wheats are selected for low water absorption and consequently for thin cell walls.



Figs. 1.7 and 1.8. Scanning electron micrographs (low magnification) of cross sections of hard winter wheat. Bar is 100 μm.

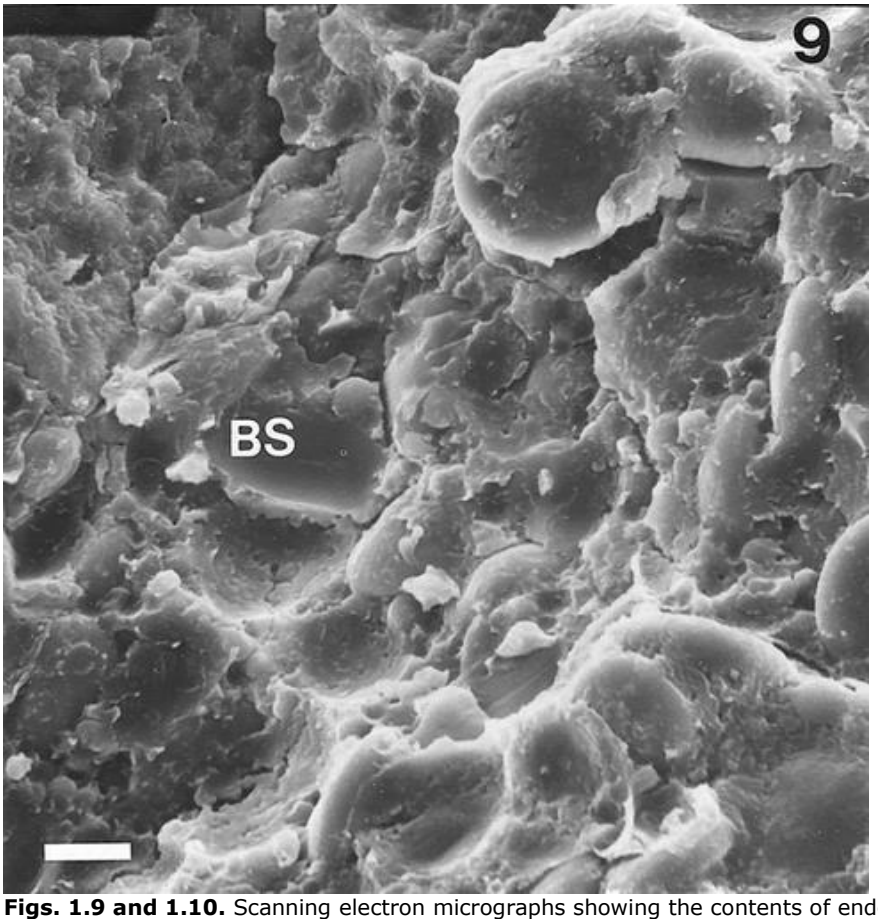
1.7. Hard wheat with breakage at the cell walls.

1.8. Soft wheat with breakage through the cells.



Another difference between hard (Fig. 1.7) and soft (Fig. 1.8) *T. aestivum* wheats is the way the cells fracture when the kernels are crushed. In hard wheat kernels, the first point of fracture occurs at the cell wall rather than through the cell contents. This is particularly evident in those cells just below the aleurone. In soft wheat endosperm, fracture occurs primarily through the cell contents. This is evidence that the cell contents are more firmly bound to each other in hard *T. aestivum* wheats, resulting in a plane of weakness between the cell walls. Of course, as the endosperm is reduced to flour size, the hard wheat cell contents are also fractured.

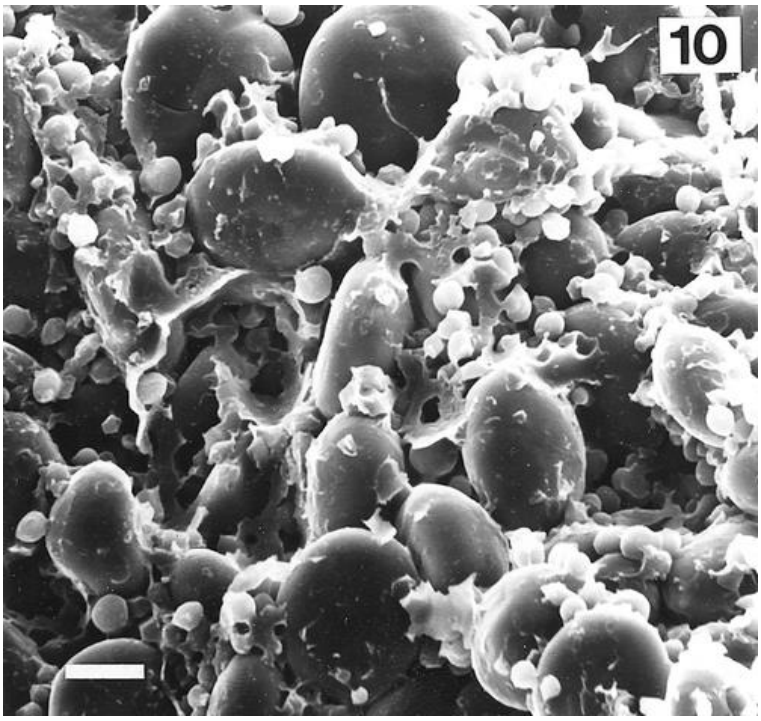
Figure 1.9 shows the tight adherence of the protein and starch in hard wheat. The protein appears to wet (coat or adhere to) the starch surface very well. This is characteristic of hard wheats. In addition, the bond between the two is strong. Evidence for the strength of the bond is the tendency of hard wheats to break at the cell wall or through some starch granules (note the broken starch granule [BS] in Fig. 1.9) rather than at the starch-protein interface. In progressively harder wheats, the protein-starch bond is increasingly strong, and relatively more broken starch granules can be seen on the fractured surface.



Figs. 1.9 and 1.10. Scanning electron micrographs showing the contents of endosperm cells. Bar is 10 Mm. (Reprinted, with permission, from Hoseney and Seib 1973)

1.9. Hard winter wheat. Note the broken starch (BS) granule.

1.10. Soft winter wheat.



In a similar micrograph of soft wheat (Fig. 1.10), the appearance is quite different. The starch and protein themselves are similar in appearance, but the protein does not wet the surface of the starch. No starch granules are fractured, as the bond between the protein and starch ruptures easily, showing that it is not strong.

In *T. durum* wheat, which is much harder than the common *T. aestivum* hard wheats, a much larger number of broken starch granules result when the kernel is fractured (Fig. 1.11). When sufficient force is applied across an endosperm cell, starch granules break, not the starch-protein bond.

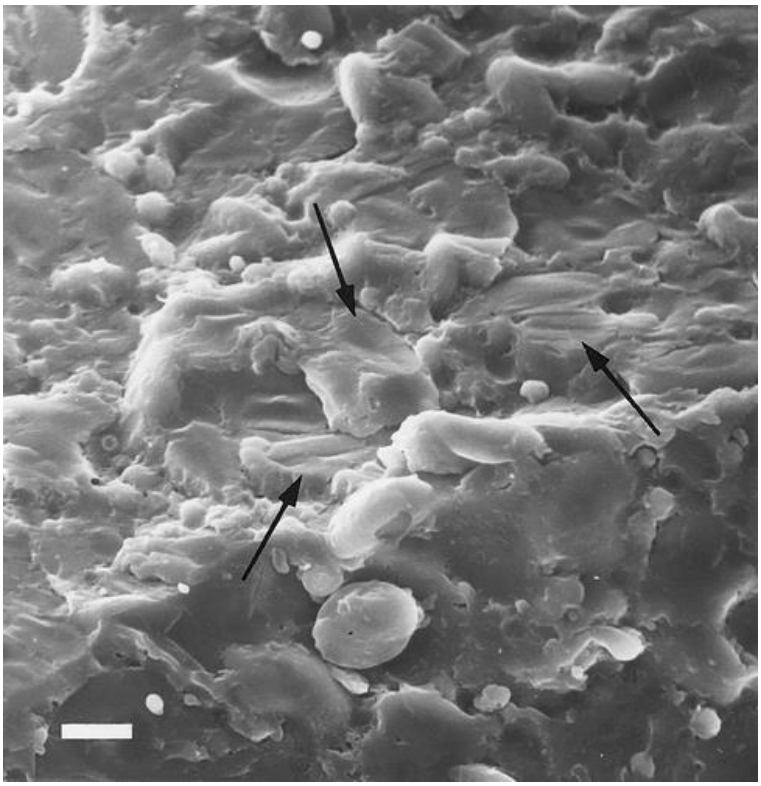


Fig. 1.11. Scanning electron micrograph of a durum wheat kernel, showing the contents of an endosperm cell. Note the large number of broken starch granules (arrows). Bar is 10 μm. (Reprinted, with permission, from Hoseney and Seib 1973)

The strength of the protein-starch bond appears to explain kernel hardness, but the nature of the starch-protein bond is not known. However, the fact that protein and starch can be easily separated from each other after treatment of flour with water seems to indicate that the bond is broken or weakened by water.

Wheat Endosperm Visual Appearance

In addition to the differences in hardness, another important characteristic of the wheat endosperm is its appearance. Some wheats are vitreous (also called horny or translucent) in appearance, while others are opaque (mealy or floury). Traditionally, vitreousness has been associated with hardness and high protein content and opacity with softness and low protein. However, vitreousness and hardness are not the result of the same fundamental cause, and it is entirely possible to have hard wheats that are opaque and soft wheats that are vitreous, although these are somewhat unusual.

Opaque (or floury) kernels have air spaces that diffract and diffuse light. In tightly packed kernels, with no air space, light is diffracted at the air-grain interface but then travels through the grain without being diffracted again and again. The result is a translucent or vitreous endosperm. As expected, air spaces within the grain make opaque grain less dense than vitreous grain. The spaces are apparently formed during the drying of the grain. As the grain loses water, the protein shrinks, ruptures, and leaves air spaces. With vitreous endosperm, the protein shrinks but remains intact, giving a denser kernel. If grain is harvested before it has dried and is subsequently dried by freeze-drying, it is opaque. This shows that the vitreous character develops during final drying in the field. It is also well known that wetting and drying vitreous grain in the field (or in the laboratory) make it lose its vitreousness.

Wheat Endosperm Texture and Visual Appearance

In summary, the wheat endosperm varies both in hardness and vitreousness. In general, high-protein hard wheats tend to be vitreous, and low-protein soft wheats tend to be opaque. However, the causes of hardness and vitreousness are different, and the two do not always go together. There is no causal relationship. Hardness is caused by the genetically controlled strength of the bond between protein and starch in the endosperm. Vitreousness, on the other hand, results from lack of air spaces in the kernel. The controlling mechanism is not clear but appears to be at least partially related to the level of protein in the sample. For example, high-protein soft wheats are more vitreous than low-protein soft wheats, and low-protein hard wheats have more yellow-berry (opacity) than their high-protein counterparts. It is also clear that both genetic and environmental conditions affect the vitreous properties of wheat.

Maize

Many types of maize (*Zea mays* L., also referred to as "corn") are grown around the world. This discussion is limited to the dent type. Popcorn is discussed in Chapter 16.

THE MAIZE KERNEL

Dent maize has a large, flattened seed. It is by far the largest of the common cereal seeds, weighing an average of 350 mg. The kernel (Fig. 1.12) is made up of four principal parts: bran (pericarp, epidermis, and seed coat) or hull, germ, endosperm, and tip cap. For maize, the term *hull* is a misnomer. It is not synonymous with the hull of barley or oats but more akin to the *bran* of wheat milling terminology. However, the use of the term *hull* is strongly ingrained in the wet-milling industry and thus will persist. The tip cap, the attachment point of the cob, may or may not stay with the kernel during removal from the cob. The botanical parts of the maize caryopsis (pericarp, endosperm, and germ) are the same as those found in wheat.

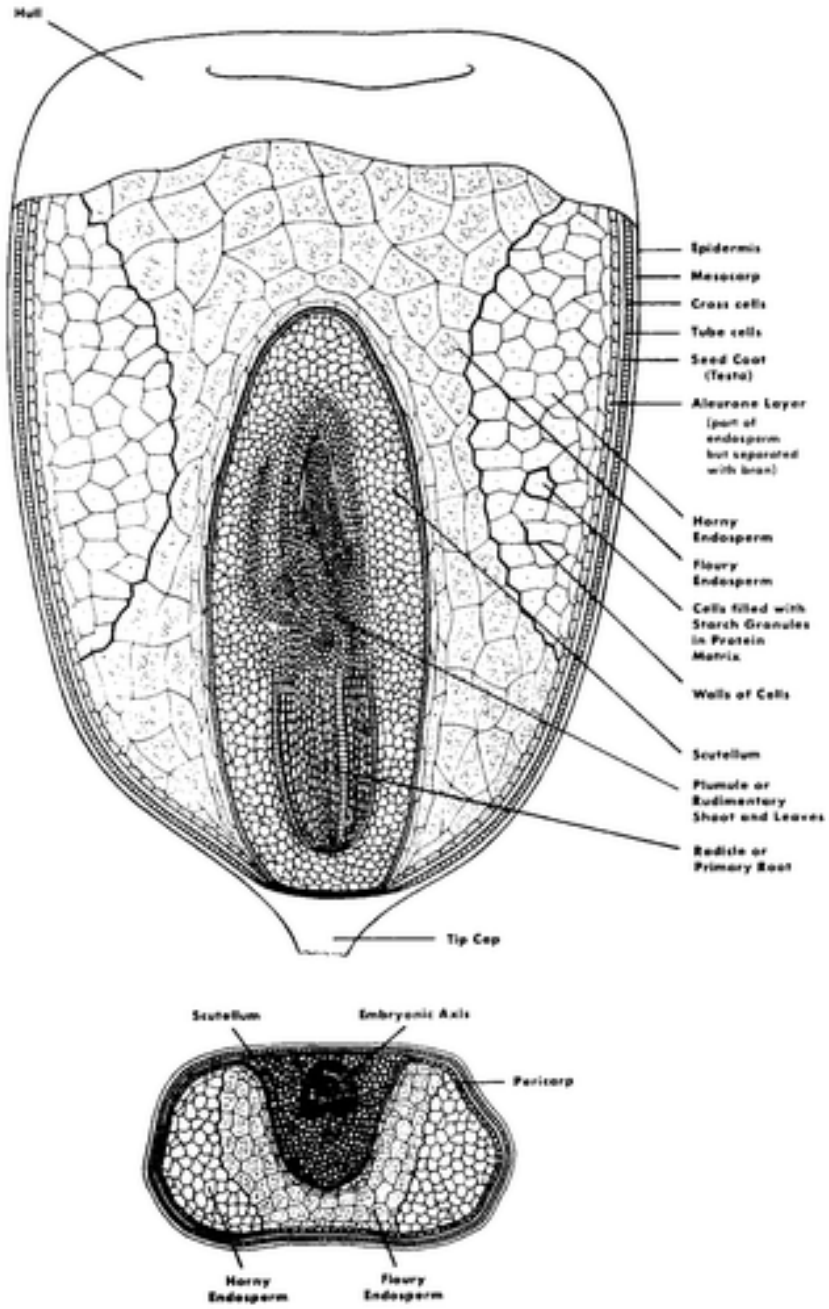
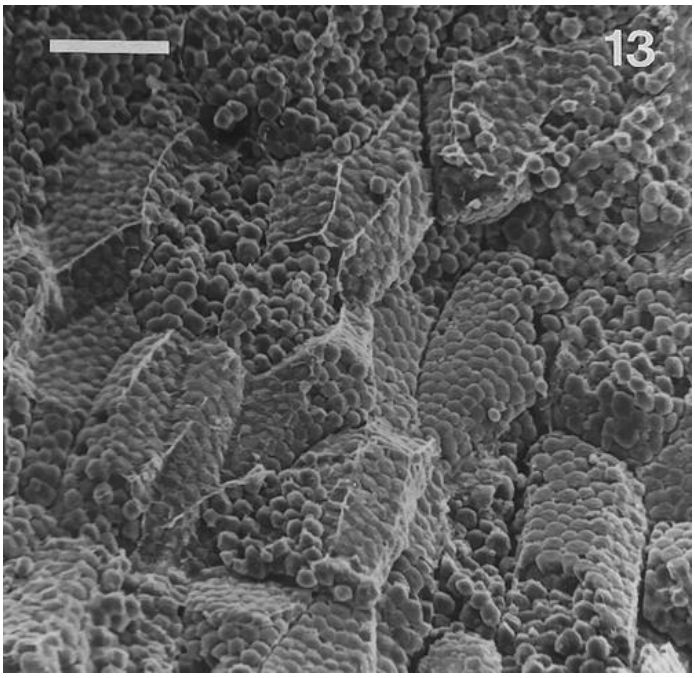


Fig. 1.12. Longitudinal and cross sections of a maize kernel. (Courtesy Corn Refiners Association, Washington, D.C.)

The color of the maize kernel can be quite variable. It may be solid or variegated and can be white, yellow, red, blue, dark brown, or purple. Yellow is the most common color, followed by white. The hull, or pericarp, makes up about 5–6% of the kernel and is coated with a layer of wax. The germ is relatively large, composing 10–14% of the kernel. The remaining part of the kernel is endosperm.

MAIZE TEXTURE AND VISUAL APPEARANCE

The cellular nature of maize endosperm is shown in Figure 1.13. The cells are large with very thin cell walls. Maize differs from wheat in that both translucent and opaque areas are found in the endosperm of a single kernel. In general, the translucent part is near the aleurone, and the opaque part is near the center of the kernel.



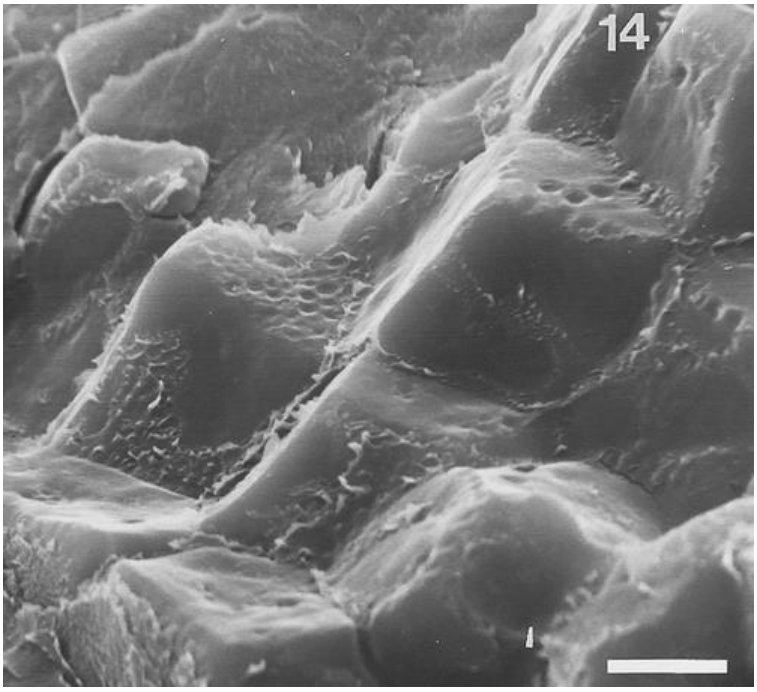
Figs. 1.13–1.16. Scanning electron micrographs of maize kernels. Each bar is 5 μm. (Reprinted from Robutti et al 1974)

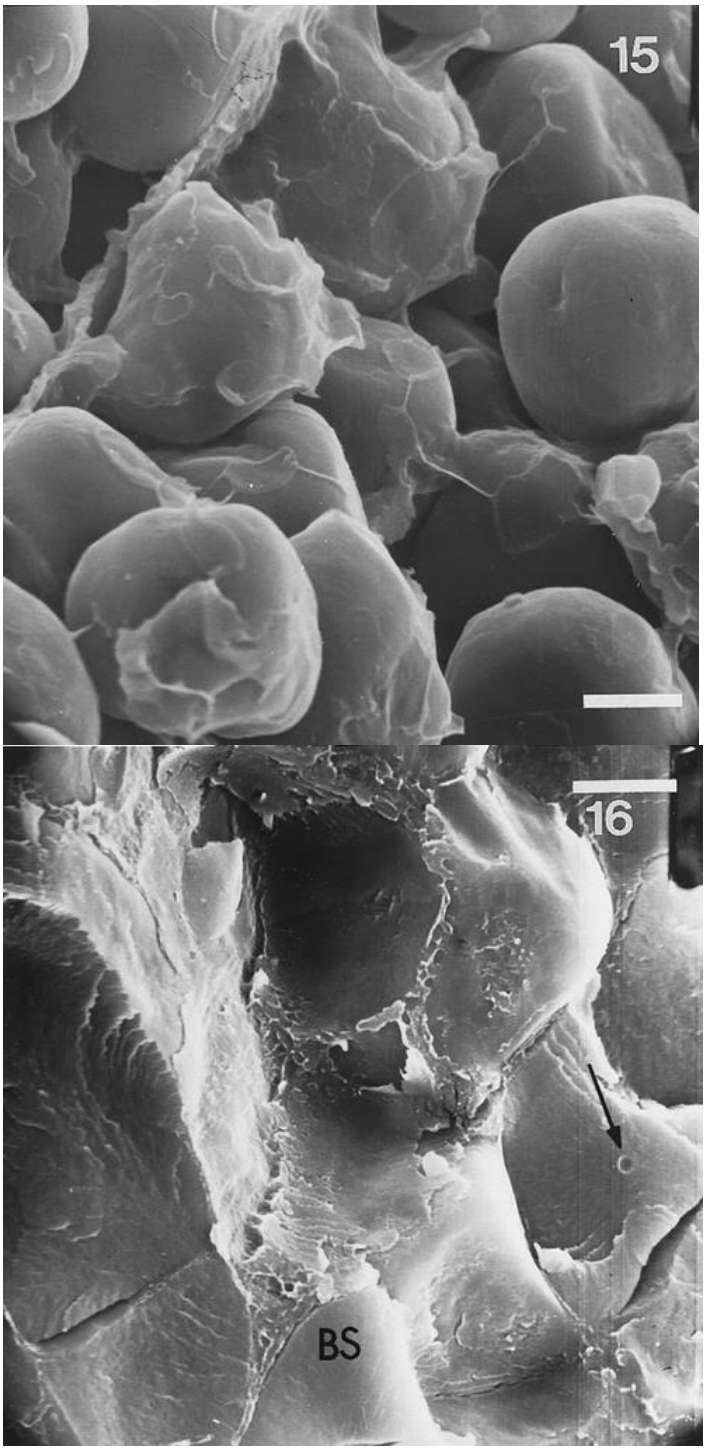
1.13. A broken kernel, showing the cellular nature of the endosperm.

1.14. Cross section of the vitreous part of a maize kernel, showing the polygonal shape of the starch granules, the indentation in the starch, and the tight compact structure.

1.15. Cross section of the opaque part of a kernel, showing the spherical shape of the starch granules, the protein, and the large number of air spaces.

1.16. Cross section of the hard endosperm of a kernel, showing the starch hilum (the point from which the starch granule grew, arrow) and broken starch (BS).





The translucent, or vitreous, endosperm (Fig. 1.14) is tightly compact, with few or no air spaces, as one might predict. The starch granules are polygonal in shape and held together by a protein matrix. Protein bodies are quite noticeable in the photomicrograph. These have been identified as bodies of zein (the prolamin protein fraction of maize; see Chapter 3). Also noticeable are indentations in the starch. In the opaque endosperm (Fig. 1.15), the starch granules are spherical and are covered with matrix protein that does not contain protein bodies. The many air spaces lead to opacity. Chemical analysis of the separated opaque and translucent parts of the endosperm has shown that the two have similar protein concentrations but that the protein types are quite different in terms of protein distribution and amino acid composition.

In general, maize kernels are quite hard. The large number of broken starch granules in Figure 1.16 shows that the bond between the protein and starch must be quite strong. The fact that water alone will not allow a good separation of protein and starch during wet milling suggests that the bond is different in maize and wheat. The opaque endosperm in maize is generally referred to as the "soft" endosperm. The particle size of ground maize from a mutant with a completely opaque endosperm suggests a soft endosperm, and photomicrographs of the

opaque section of a normal kernel (Fig. 1.15) show no broken starch granules (which is consistent with a soft endosperm). However, since opaqueness and hardness are caused by different mechanisms, it appears prudent to call this part of the endosperm "opaque" and not assume that it is soft simply because it is opaque.

The starch granules in the opaque and translucent parts of the endosperm differ in shape. One possible explanation for two starch-granule shapes in a single kernel is that, during the natural drying process, the protein loses water and shrinks. The adhesion between protein and starch is strong enough to pull the starch granules closer and closer together. At this stage, the starch granules are pliable and, as they are tightly packed, they become polygonal in shape. Further evidence of their plasticity before maturity is the fact that the zein bodies make indentations on the starch granules in the translucent endosperm.

In the opaque endosperm, protein-protein bonds rupture during drying, giving intergranular air spaces and maintaining spherical starch granules. If maize is harvested before it dries, essentially all of its starch granules are spherical, showing that the differentiation of granule shape occurs during grain drying.

Rice

THE RICE KERNEL

Rice (*Oryza sativa* L.) is harvested with the hull, or husk, attached (Fig. 1.17) and is called "paddy" or "rough rice." The hull (Fig. 1.18), which constitutes about 20% of the weight of rough rice, is made up of the floral envelopes, i.e., the lemma and palea. The hulls are high in cellulose (25%), lignin (30%), arabinoxylans (15%), and ash (21%). The ash is unique, as it contains about 95% silica. The high levels of lignin and silica make the rice hull of rather low value both nutritionally and commercially.

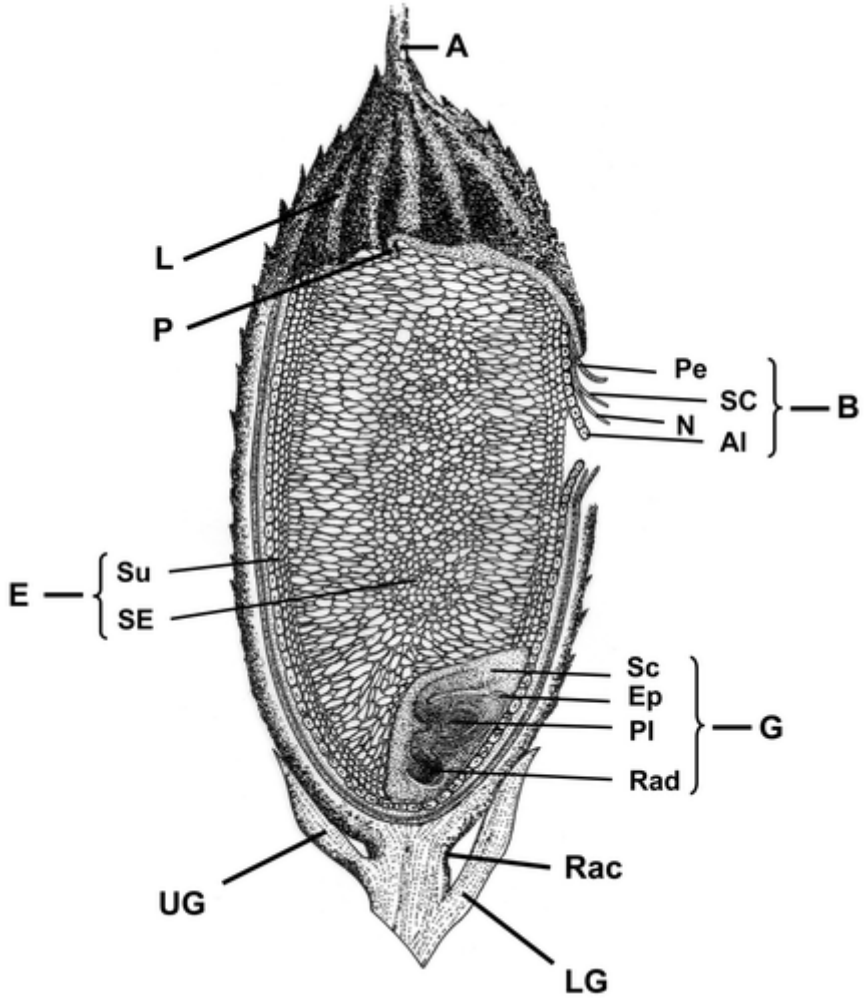
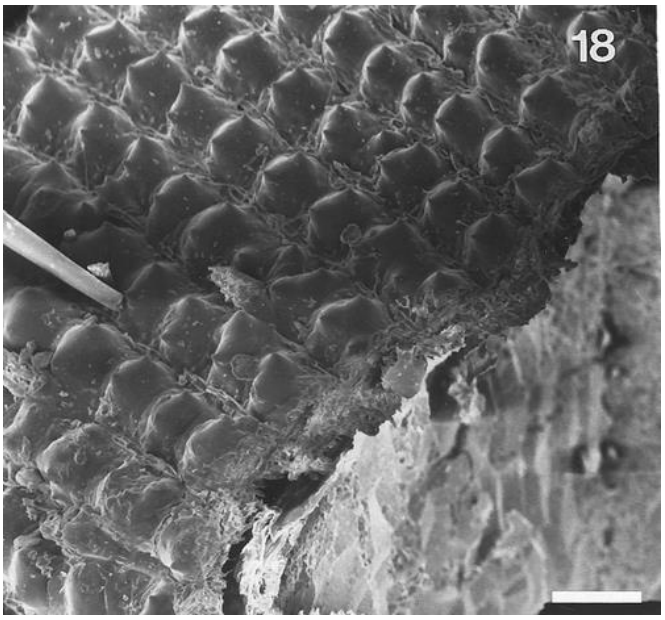


Fig. 1.17. Longitudinal section of a rice kernel. From top: awn (A), lemma (L), palea (P), pericarp (Pe), seed coat (SC), nucellus (N), aleurone (Al), bran (B), subaleurone (Su), starchy endosperm (SE), and endosperm (E). From bottom: lower glume (LG), upper glume (UG), rachilla (Rac), radicle (Rad), plumule (Pl), epiblast (Ep), scutellum (Sc), and germ (G). (Courtesy L. Lamberts and L. Van den Ende; adapted from Juliano 1984)

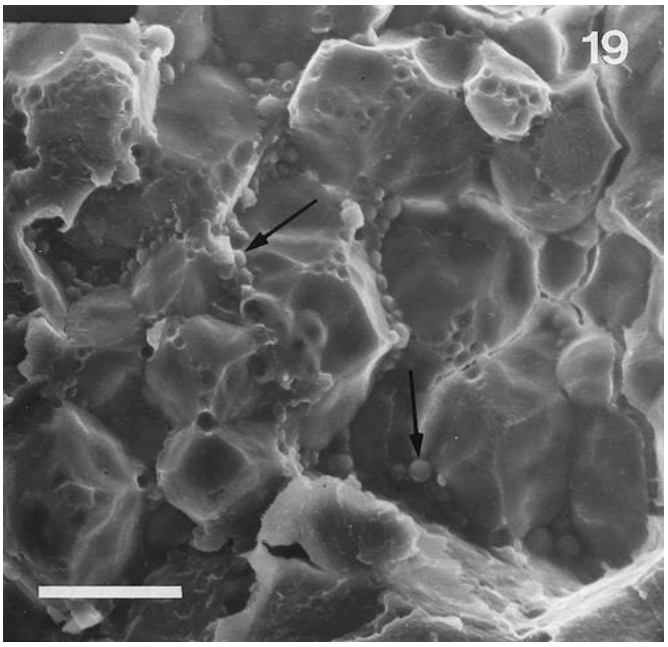


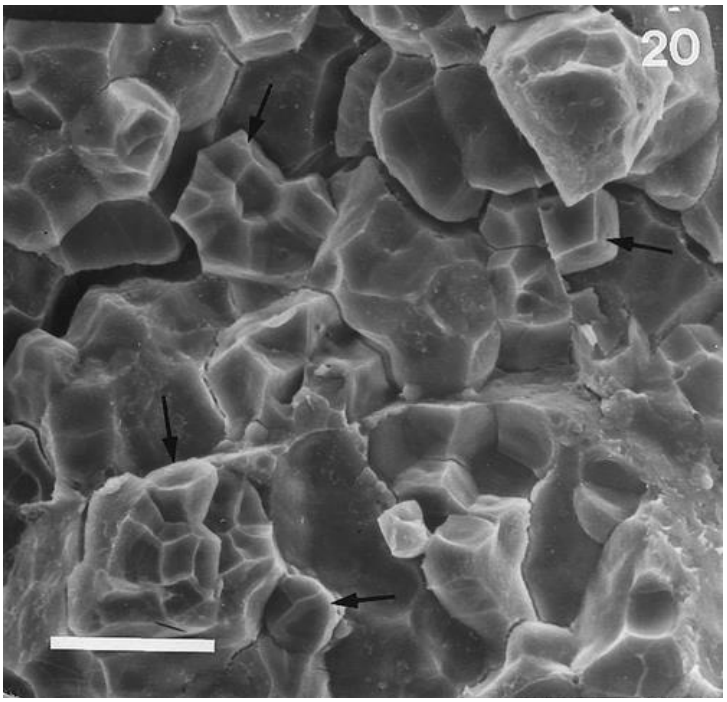
Figs. 1.18–1.20. Scanning electron micrographs of cross sections of a rice kernel.

1.18. The outer surface of the rice hull. Bar is 100 μm.

1.19. Compound starch granules and protein bodies (arrows) near the aleurone layer. Bar is 10 μm.

1.20. Compound starch granules near the center of the kernel, with certain granules broken, showing the individual granules (arrows). Bar is 10 μm.





Brown rice (rice after the hull is removed) has the same gross structure as that of the other cereals. However, the caryopsis does not have a crease. It varies from 5 to 8 mm in length and weighs about 25 mg. Brown rice consists of a pericarp (about 2%); seed coat, nucellar epidermis, and aleurone (about 5%); germ (2–3%); and endosperm (89–94%). As with the other cereals, the aleurone is the outermost layer of the endosperm, but it is removed with the pericarp and seed coat during abrasive milling to produce white rice.

RICE ENDOSPERM TEXTURE AND VISUAL APPEARANCE

In general, the endosperm of rice is both hard and vitreous. However, opaque cultivars are known, and some cultivars have opaque areas, referred to as "white belly." As in previous examples, the opacity is caused by air spaces in the endosperm. The thin-walled endosperm cells are tightly packed, with polygonal starch granules, protein matrix, and protein bodies. Comparison of Figures 1.19 and 1.20 reveals that the protein bodies are more numerous in the cells just inside the aleurone than in cells near the center of the endosperm. The polygonal starch granules may be formed by compression of the starch granules during grain development. Rice and oats are the only two cereals with compound starch granules (i.e., large granules made up of many small granules). The compound granules appear to result from many small individual granules being synthesized in a single amyloplast, i.e., an organelle containing starch granule(s). The individual rice starch granules are small, averaging 2–4 μm.

Barley

Barley (*Hordeum vulgare* L.), like rice and oats, is harvested with the hull (or husk) intact. The tightly adhering hull consists of the lemma and palea. Unlike rice and oats, in which the hull is relative loose and can be separated, the hull of barley is cemented to the pericarp and difficult to separate. However, hull-less barleys, which lose the hull during threshing, have been developed. The caryopsis is composed of pericarp, seed coat, nucellar epidermis, germ, and endosperm (Fig. 1.21). The aleurone cells in barley are composed of two to three layers of cells (Fig. 1.22). Medium-sized kernels weigh about 35 mg. The aleurone of some cultivars is blue, whereas, in others, it is colorless. The endosperm cells are packed with starch embedded in a protein matrix (Fig. 1.23). Like wheat and rye starch, barley starch has both large lenticular granules and small spherical granules.

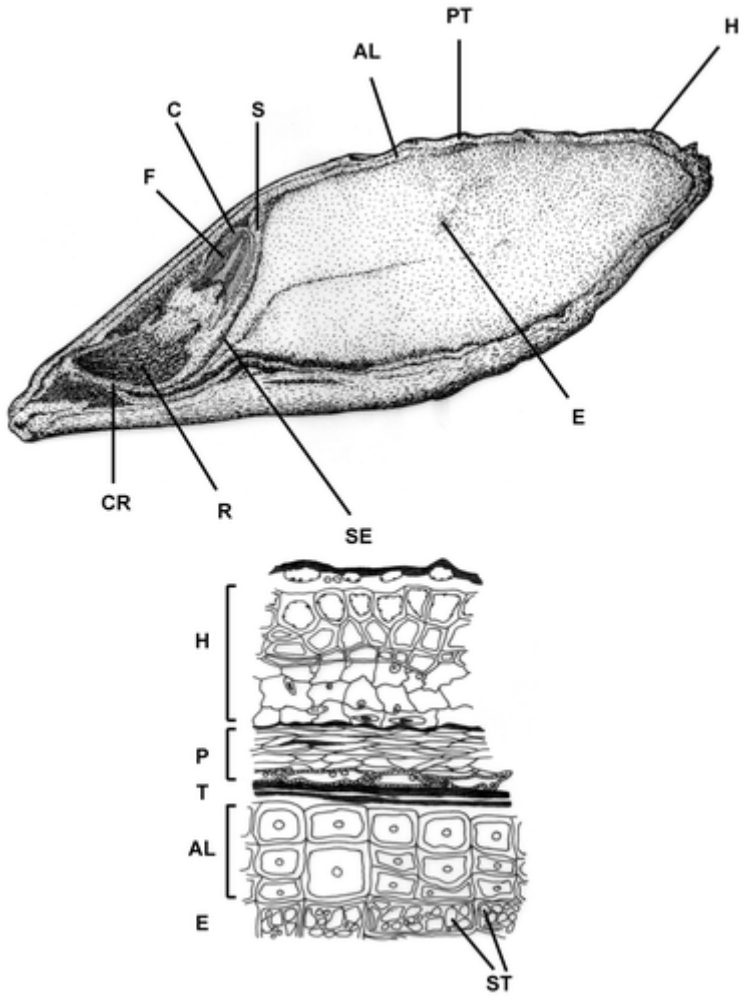
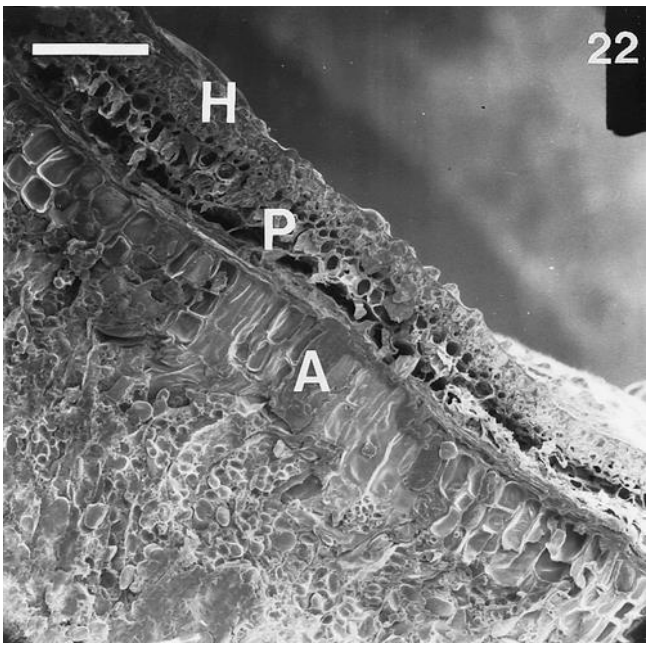


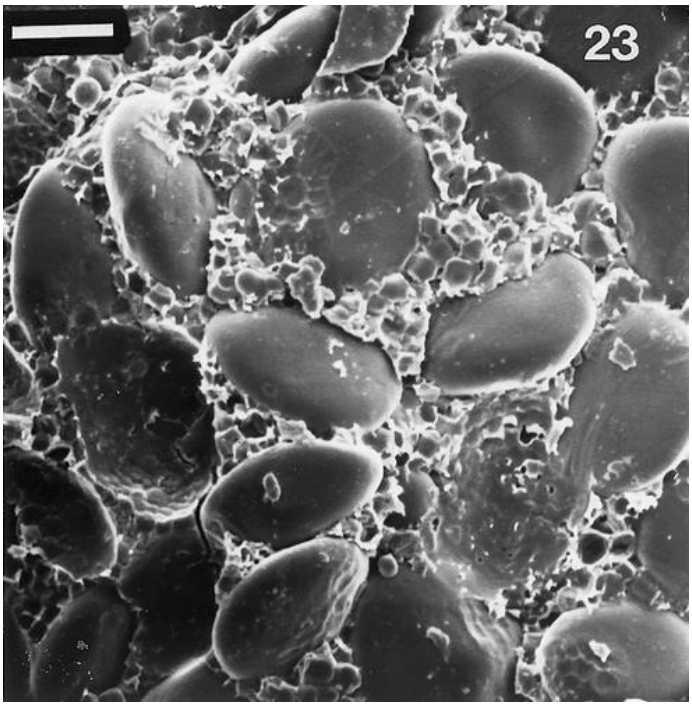
Fig. 1.21. Longitudinal section of a barley kernel **(top)** and outer layers **(bottom). Top:** kernel with indication of coleoptiles (C), foliar shoot (F), coleorhizae (CR), root (R), scutellum (S), scutellar epithelial cells (SE), husk (H), pericarp-testa (PT), aleurone layer (AL), and starchy endosperm (E). (Courtesy I. Celus and L. Van den Ende) **Bottom:** outer layers of the kernel with indication of husk (H), pericarp (P), testa (T), aleurone cells (AL), starchy endosperm (E), and starch granules (ST). (Adapted from Palmer and Bathgate 1976)



Figs. 1.22 and 1.23. Scanning electron micrographs of cross sections of a barley kernel.

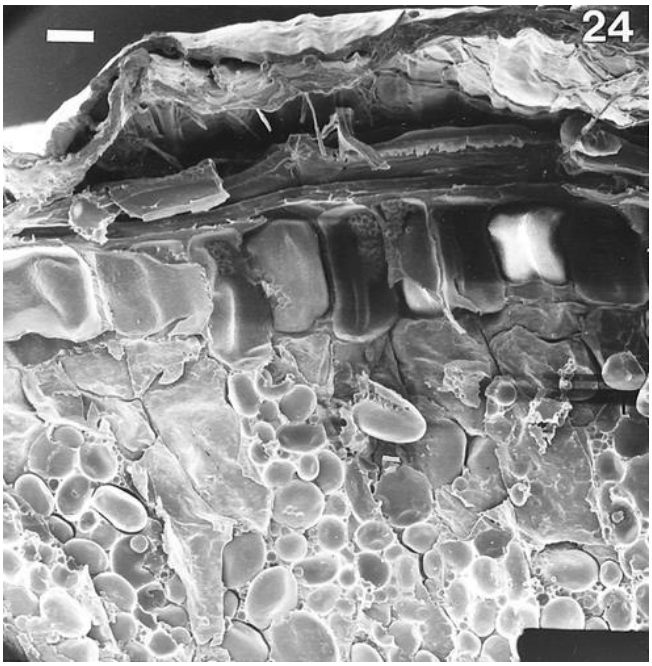
1.22. Hull (H), pericarp (P), and multilayered aleurone cells (A). Bar is 100 µm.

1.23. Contents of an endosperm cell. Bar is 10 µm.



Rye

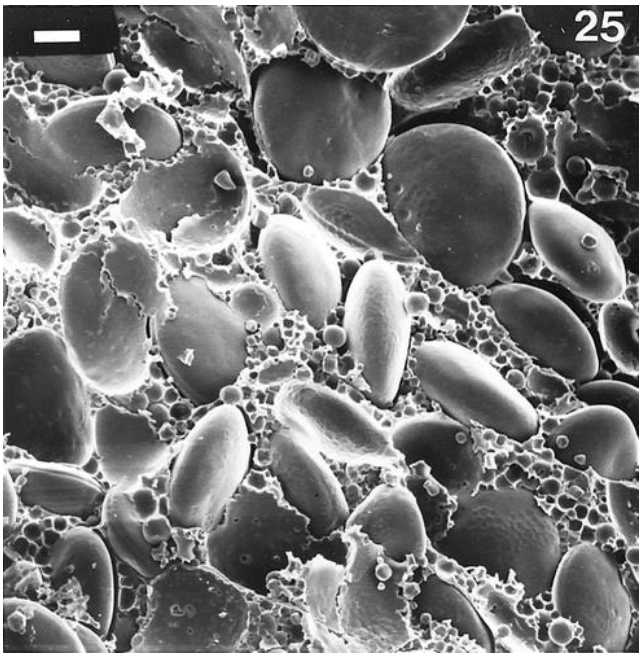
The rye (*Secale cereale* L.) kernel is a caryopsis 6–8 mm in length and 2–3 mm in width. The kernel threshes free of glumes, has no hull, and, like wheat, possesses a ventral crease. Its color is grayish yellow. Like the other cereals, rye has a caryopsis consisting of pericarp, seed coat, nucellar epidermis, germ, and endosperm. The endosperm is surrounded by a single layer of aleurone cells. Scanning electron micrographs of the outer areas of the grain (Fig. 1.24) and of the endosperm (Fig. 1.25) show that they are similar to those of wheat. The starch in the endosperm cells is embedded in a protein matrix. Like wheat and barley starches, rye starch has large lenticular and small spherical granules. Rye flour generally has much higher contents of arabinoxylan cell wall constituents than wheat flour.



Figs. 1.24 and 1.25. Scanning electron micrographs of cross sections of a rye kernel.

1.24. Outer part of the kernel. Bar is 20 μm.

1.25. Contents of an endosperm cell. Bar is 10 μm.



Triticale

Triticale (*Triticale hexaploide* Lart.) is a cereal produced by crossing wheat (*Triticum*) and rye (*Secale*). In general morphology, the grain closely resembles its parent species. The caryopsis threshes free of glumes, is generally larger than the wheat caryopsis (10–12 mm in length and 3 mm in width), and weighs about 40 mg. It consists of a germ attached to an endosperm, which has aleurone as the outer layer. Outside the aleurone are the seed coat, a pericarp, and the remains of the nucellar epidermis. Thus, triticale closely resembles the other cereal grains in structure. The kernel has a crease that extends its full length. The yellowish brown grain is characterized by folds or ripples on the outer pericarp, apparently caused by shriveling of the grain.

Grain shriveling is a major problem with triticale. It leads to low test weight, poor appearance, and unsatisfactory milling performance. The aleurone layer in triticale is more irregular in shape than is that in wheat. The cells vary in size, and the cell walls tend to vary in thickness. In shriveled grain, the aleurone cells are badly distorted, and lesions have been noted in which complete sections of aleurone and associated endosperm cells are missing.

Oats

Oats (*Avena sativa* L.), like barley and rice, is harvested with the caryopsis enclosed in a floral envelope, the hull. The hull represents about 25% of the total weight. The caryopsis itself is called a "groat." The oat groat is similar in appearance to kernels of wheat or rye except that it is covered with numerous trichomes (hairlike protuberances, Fig. 1.26). The germ extends about one-third the length of the groat, being larger and narrower than the germ of wheat. The oat groat consists of pericarp, seed coat, nucellar epidermis, germ, and endosperm. As with all cereals, the aleurone makes up the outer layer of the endosperm. Oat groats have higher fat and protein contents than do other cereals. They are also a good source of several enzymes. The most troublesome of these is lipase, which is very active. Unless the lipase is denatured, milled products have a very short shelf life because of the production and subsequent oxidation of fatty acids.

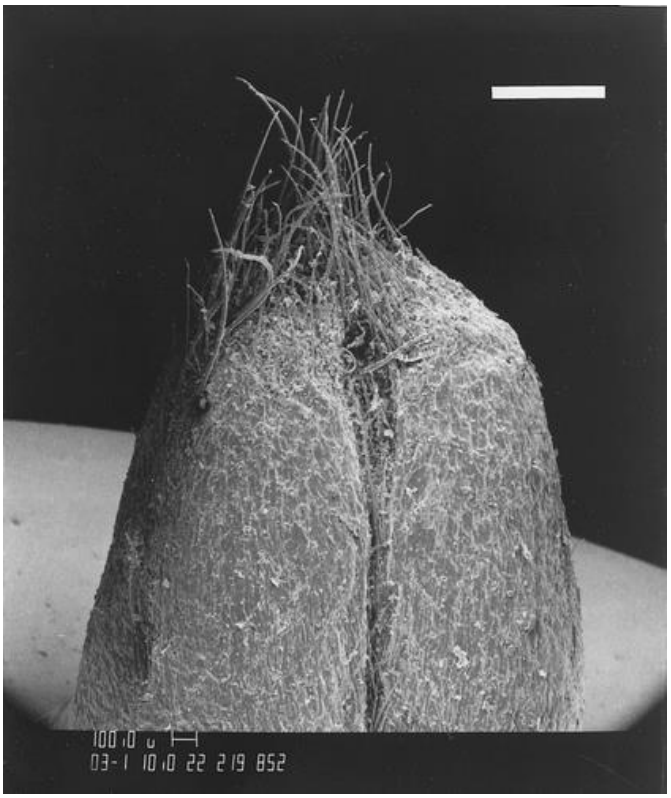
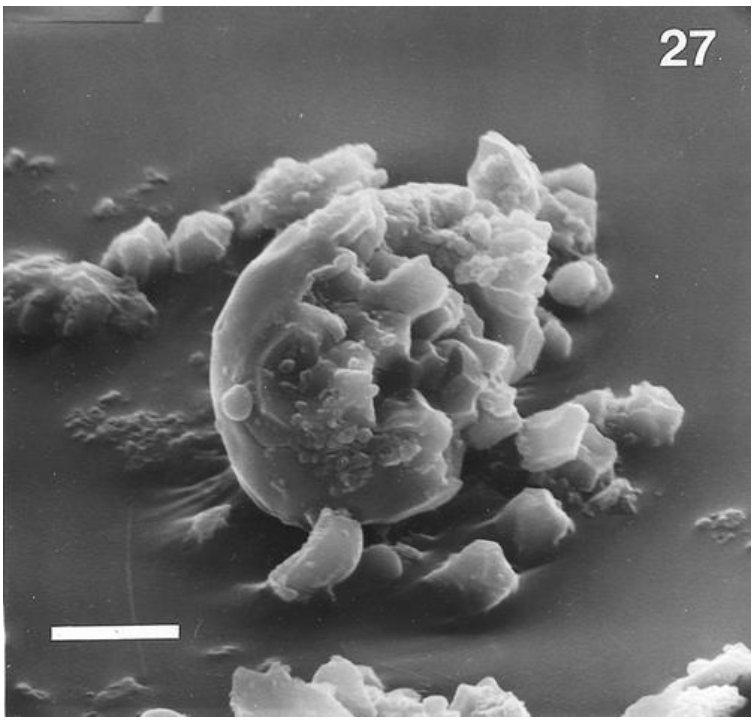


Fig. 1.26. Scanning electron micrograph of the outer surface of an oat groat, showing the hairlike protuberances, or trichomes. Bar is 500 μm.

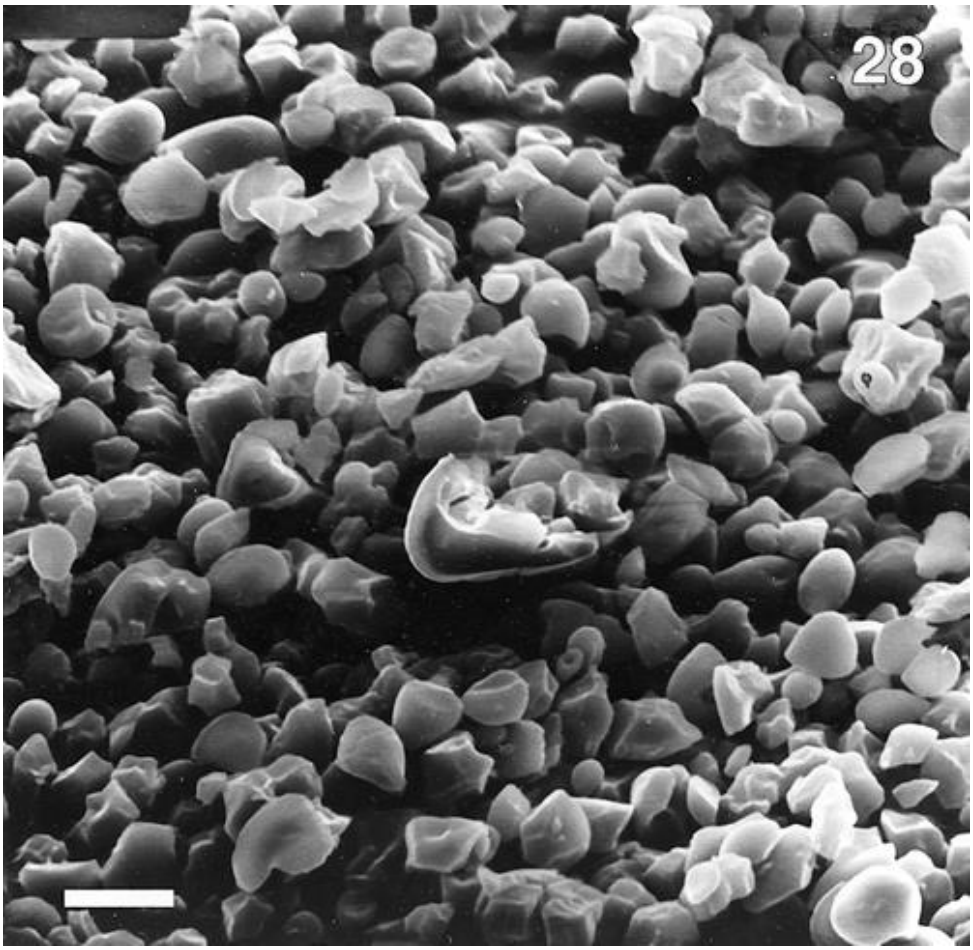
The starch is present as large compound granules that are smooth and irregular in shape (Fig. 1.27). Each compound granule is made up of many small individual granules. The small granules are polygonal in shape and range in size from 3 to 10 μm (Fig. 1.28).



Figs. 1.27 and 1.28. Scanning electron micrographs of oat starch. Each bar is 10 μm.

1.27. A partially intact compound granule.

1.28. Isolated starch granules resulting from the disintegration of compound granules during oat starch isolation.



Sorghum

THE SORGHUM KERNEL

The kernels of sorghum (*Sorghum bicolor* (L.) Moench) thresh free of hulls or glumes. They are generally spherical, range in weight from 20 to 30 mg, and may be bronze, white, red, yellow, or brown. Figure 1.29 shows the various parts of the sorghum kernel. A hand-dissected kernel was found to consist of 7.9% pericarp (presumably pericarp plus seed coat), 9.8% germ, and 82.3% endosperm. However, other samples would be expected to vary in composition. Scanning electron micrographs of the outer layers of sorghum kernels reveal a thick pericarp, in most varieties, consisting of three layers: the epicarp, the mesocarp, and the endocarp (Fig. 1.30). Unlike other cereals, some sorghum varieties contain starch granules in the pericarp. These granules, ranging in size from 1 to 4 μm, are located in the mesocarp.

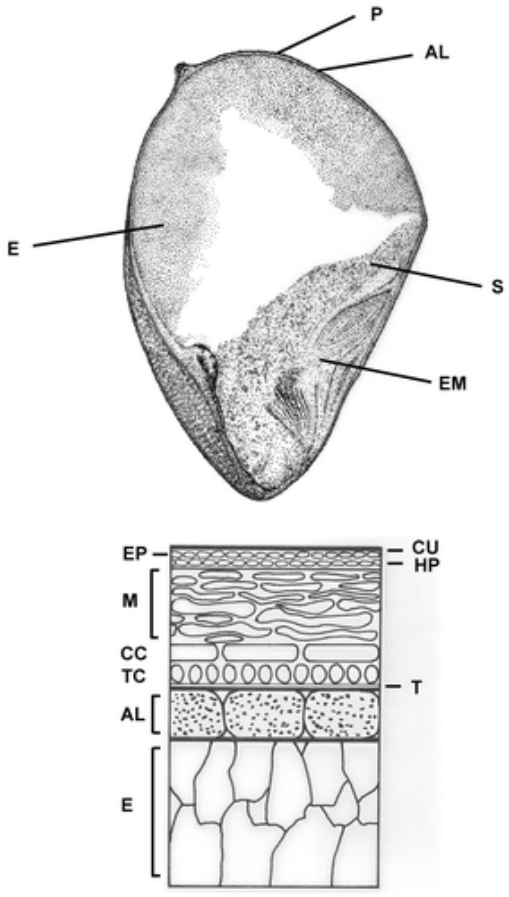
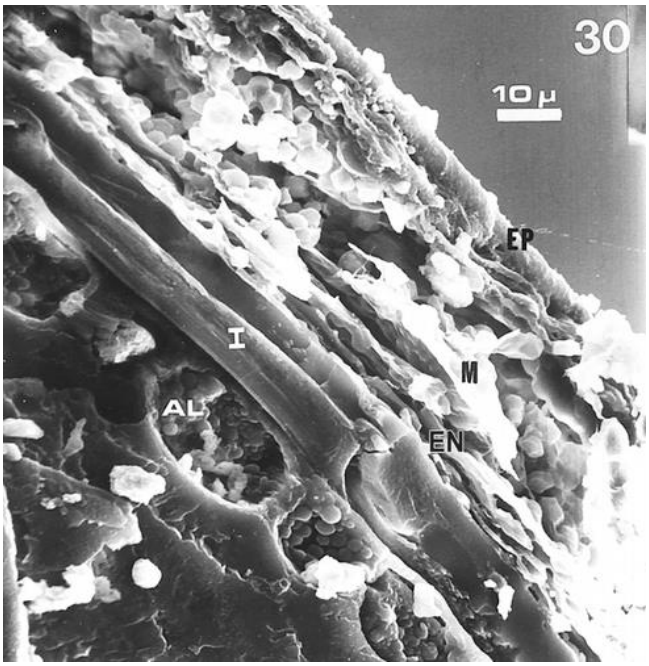


Fig. 1.29. Longitudinal section of a sorghum kernel **(top)** and outer layers **(bottom). Top:** kernel with indication of pericarp (P), aleurone (AL), starchy endosperm (E), embryo (EM), and scutellum (S). (Courtesy I. Celus and L. Van den Ende). **Bottom:** outer layers with indication of cutin (CU), epicarp (EP), hypodermis (HP), mesocarp (M), cross cells (CC), tube cells (TC), testa (T), aleurone layer (AL), and peripheral endosperm (E). (Adapted from Earp et al 2004)



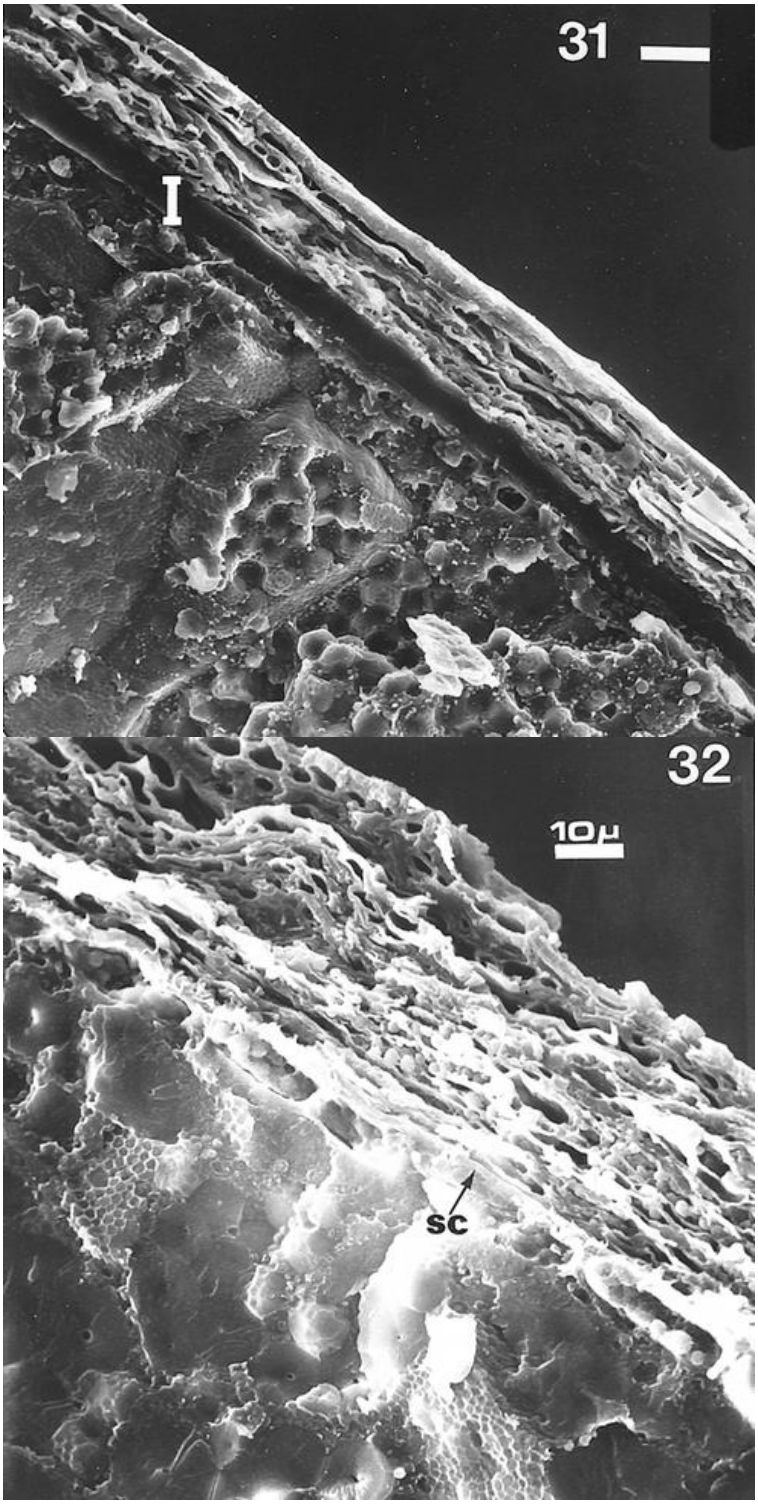
Figs. 1.30–1.33. Scanning electron micrographs of cross sections of a sorghum kernel. (Figs. 1.30, 1.32, and 1.33 reprinted from Hoseney et al 1974)

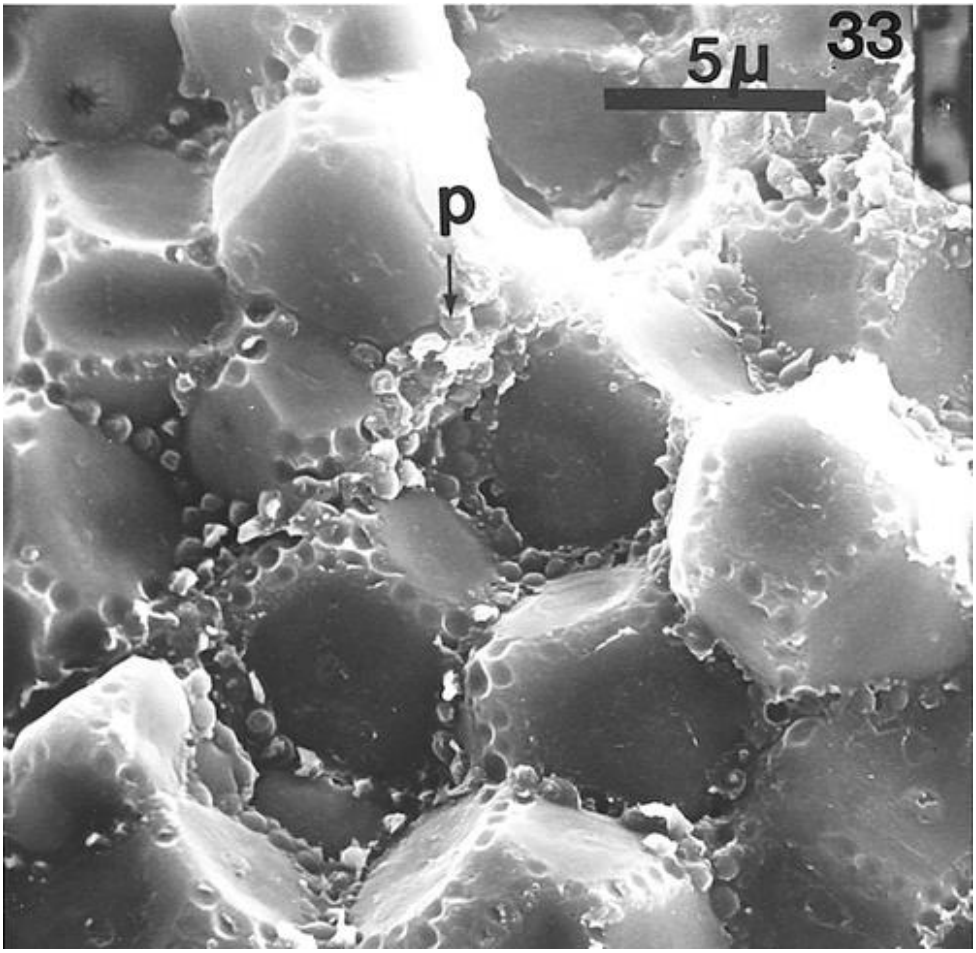
1.30. The outer edge of the kernel, showing the epicarp (EP), mesocarp (M), endocarp (EN), inner integument (I), and aleurone cells (AL). Note the small starch granules in the mesocarp. Bar is 10 µm.

1.31. The outer edge, showing the presence of a thick, pigmented inner integument (I). Bar is 20 µm.

1.32. A sorghum kernel containing no inner integument. The seed coat (SC), or testa, is shown. Bar is 10 µm.

1.33. The vitreous part of the kernel, showing the content of an endosperm cell. Note the lack of air spaces, the polygonal starch granules, and protein bodies (P). Bar is 5 µm.





The mature sorghum caryopsis may (Fig. 1.31) or may not (Fig. 1.32) have a pigmented inner integument, its presence or absence being under genetic control. The inner integument is often erroneously called a "testa layer." The testa is the seed coat, which is joined to the outer edge of the inner integument. While all mature sorghum seeds have a testa (seed coat), certain cultivars lack a pigmented inner integument. The pigmented inner integument often contains high levels of proanthocyanidins, which are also referred to as "condensed tannins." Cultivars that have a large pigmented inner integument are called "bird-resistant sorghums." Birds do not like the bitter and astringent tannins. However, if no other feed is available, they will eat the bird-resistant types. As in other cereals, the aleurone cells are the outer layer of the endosperm. In the starchy endosperm, cells containing high concentrations of protein and few starch granules are found just beneath the aleurone layer. Much of the protein is in the form of protein bodies, which are 2–3 μm in diameter (Fig. 1.33).

SORGHUM TEXTURE AND VISUAL APPEARANCE

Sorghum kernels, like maize kernels, contain both translucent and opaque endosperm within an individual kernel. The opaque endosperm has large intergranular air spaces (Fig. 1.34), which are responsible for its opaque appearance. In general, grain sorghum has not been selected or bred as extensively as other cereals. Thus, it is not surprising that there is much diversity in the size, texture, and shape of sorghum kernels.

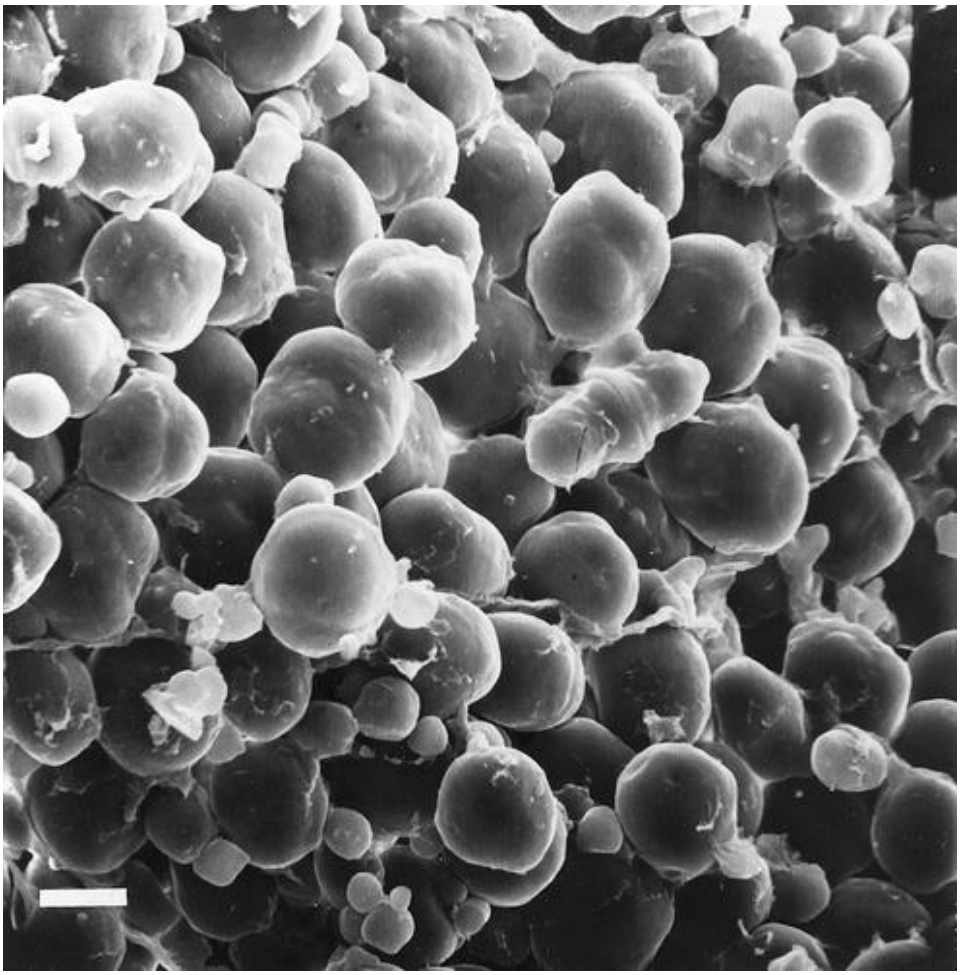


Fig. 1.34. Scanning electron micrograph of a cross section of the opaque part of a sorghum kernel. Note the air spaces and more-or-less spherical starch granules. Bar is 10 µm. (Reprinted from Hoseney et al 1981)

The terms *hard* and *soft* have been used to designate the vitreous and opaque areas of sorghum endosperm as well as the general appearance of kernels. However, as discussed previously for wheat, the factors determining vitreousness and physical hardness are different. Therefore, some kernels may appear vitreous but be classified soft by objective measurements. Visual determination of hardness or softness in sorghum kernels is based on the assumption that hardness and vitreousness are the same. This appears to be an unwarranted assumption.

Pearl Millet

Pearl millet (*Pennisetum glaucum* (L.) R. Br.) consists of small (average about 8.9 mg), tear-shaped kernels that thresh clean of their hull. They vary in color, with slate gray being most common, although yellow, white, and brown varieties are also known. The caryopsis is similar to those of the other cereals. Millet pericarp does not contain starch, as the pericarp of sorghum does, nor does pearl millet contain a pigmented inner integument. The germ in pearl millet is large (17%) in proportion to the rest of the kernel (Fig. 1.35). Its endosperm has both translucent and opaque endosperm, as do those of sorghum and maize. The opaque endosperm contains many air spaces and spherical starch granules (Fig. 1.36). The translucent (vitreous) endosperm (Fig. 1.37) is void of air spaces and contains polygonal starch granules embedded in a protein matrix. The matrix also contains protein bodies ranging in size from 0.3 to 4 µm. The protein bodies have a well-defined internal structure, as shown by the pattern of electron scattering in transmission electron micrographs.

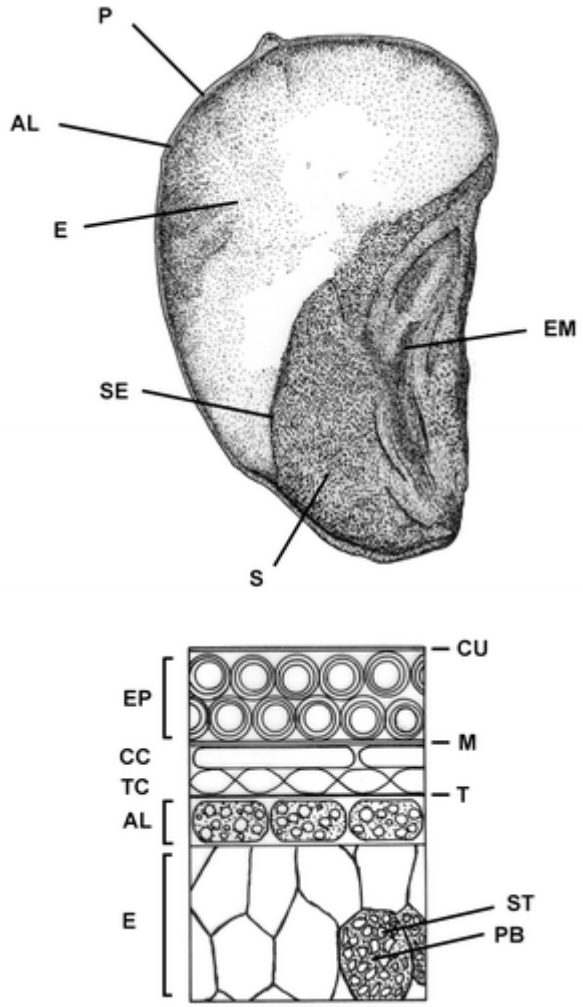
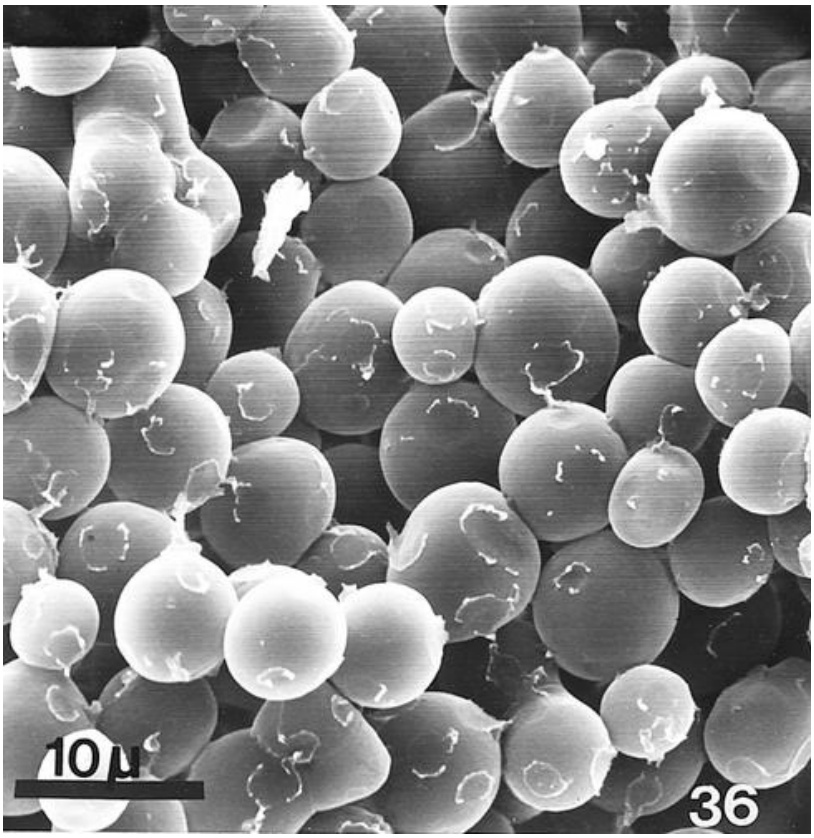


Fig. 1.35. Longitudinal section of a pearl millet kernel **(top)** and outer layers **(bottom).**

Top: kernel with indication of pericarp (P), aleurone (AL), starchy endosperm (E), scutellar epithelial cells (SE), scutellum (S), and embryo (EM). (Courtesy I. Celus and L. Van den Ende)

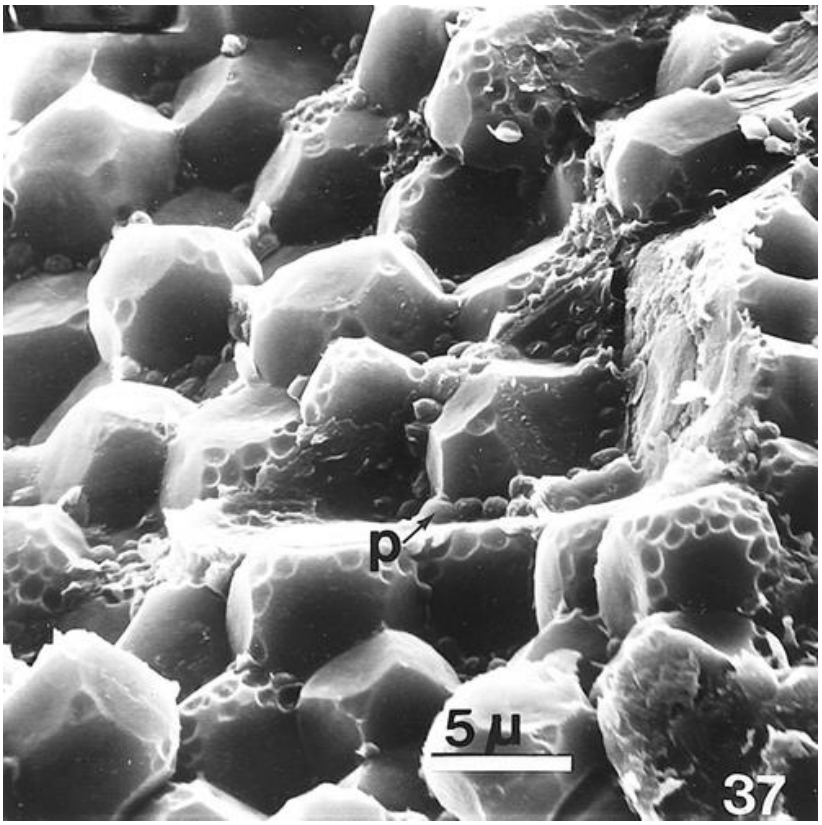
Bottom: outer layers with indication of cutin (CU), epicarp (EP), mesocarp (M), cross cells (CC), tube cells (TC), testa (T), aleurone layer (AL), peripheral endosperm (E), starch granules (ST), and protein bodies (PB). Also indicated are protein bodies and starch granules within one endosperm cell. (Adapted from McDonough and Rooney 1989)



Figs. 1.36 and 1.37. Scanning electron micrograph of a cross section of a pearl millet kernel. (Reprinted from Badi et al 1976)

1.36. The opaque part. Note the air spaces and the spherical starch granules.

1.37. The vitreous part. Note the lack of air space, the polygonal starch granules, and the protein bodies (P).



CHAPTER 2: Starch

Starches from Cereals

In cereals and other higher plants, starch granules are formed in amyloplasts. In the cereals with simple starch granules (wheat, maize, rye, barley, sorghum, and millets), each amyloplast contains one granule. In rice and oats, which have compound starch granules, many granules are found in each amyloplast. The starches from different cereals vary widely in size and shape (Table 2.1).

TABLE 2.1
Properties of Certain Starches[a]

Source of Starch	Gelatinization Temperature Range (°C)	Granule Shape	Granule Size (μm)
Barley	51–60	Round Elliptical	20–25 2–6
Triticale	55–62	Round	19
Wheat	51–60	Lenticular Round	20–35 2–10
Rye	51–60	Round Lenticular	28 28
Oats[b]	53–59	Polyhedral	3–10
Maize	62–72	Round Polyhedral	 15
Waxy maize	63–72	Round	15
Sorghum	68–78	Round	25
Rice[b]	68–78	Polygonal	3–8

[a] Adapted from Lineback (1984).
[b] Data are for isolated individual granules and not for compound granules.

Wheat, barley, and rye all have two types and sizes of starch granules, as shown inFigure 2.1 for wheat starch. The large, lenticular (lens-shaped) granules are 25–40 μm in the long dimension; the small, spherical granules are 5–10 μm in diameter.Figure 2.2 shows a scanning electron micrograph of isolated wheat starch granules. In barley, the lenticular granules are formed during the first 15 days after pollination. The small granules, representing about 88% of the total number of granules, appear 18–30 days after pollination. Amyloplasts in barley and wheat each initially form a large, lenticular starch granule. Later, they form evaginations (outgrowths) in which small granules are formed. These much smaller amyloplasts separate from the mother plastid by constriction.

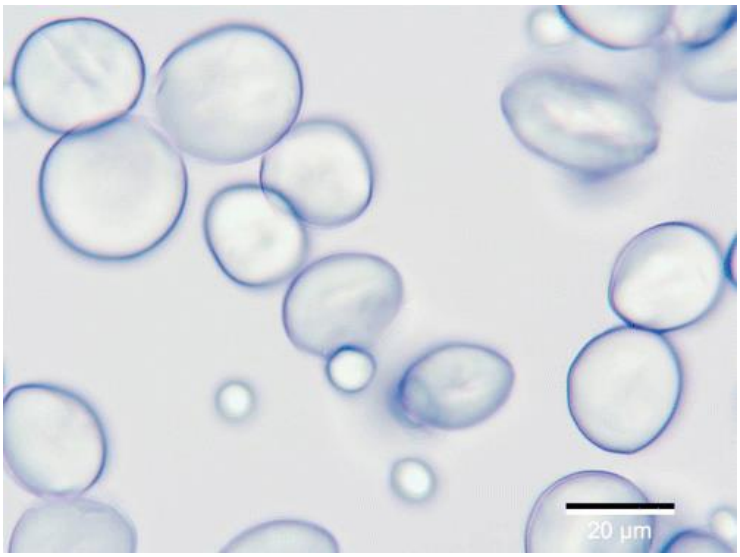


Fig. 2.1. Light photomicrograph of wheat starch granules, showing large lenticular and small spherical granules. Bar is 20 µm. (Courtesy S. Gomand)

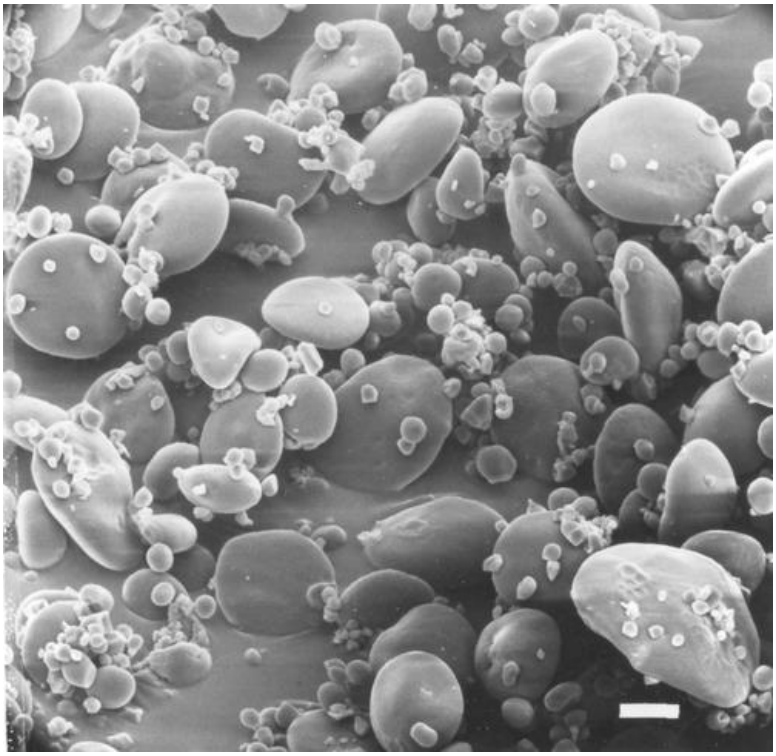


Fig. 2.2. Scanning electron photomicrograph of isolated wheat starch granules. Bar is 10 µm.

The starch granules of maize and sorghum are similar to each other in size and shape. They average about 20 µm in diameter, as shown in a light micrograph of maize starch (Fig. 2.3), and their shape varies from polygonal to almost spherical, also shown by scanning electron microscopy (Fig. 2.4). Starch granules in cells near the outside of the kernel (i.e., in the vitreous endosperm) tend to be polygonal (Fig. 1.14), whereas those in cells from the center of the kernel (in the opaque endosperm) tend to be spherical (see Figs. 1.13 and 1.15). As far as we know, the properties of the differently shaped granules are the same. Pearl millet starch is also similar to that of maize and sorghum, except that its granules are smaller, averaging about 12 µm in diameter (Fig. 2.5).

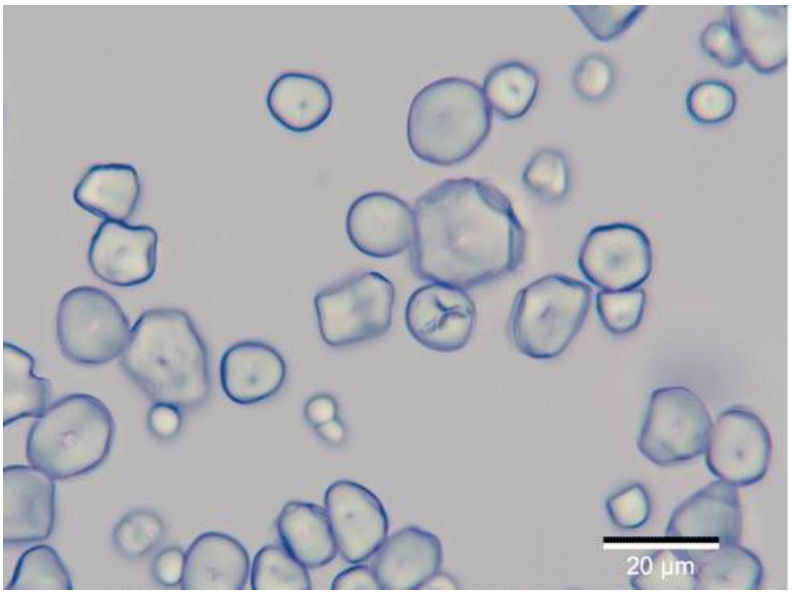


Fig. 2.3. Light photomicrograph of isolated maize starch granules. Bar is 20 µm. (Courtesy S. Gomand)

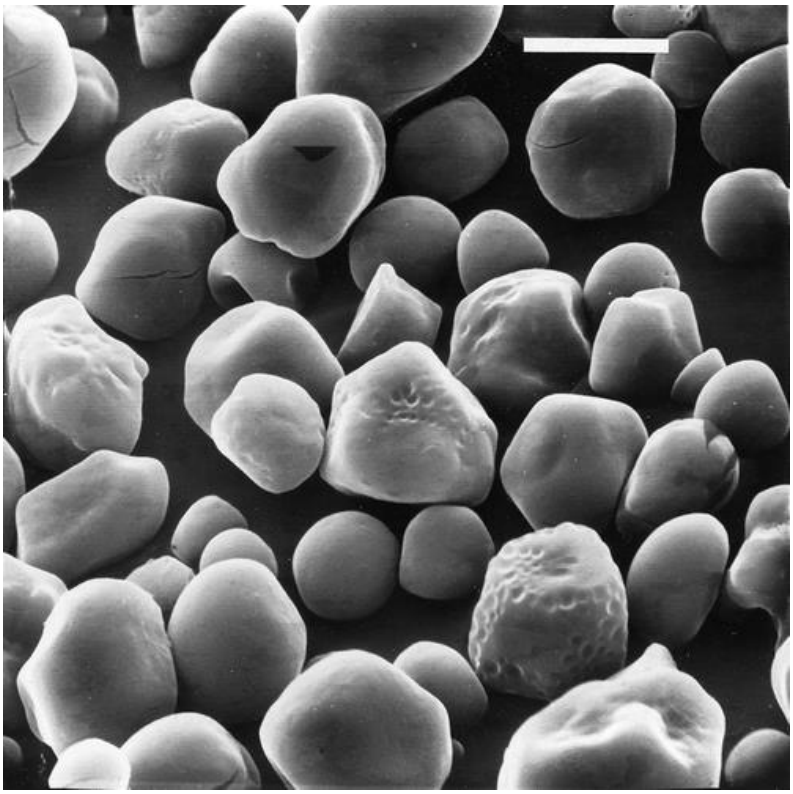


Fig. 2.4. Scanning electron photomicrograph of isolated maize starch granules. Bar is 10 µm. (Reprinted from Robutti et al 1974)

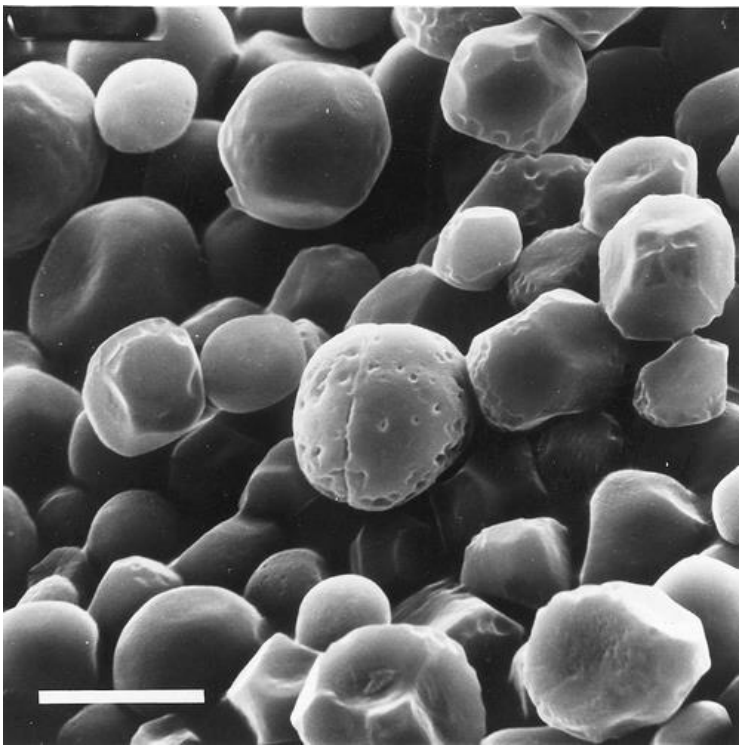


Fig. 2.5. Scanning electron photomicrograph of isolated pearl millet starch granules. Bar is 5 μm. (Reprinted from Hoseney et al 1981)

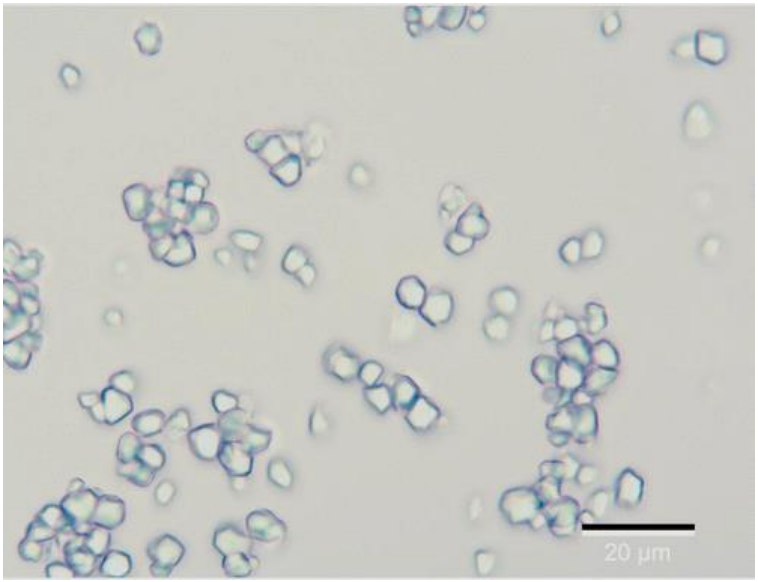


Fig. 2.6. Light photomicrograph of isolated rice starch granules. Bar is 20 μm. (Courtesy S. Gomand)

Individual starch granules of rice and oats are similar to each other in that they are small (2–5 μm), are polygonal in shape, and occur in the grain as compound granules. Figure 2.6 shows isolated individual rice starch granules. The compound granules (see Figs. 1.19 and 1.27), however, are quite different. While those of oats are large and spherical, those of rice are smaller and polygonal.

Composition of Granular Starch

Most common starches, apart from a number of minor constituents, consist primarily (about 98%) of polymeric carbohydrate material, built up of α-D-glucopyranosyl units. Each individual starch molecule has only one hemiacetal group, more commonly referred to as the "reducing end," which confers reducing power to the molecule. The reducing power of many carbohydrate molecules is a basis for their quantitative estimation. The monomers are glycosidically linked to either position 4 or position 6 of the neighboring glucose (Fig. 2.7).

Linkages have the α orientation, and α-1,4 and α-1,6 bonds are customary said to result in linear and branched structures, respectively.

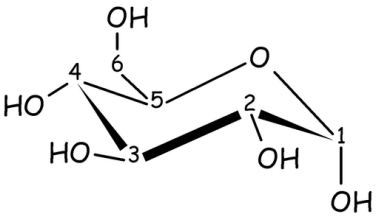


Fig. 2.7. Depiction of an α-D-glucopyranose unit, showing the numbering of its carbon atoms. (Courtesy M. Verswyvel)

Two polymers can be discerned, i.e., amylose and amylopectin.

AMYLOSE

Amylose is generally thought of as a linear polymer of α-D-glucose linked by α-1,4 bonds. Its molecular weight varies between about 80,000 and about 1,000,000 (500–6,000 anhydroglucose units). The molecular weight varies not only among species of plants but also within a species and depends upon the stage of grain maturity. Although the polymer is generally assumed to be linear, this appears to be true for only part of the amylose. Indeed, 25–55% of the molecules have secondary chains attached through occasional α-1,6 branch points. When, in excess water, amylose is leached from starch by being heated slightly above the starch's gelatinization temperature (see below), the amylose solubilized is essentially linear. As the leaching temperature is increased, amylose of higher molecular weight and more branching is extracted. Both enzyme and viscosity studies have indicated that the branches are of long-chain length, with the side chains containing hundreds of glucose residues (Fig. 2.8). However, the branches on amylose are so long and so few that, in many ways, the molecule acts as an unbranched entity.

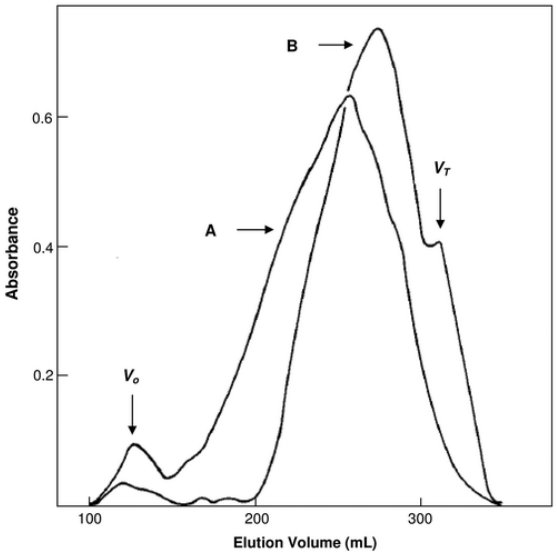


Fig. 2.8. Elution profile of amylose (A) and debranched amylose (B) from Sepharose CL-2B, with indication of the column's void (V_o) and total (V_T) volumes. (Adapted from Ghiasi et al 1982b)

The long, linear nature of amylose gives it unique properties, such as its ability to form complexes with iodine, organic alcohols, or fatty acids (Fig. 2.9). Such complexes are called "clathrates" or "helical inclusion compounds." The well-known blue color given by a mixture of iodine and starch is thought to be due to polyiodide ions in the central core of the amylose helix. Nuclear magnetic resonance studies have revealed that amylose-lipid complexes also occur in native cereal starches, and free lipids occurring in the cereal starch may form additional amylose-lipid complexes during starch gelatinization (see below).

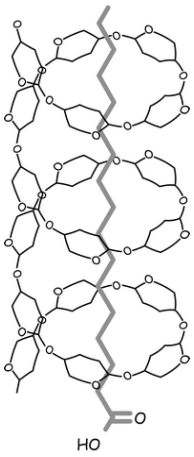


Fig. 2.9. Depiction of an organic acid forming a clathrate, i.e., an inclusion complex, with amylose. (Courtesy M. Verswyvel)

AMYLOPECTIN

Like amylose, amylopectin is composed of α-D-glucose linked primarily by α-1,4 bonds. Amylopectin is branched to a much greater extent than is amylose, with 4–5% of the glycosidic bonds being α-1,6 bonds. This level of branching means that the average unit chain in amylopectin is only 20–25 glucose units long. The molecular weight of amylopectin has been reported to be as high as 10^8. It is truly a huge molecule, one of the largest found in nature. If the above figure for molecular weight is correct, the molecule would have more than 617,000 glucose residues ($10^8 \div 162$; 162 is the molecular weight of an anhydroglucose unit incorporated into the structure) or more than 30,000 chains with an average degree of polymerization (DP, i.e., number of glucose units per chain) of 20.

The amylopectin molecule has three types of chains (Fig. 2.10). A chains are composed of glucose linked α-1,4; B chains are composed of glucose linked α-1,4 and α-1,6; and C chains are made up of glucose with α-1,4 and α-1,6 linkages plus the reducing group. Thus, A chains do not carry branches, and B chains do. The C chain is branched and also has the only reducing group (unbound C-1) in the molecule. Based on the mutual organization of A and B chains, a laminated, a herringbone, and a randomly branched structural model (further referred to as Meyer's model) were originally proposed for amylopectin. Over time, more insight into the exact structure of amylopectin has been gained by use of a series of enzymes that partially degrade the molecule in very specific ways.

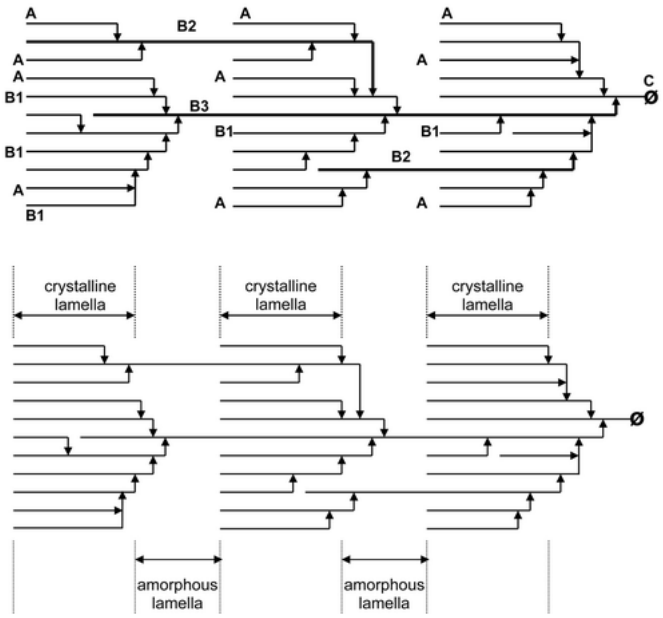


Fig. 2.10. Cluster structure of amylopectin, with indication of A, B, and C chains and illustration of crystalline and amorphous lamellae. The solid lines represent α-1,4-linked glucose units; arrows indicate α-1,6 linkages. The only chain carrying a reducing end (ø) is the C chain. The external chains are A chains. B1 chains expand

over one cluster only, while B2 and B3 chains expand over two and three clusters, respectively. (Courtesy G. Vandeputte and H. Goesaert; adapted from Hizukuri 1986)

The first enzyme is β-amylase. Its Enzyme Convention (EC) classification number is EC 3.2.1.2. It is an exoacting enzyme, which attacks starch chains from their nonreducing end, and it breaks every second α-1,4 bond. β-Amylase cannot pass a branch point (an α-1,6 bond) on the starch chain. Thus, it reduces a linear chain to maltose (two glucose molecules linked α-1,4) and leaves residues of two or three glucose residues, depending upon whether the original chain had an even or odd number of glucose residues outside the branch point (Fig. 2.11). Because of its high degree of branching, amylopectin is degraded only about 55% by β-amylase. The products are maltose and a large residue, the β-limit dextrin, which is enriched in α-1,6 bonds. In agreement with the above, it has short A chains with either two or three glucose units and still has a very large molecular weight (about 10^4).

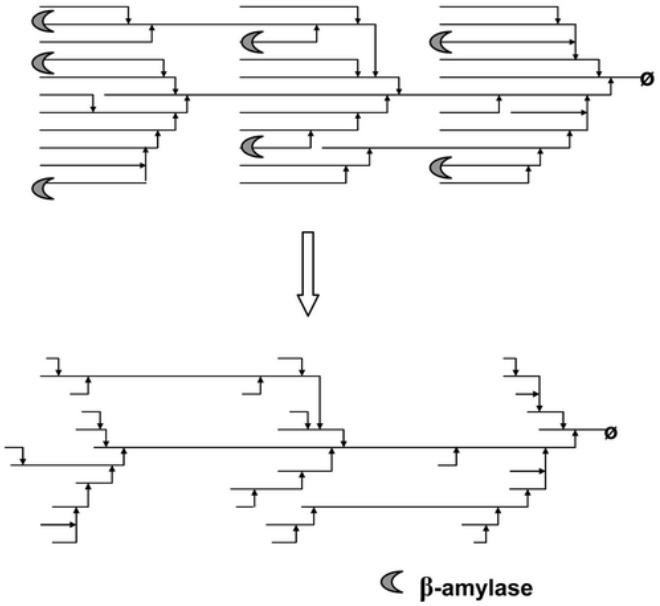


Fig. 2.11. Action of β-amylase on amylopectin, producing a β-limit dextrin. The solid lines represent a-1,4-linked glucose units; arrows indicate α-1,6 linkages. Both amylopectin and β-limit dextrin molecules have only one reducing end (0). Maltose molecules released by the enzyme action are not shown. (Courtesy A. Bijttebier)

Another enzyme that has been helpful in determining the structure of amylopectin is the debranching enzyme pullulanase (EC 3.2.1.41). It hydrolyzes the α-1,6 bonds but not the α-1,4 bonds. Thus, treating amylopectin with this enzyme releases all linear A and B chains, each of which now has a reducing end and hence possesses reducing power. By determining the reducing power per unit weight, the average chain length can be calculated. Amylopectin has an average chain length of about 25. The size distribution of the chains can be studied by gel permeation chromatography. The distribution is bimodal, with most (by weight) of the chains being about 19 glucose units in length and the others about 60 glucose units.

To determine the ratio of A to B chains in amylopectin, one can produce the β-limit dextrin, debranch it with pullulanase, and subject it to gel permeation chromatography to separate the component polymers. The sum of the maltose and maltotriose molecules gives the number of A chains. The number of larger molecules gives the number of B chains. The ratio of the reducing power of the (outer) small chains (maltose and maltotriose) to that of the large chains (larger than maltotriose) is the A to B chain ratio (each reducing group comes from one chain).

Approaches such as outlined here have shown that the ratio of A to B chains ranges from 1.0:1 to 1.5:1, consistent with Meyer's structure. However, complete debranching of amylopectin yielded chains with a polymodal chain length distribution, suggesting that the branching pattern is not completely random. Extensive amylolysis of waxy rice and maize amylopectins furthermore showed that significant numbers of amylopectin branch points were retained in single-limit dextrins. In accordance with these observations, the Meyer model was abandoned in favor of the cluster model (Fig. 2.10), which is widely accepted today. Its name indicates that the branching points occur in clusters.

AMYLOSE AND AMYLOPECTIN CONTENTS IN STARCHES

Most common starches, apart from several minor constituents, contain the two distinct polymer fractions amylose and amylopectin, with clear differences in molecular weight and in structural organization. For regular starches, amylose typically makes up 18–33% of the carbohydrate moiety. With the exception of rice starches, the varietal variation of amylose content in regular starches of a single plant species is quite limited. In maize, sorghum, rice, barley, and wheat, mutants that have starches with essentially 100% amylopectin have been discovered. Such starches are called "waxy starches," and the cereals that contain them are called waxy maize, waxy barley, etc. Mutants that have starches with unusually high levels of amylose are also known. Certain lines of maize have starch containing 70% amylose. Such cereals are known as "amylotypes."

If one were to consider a hypothetical starch containing 25% amylose and 75% amylopectin, one could, at first glance, be inclined to consider amylopectin much more important for the properties of this particular starch than amylose. However, that is not necessarily the case, as shown by the following reasoning. Assuming that each of the amylose molecules in the hypothetical starch consists of 3,000 glucose units, while those of amylopectin consist of 300,000 glucose units, one sees that the molar ratio of amylose to amylopectin in the starch is

$$\frac{0.25 / 3{,}000}{0.75 / 300{,}000} = \frac{0.0000833}{0.0000025} = 33.333.$$

Thus, on a molar basis there are roughly 33 times as many relatively mobile amylose molecules as relatively immobile amylopectin molecules.

MINOR CONSTITUENTS

Although starch contains several minor constituents, these occur at such low levels that it can be debated whether they are trace constituents of the starch or contaminants not completely removed during the isolation process. Even though these minor constituents are present only in small concentrations in the starch, they can and do affect the starch properties.

Generally, the level of lipids in cereal starch is between 0.5 and 1.0%. The lipids associated with starch are generally polar and hence are best extracted with polar solvents such as methanol-water. In some cases, even more polar solvents are necessary to extract all the lipids. In cereal starches, lipids are prevalent inside the starch granules. They consist mainly of lysophospholipids and free fatty acids and are present in proportions positively correlated with amylose content. Irrespective of the lipid class, the most abundant fatty acids in cereal starches are linoleic and palmitic acids. In wheat, barley, rye, and triticale starches, lysophospholipids are present almost exclusively, while maize and rice starches contain significant proportions of free fatty acids. The lipids in starch can occur either free or as amylose-lipid complexes (see below). In contrast, noncereal starches contain essentially no lipids.

Phosphorus is the most abundant mineral in starch. Normal starch contains lysophospholipids (see above) and variable levels of esterified phosphate. The monoesterified phosphate groups are found exclusively on amylopectin, with preference for the longer amylopectin branches. Potato amylopectin contains 200–1,000 ppm of monoesterified phosphorus, compared to 40–150 ppm for root starches and 0–20 ppm for cereal starches.

All starches also contain low levels of nitrogen (<0.05%). Part of this is from the lipids, and the remainder is mostly proteinaceous. A considerable part of the nitrogen stems from granule-bound starch synthase, a starch-synthesizing enzyme associated with amylose. The absence of this enzyme in waxy starches results in intrinsically lower protein contents.

FRACTIONATION OF STARCH INTO AMYLOSE AND AMYLOPECTIN

Two general techniques are used to fractionate (separate) starch into amylose and amylopectin. In the first, amylose is selectively leached from granules heated to slightly above the gelatinization temperature (see below). A higher leaching temperature solubilizes amylopectin in addition to amylose, and thus further purification is required. The fractionation achieved by leaching is not quantitative.

In the second approach, granular starch is completely dispersed before the amylose and amylopectin are separated. Cereal starches are particularly difficult to disperse completely. Because several hours at autoclave temperatures (130°C) are required, care must be taken that the starches are not degraded. Preventive measures include starch defatting, buffering, and protection from oxygen. Several pretreatments (such as the use of liquid ammonia, dimethylsulfoxide, or dilute base) have been used to help completely disperse the starch. After the starch is completely dispersed, the most common separation technique is to precipitate the

amylose as its *n*-butanol or thymol complex. These components form an inclusion complex with amylose, the nature of which is similar to that shown in Figure 2.9. Several reprecipitations are necessary to obtain pure amylose; the amylopectin can be recovered by lyophilization or precipitation with alcohol.

Organization of the Starch Granule

Several levels of organization of the starch granule can be distinguished. We here cover what is known based on microscopic and X-ray diffraction studies as well as from more advanced work.

STARCH HILUM AND GROWTH RINGS

In developing cereal endosperm tissue, a high positive correlation exists between sucrose concentration and rate of starch synthesis. Starch biosynthesis is initiated at the hilum, a site easily recognizable in the mature granule. A granule grows from the hilum by apposition of carbohydrate material at its expanding surface. The new layer deposited on the outside of the growing granule varies in thickness. The layers become apparent after treatment of the starch with dilute acid or enzymes (Fig. 2.12). The more-resistant shells are more crystalline (see below) than the rapidly degradable more-amorphous shells, which, in spite of their name, contain some crystallites.

Fig. 2.12. Scanning electron micrograph of a cross section of a grain sorghum kernel that has been treated with α-amylase. Note the rings in the broken starch granules. Bar is 10 μm.

In potato starch, the layers are obvious and easily seen in the intact starch under a light microscope (Fig. 2.13). The nature and cause of the layers in starch are still uncertain, but they presumably represent growth rings, as early observations on wheat and barley starch suggest one growth ring for each day after granule initiation. Furthermore, growth rings are not visible in granules from most plants grown at constant light and temperature. For potato, however, ring formation is not abolished under such conditions.

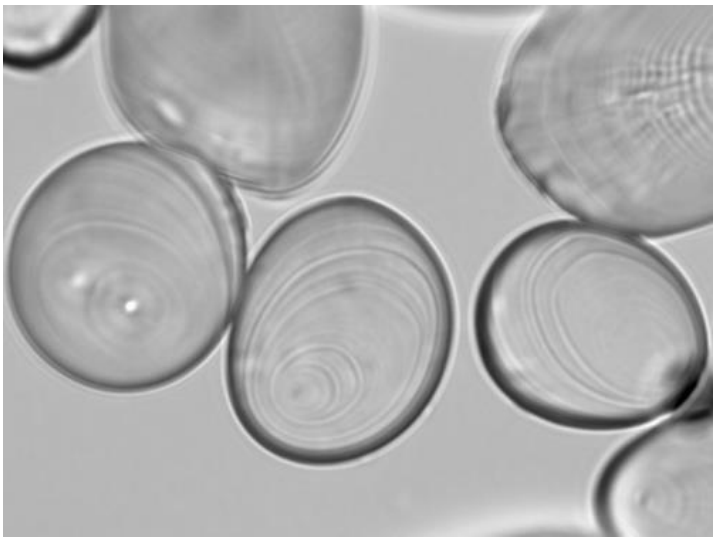


Fig. 2.13. Light photomicrograph of potato starch granules. Note the concentric rings. (Courtesy S. Gomand)

BIREFRINGENCE

When viewed in polarized light, starch granules show birefringence in the form of the typical Maltese cross (Fig. 2.14). The birefringence indicates that the starch granule has a high degree of molecular order but not necessarily that the granules are crystalline; things can be very ordered and yet not be crystalline. If they are highly ordered, they will be birefringent. On the other hand, the cellulose in a piece of paper is semicrystalline and, although the crystallites themselves are birefringent because they are ordered, the paper as a whole is not birefringent because the crystallites are randomly oriented.

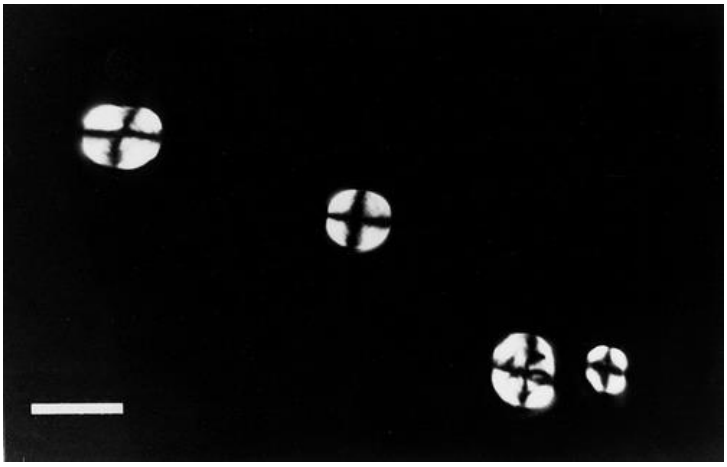


Fig. 2.14. Light photomicrograph of wheat starch granules taken with crossed nichol prisms showing the Maltese cross. Bar is 10 μm. (Courtesy N. Martin)

CRYSTALLINITY

That starch is a semicrystalline material has been clear since the classic work of Katz and his collaborators in the 1930s. In their work, they observed that intact starch granules of different botanical origins gave three types of X-ray patterns (designated A, B, and C). The crystallinity of starch granules can be destroyed by mechanical means. Ball milling starch at room temperature eventually completely destroys both the birefringence and the X-ray pattern. In general, we do not have a good explanation for this phenomenon, although it is clear that, when the ball strikes the starch, friction heat is generated.

Most cereal starches give A patterns (Fig. 2.15). Potato, other root starches, and retrograded (see below) starch give B patterns, while smooth pea and bean starches give C patterns. The C pattern is an intermediate form, probably a mixture of the A and B types. The A-type unit cell has 12 glucose residues and four water molecules, which are buried deep in the crystalline structure and cannot be removed without complete destruction of that structure. The B polymorph has 12 glucose residues and 36 water molecules, which are located in a channel surrounded by six double helices and hydrogen-bonded to glucose residues and/or other water molecules; hence, they cannot move freely in the channel. The B pattern of potato starch can be

converted to an A pattern by heat-moisture treatments. Small dextrins (12–15 glucose units) can yield any of the three patterns, depending on their crystallization conditions.

The fact that selective leaching of amylose from granular starch increases its crystallinity implies that amylopectin structural elements have a predominant role in imparting crystallinity to starch. Moreover, mild acid hydrolysis has been used to relate the starch crystalline properties and the molecular structure of starch polymers (i.e., amylopectin clusters, amylose), as the acid acts homogeneously throughout the granule and preferentially etches the amorphous zones. Insoluble residues after acid hydrolysis are referred to as "lintnerized starches" (lintners) or "Naegeli amylodextrins," depending on the acid used (hydrochloric or sulfuric acid, respectively). Combined chromatographic and enzymatic analysis of waxy maize Naegeli amylodextrins, regular cereal and potato lintners, and lintners of regular legume starches revealed two main populations of chains: a fraction of linear chains with an average DP of 13–15 and a fraction of singly branched chains with an average DP of 25. It is now accepted that, for starches with regular or low amylose contents, short external amylopectin chains intertwine to form double helices. It is equally accepted that double helices belonging to the same cluster are arranged such that either the A or B crystalline unit cell is formed. Individual crystallites are thought to be aligned in high-density "crystalline" lamellae, while amylopectin branching points reside in the low-density "amorphous" lamellae (Fig. 2.16). Hence, it is accepted that the amylopectin fraction of starch accounts for (most of) the granular crystallinity.

In line with the above, variations in chain length distribution among amylopectins are accompanied by differences in the prevailing crystalline polymorph of the starch (A-type or B-type polymorph, see above). Moreover, it has recently been established that, on top of the differences in chain length distribution, starches bearing A- and B-type crystallites may also show a different branching pattern.

X-ray diffraction of crystalline amylose helical inclusion compounds (see above) results in the V pattern (Fig. 2.15). Such patterns can be found after gelatinization (see below) and complexing with lipid or related compounds.

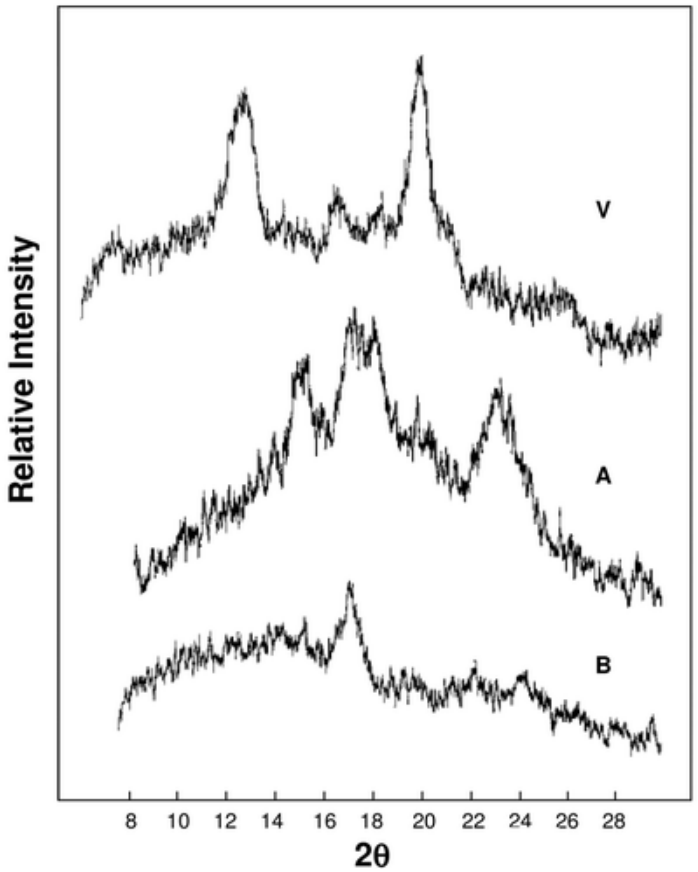


Fig. 2.15. X-ray diffraction patterns of starch, showing the A, B, and V patterns. (Courtesy K. Zeleznak and J.-L. Jane)

GROWTH RINGS REVISITED

Today, the starch granule can be defined in terms of alternating amorphous and semicrystalline growth rings, or shells, with a radial thickness of 120–400 nm (Fig. 2.16). The amorphous shells are less dense and contain amylose and probably less-ordered (amorphous) amylopectin, while the semicrystalline shells are composed of alternating amorphous and crystalline lamellae of about 9–10 nm in length. The latter are made up of amylopectin double helices packed in a parallel fashion, while the former consist of the amylopectin branching regions (and possibly some amylose). There are indications that these lamellae are organized into larger, somewhat spherical structures, named "blocklets," which range in diameter from 20 to 500 nm.

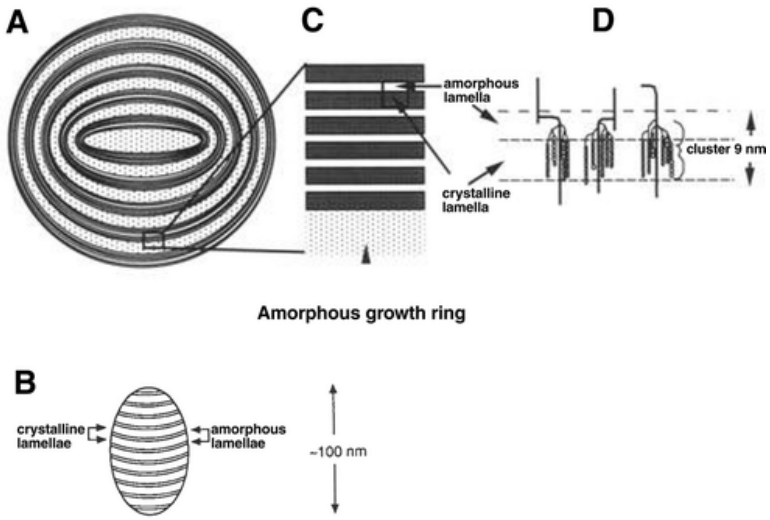


Fig. 2.16. Schematic representation of the starch granule, showing amorphous and semicrystalline growth rings in a starch granule **(A),** blocklet **(B),** amorphous and crystalline lamellae in a stack and part of an amorphous growth ring **(C),** and aligned double helices (from amylopectin side chains) within a crystalline lamella and amylopectin branch points within an amorphous lamella **(D).** (Adapted from Donald et al 1997 and Myers et al 2000)

Starch in Excess Water Systems

In the preparation of most cereal-based food systems, the starch-containing cereal or fractions thereof are, at some point in time, heated in the presence of water and cooled to a variable degree before consumption. The unique character of many of our foods results from the changes that starch undergoes, especially when it is heated and subsequently cooled. Some obvious examples are the viscosity and mouthfeel of gravies and puddings and the texture of gum drops and pie filling. It is therefore important to understand what happens to starch under conditions relevant for various food systems.

STARCH GELATINIZATION AND COOKING

When excess water is added to starch at room temperature, the water molecules (or, for that matter, most small molecules up to a molecular weight of about 1,000) freely penetrate the granule. Upon hydration, the starch can hold about 30% of its dry weight as moisture. The granule swells slightly. Under such conditions, its volume increase is generally considered to be about 5%, and the volume change and water absorption are reversible.

The phenomena that occur when starch is heated in excess water can be studied using a variety of experimental techniques, including optical microscopy, amylography, and rapid viscoanalysis, as well as differential scanning calorimetry and time-resolved X-ray diffraction analysis. The present discussion focuses on optical microscopy, as it allows introduction of the definition of gelatinization. It further deals with amylography and rapid viscoanalysis, as both techniques are widely used to predict starch functionality.

Optical Microscopy

When viewed in a polarization microscope as a function of temperature, individual granules dispersed in excess water lose their birefringence first at the hilum and then in the rest of the granule over a small temperature interval (<1 degree C). The granule is said to gelatinize, and the process it undergoes is defined as gelatinization. The gelatinization temperature of a starch granule is therefore the temperature at which the birefringence is lost. However, for a given starch sample consisting of a normal granule population, the loss of

birefringence occurs over a much wider temperature range (7–10 degrees C), showing that gelatinization is a granule-by-granule event. It is hence common practice to record gelatinization temperature ranges and/or the temperatures at which increasing percentages of starch granules lose their polarization cross.

The starches from different cereals vary widely in their gelatinization properties (Table 2.1). Wheat, barley, and rye all have similar gelatinization properties: during heating in excess water, 50% of the granules lose their birefringence by the time 53°C is reached. Triticale starch appears to be very similar to these starches. Taken together, the starch granules of maize, sorghum, and pearl millet are very similar to each other in gelatinization properties: all three starches have a similar temperature (67°C) at which 50% of the granules have gelatinized, which is somewhat higher than that of wheat, barley, and rye. The starches of oats and rice differ quite widely in their gelatinization properties. Oat starch gelatinizes at a relative low temperature (50% gelatinization at about 55°C) and rice starch at a higher temperature (50% gelatinization at about 70°C).

In essence, gelatinization is an irreversible process, which destroys the molecular order of the starch, but it clearly affects all structural levels. Along with the disruption of molecular order, the loss of birefringence is accompanied by the melting of crystallites, absorption of water, swelling of granules, and the progressive solubilization of the starch.

Amylography or Rapid Viscoanalysis

As outlined above, heating of starch granules above their gelatinization temperature results in irreversible changes. These can be shown by either an amylograph or a Rapid Visco Analyser.

Both instruments measure the relative viscosity of a starch and water (buffer) system as it is subjected to shear during a controlled heating, a holding period at a constant temperature, and then a controlled cooling. The relative viscosities measured with these instruments are a function of the temperature profile and the shear used. In addition, they drastically change with the concentration of the starch used in the analysis. In essence, we can distinguish three concentration regimes. The first is a very dilute one and is defined as that in which the starch concentration is insufficient to give rise to a signal in either the amylograph or the Rapid Visco Analyser. The second regime is a dilute-concentration regime. Under such conditions, the fully swollen granules do not occupy the full space available to them, and their swelling is, accordingly, not limited by space constraints. In both the very dilute and the dilute regime, the rheology of the starch-water system is said to be governed by the swelling power of the granules as well as by the amylose fraction that is solubilized. The third and last regime is the concentrated regime. Under these conditions, the starch concentration is such that the granules cannot swell to their full extent. It follows that the rigidity of the granules drastically impacts the rheology of the system. However, while the concept of separate concentration regimes is useful for our understanding, it should be kept in mind that the concentration effects are a continuum from one regime to another.

As outlined above, in the very dilute concentration regime, the instruments are not sensitive enough to measure small changes at low relative viscosity; therefore, a material such as carboxymethyl cellulose is often added to the buffer (often a phosphate buffer, pH 6.8) to produce a baseline viscosity that is in the instrument's measurement range.

When wheat starch is added to water, changes occur as the temperature is increased (Fig. 2.17). Between 50 and 57°C, viscosity increases. This coincides with the loss of granular birefringence; i.e., the starch gelatinizes. The events occurring during heating but after gelatinization, or loss of birefringence, are referred to as "pasting." Continued heating in excess water gives rise to an additional, larger increase in viscosity.

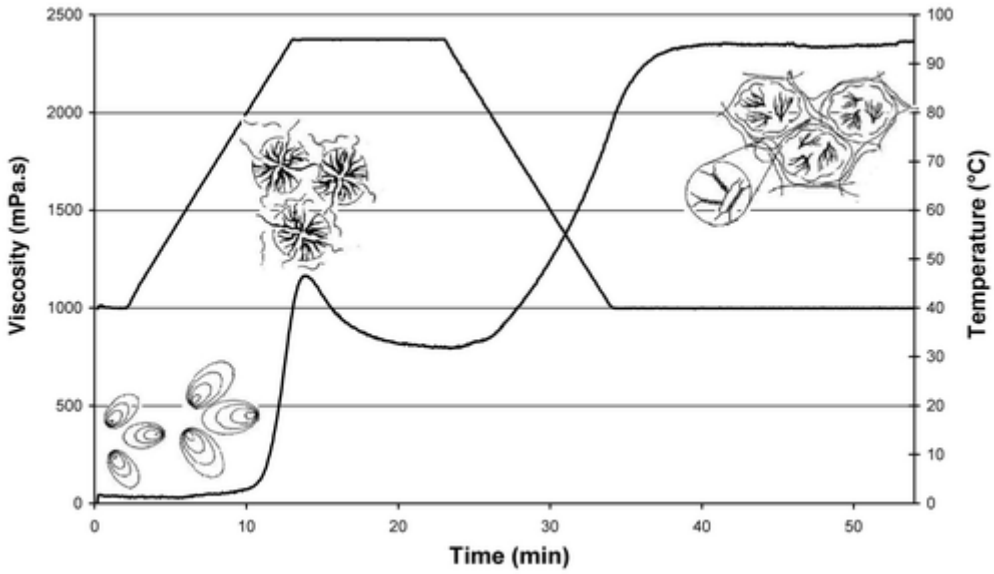


Fig. 2.17. Conceptualized rapid viscogram of a starch suspension, showing the different phases of swelling, pasting, and setback (gel formation) as a function of the heating, constant temperature, and cooling profile used. At left, intact starch granules are shown, followed by gelatinized granules with leached amylose, and finally starch gel with indications of starch granule remnants containing intergranular crystalline amylose. (Courtesy G. Gelders)

The viscosity increase that occurs when starch is heated in water is the result of the starch taking up water and swelling substantially. With continued heating, the starch granule becomes distorted, and soluble starch (mainly leached-out amylose) is released into the solution. The soluble starch and the continued uptake of water by the remnants of the starch granules are responsible for the increase in viscosity. Solubilization of starch is continuous during pasting. Even in excess water, the granule is not completely soluble until a temperature in excess of 120°C is reached. Thus, in any food system, complete pasting or complete solubilization of starch would not occur. In cooked food, the starch occurs as remnants of the granule, with a small level of soluble starch.

In the instruments, as in all food systems except those cooked under pressure, the temperature cannot materially exceed 100°C or the system will boil. So, heating is discontinued at 95°C, and the temperature is held at 95°C with continued stirring. The starch is said to be "cooked." Actually, relatively little change occurs in the nonsoluble starch. One property of starch yet to be explained adequately is that solubilization appears to be controlled mostly by temperature and not by the interaction of time and temperature. Holding starch at a specific temperature for a period of time does not increase its solubility. The temperature must be raised or the sample stirred or otherwise sheared to increase the solubility.

The rapid viscogram in Figure 2.17 shows a viscosity peak. Such a peak is generally referred to as the "swelling peak." As long as the granules remain intact as they take up water and release amylose, they increase the relative viscosity of the system. However, from a given moment onward, the relative viscosity of the starch system decreases markedly. The decrease in viscosity is caused by the molecules of soluble starch orienting themselves in the direction that the system is being stirred, as well as by shear-induced destruction of the (not necessarily fully) swollen (and hence fragile) granules. This phenomenon, called "shear thinning," is an important property of starch pastes. It is of practical relevance for many food systems. If one wants to make a thick soup, one must not stir excessively or pump the paste through a pipe, as, in both cases, shear thinning will occur, giving a lower viscosity. Different starches vary in the amount of shear thinning that they show, and starch modification (see below) affects this property. Generally, the more soluble the starch, the more it will thin on shearing.

Finally, it is of note that, while amylose-lipid inclusion complexes may be present in native starch already, additional quantities may be formed with free starch lipids during the starch gelatinization and pasting process. This complexation evidently influences the properties of starch as well. With differential scanning calorimetry (DSC, see below), which measures heat flow as a function of temperature, one can detect two types of amylose-lipid complexes. The first type typically gives rise to an endothermic transition at about 98°C, while the second type gives rise to an endothermic transition typically at about 110°C. It has been stated that the first type corresponds to noncrystalline complexes and that the lower-melting endotherm is the result of the dissociation of the complexes, while the second, higher-melting endotherm can be ascribed to the melting of crystalline amylose-lipid complexes. Whatever may be the case, it follows from the above that at least part of the amylose-lipid complexes present in the starch granules and those complexes formed during the starch gelatinization and pasting process dissociate during the cooking phase.

STARCH SETBACK, GELATION, AND RETROGRADATION

Setback

After the cooking period at 95°C, the amylograph as well as the rapid viscoanalysis procedures include a controlled cooling to 50°C. Such cooling gives rise to a rapid increase in viscosity, which is referred to as "setback" (Fig. 2.17). Starches vary in the amount of setback they display. The phenomenon is caused by a decrease of energy in the system that allows more hydrogen bonding and entanglement between starch chains.

Gelation and Retrogradation

Simply stated, a gel is a liquid system that has the properties of a solid. Some common examples are gelatins, pie fillings, and puddings. In gels, a small amount of solid material controls a large amount of water. It is amazing that water does not leak out of the gels when they are left standing. Calculations show that the distances between the starch chains in gels are very large compared to the size of the water molecule. Studies with diffusing solutes show that the water in gels has properties essentially equal to those of pure water. However, the water is held in the gels. We do not understand the forces involved in this. However, it seems very logical that hydrogen bonds are involved. One can indeed visualize a food system gel as protein or carbohydrate chains with layers of water molecules attached by hydrogen bonding.

During storage, gelatinized starch undergoes a process called "retrogradation." The term *retrogradation* means *to go back.* In starch chemistry, it was first used to describe the observation that, following gelatinization, the starch would regain crystallinity. Strictly speaking, of course, only amylopectin molecules go back to a crystalline entity; hence, the term *retrogradation* should be used only for amylopectin crystallization. Under certain conditions, amylose may also crystallize. However, since it was not crystalline to start with, this should not be referred to as retrogradation. Therefore, in this book, the terms *amylopectin retrogradation* and *amylose crystallization* are used.

The starch concentration, the temperature, and the shear applied during the steps preceding the cooling phase determine the structure of the starch suspension. The structure may vary from 1) densely packed swollen granules without a continuous amylose gel phase outside the granules, in which case the suspension forms a paste with flow properties rather than a gel, to 2) swollen granules dispersed in a continuous gel phase of leached amylose (Fig. 2.18), to 3) a macromolecular dispersion of amylose and amylopectin.

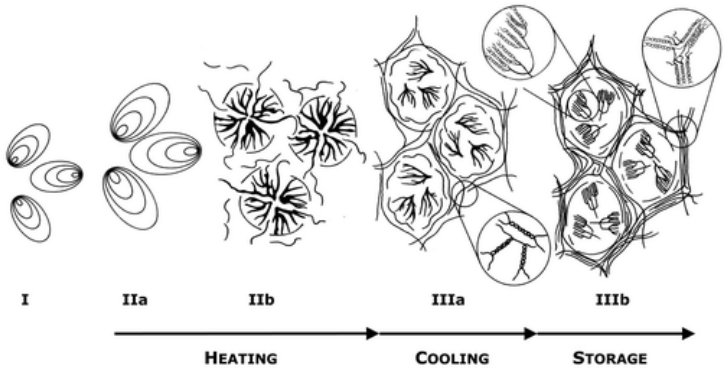


Fig. 2.18. Schematic representation of changes that occur in a starch-water mixture during heating, cooling, and storage. **I,** Native starch granules; **II,** gelatinization (i.e., loss of birefringence associated with crystal melting): swelling **(IIa)** and amylose leaching and partial granule disruption**(IIb),** resulting in the formation of a starch paste; **III,** retrogradation: formation of an amylose network (gelation) during cooling of the starch paste **(IIIa)** and formation of ordered or crystalline amylopectin molecules (amylopectin retrogradation) during storage **(IIIb).** (Adapted from Goesaert et al 2005)

In the second case (Fig. 2.18), gel formation has primarily been attributed to gelation of amylose in the continuous phase. Initially, double helices are formed between the amylose molecules that were solubilized during gelatinization and pasting, and a continuous network develops (gelation). After some hours, these double helices form very stable crystalline structures, as they have a melting temperature of about 150°C. Indeed, such crystalline amylose structures have been recovered as insoluble residues following treatment of retrograded starch with thermostable amylase at 100°C, a treatment that leads to complete dissociation of crystalline amylopectin (see below). That this process occurs fast does not need to be a surprise. It is well known that crystallization (comprising the steps of both crystal nucleation and propagation) can occur between the glass transition (see Chapter 5) temperature of a given system and the melting temperature. When applying this concept to amylose systems, one comes to the following reasoning. Because the glass transition temperature of a starch system is typically below 0°C and the melting temperature of amylose crystals is about

150°C, the temperature range between cooking starch (typically at 100°C) and its subsequent cooling and storage at room temperature (typically 20°C) is optimal for amylose crystal formation. Crystals can thus form over a broad temperature range. Similar reasoning, but now based on amylopectin crystal melting temperatures of about 50–60°C, allows one to understand that amylopectin crystallization is much slower. As long as the starch is above the melting temperature of amylopectin, new crystals would not form. The crystal nucleation and propagation temperature range between room temperature and the crystal melting is narrower than that of amylose. In practice, upon storage, gel stiffness slowly increases because of crystallization of amylopectin within the granule remnants, which, in the second case described above, are embedded in and reinforce the continuous amylose matrix. Therefore, amylose crystallization determines to a great extent the initial hardness of a starch gel, while amylopectin retrogradation determines the long-term development of gel structure and crystallinity in starch systems.

It was stated above that, during the cooking phase, at least part of the amylose lipid complexes dissociate. However, cooling of starch pastes leads to renewed formation and subsequent crystallization of amylose-lipid complexes.

Finally, as the gel ages, the starch chains have a tendency to interact strongly with each other and thereby force water out of the system.

Starch in Limited Water Systems

The above systems used to study the interaction of starch, water, and temperature work only at dilute starch-in-water concentrations. These conditions are quite different from the concentrated starch-in-water systems such as found in baked products. Little or no data suggest that results obtained in dilute systems can be used to understand what occurs in concentrated food systems. However, the changes that starch undergoes in such systems are very important. All baked products set; that is, they reach a temperature at which the dough or batter can no longer expand under the gas pressure generated by the increasing temperature. The changes that starch undergoes are at least partially responsible for that setting.

It has always been, and still is, difficult to study starch in limited water systems. Yet most, if not all, of our food systems are limited in water (less than 2:1 water to starch). DSC has been quite beneficial for studying starch in such concentrated systems.

DIFFERENTIAL SCANNING CALORIMETRY STUDIES

DSC instrumentation is useful for following gelatinization, retrogradation, and crystallization of starch polymers. It can measure the enthalpies (heat flows) associated with melting of both crystalline amylose and amylopectin (melting temperatures of about 150°C and 50–60°C, respectively), as well as the dissociation and melting enthalpies of amylose-lipid complexes (see above).

When starch is heated in excess water (water-starch, 2:1) in a DSC instrument, a sharp endothermic peak is obtained (Fig. 2.19A). The start of the peak (where it deviates from the base line) corresponds to the start of birefringence loss. The area under the curve is a measure of the energy (enthalpy, ΔH) required for the transition from an ordered to a disordered state (crystalline to melted state). The end point of the loss of birefringence and the end of the peak are not quite the same, as there is a considerable lag in the DSC instrument. However, in general, the two correlate well.

As the amount of water in the sample is reduced, the DSC peak widens and becomes clearly bimodal (Fig. 2.19B). At low water contents (water-starch, 0.35:1), the loss of birefringence, as reflected by the endothermic peak in the DSC thermogram, occurs over a temperature range of more than 30 degrees C (Fig. 2.19F). The slow loss of birefringence can also be seen directly in light photomicrographs. The amount of water above 30% available to the starch does not affect the temperature at which birefringence starts to disappear, but it does greatly affect the completion of the process.

For some waxy and regular cereal starches, gelatinization enthalpy correlates significantly with crystallinity, as expected because hydrogen bonding between adjacent double helices has marked effects on stability. After partial gelatinization, the residual enthalpy correlates both with crystallinity and double-helical order.

Several views on the impact of moisture content on DSC enthalpic transitions have been formulated. One of these maintains that, initially, water enters in the more-accessible, amorphous regions of the starch granules. Swelling of the amorphous regions induces stress on the crystallites, and starch chains are stripped from the surface of crystallites, thereby reducing the crystallinity and causing the loss of birefringence of the starch granules. In excess water, the degree of swelling is sufficient to completely gelatinize the granule. At lower water levels, swelling is insufficient to completely disrupt the starch granule. The remaining order is then

disrupted at higher temperatures by a conventional melting transition. At very low moisture contents (<30%, based on starch), only the latter process takes place.

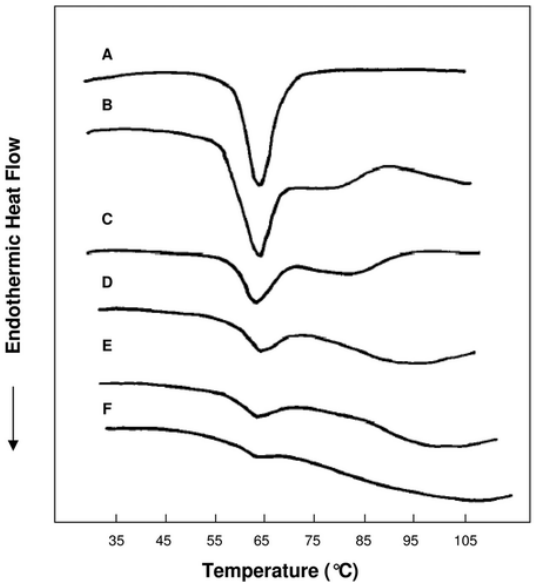


Fig. 2.19. Differential scanning calorimeter thermograms of wheat starch heated with water-to-starch ratios of 2.0 (A), 1.0 (B), 0.75 (C), 0.5 (D), 0.44 (E), and 0.35 (F). (Reprinted from Ghiasi et al 1982a)

Starch-Degrading Enzymes

Carbohydrate-hydrolyzing enzymes have, in the recent past, been grouped into glycoside hydrolase families, based on genetic information, structural and amino acid sequence similarities, and hydrophobic cluster information. In the particular case of starch-degrading enzymes, glycoside hydrolase families 13, 14, and 15 are of particular relevance. Depending on the enzyme, an endoaction or an exoaction pattern can be discerned. Enzymes that display an endoaction can hydrolyze the starch chain internally, while enzymes displaying an exoaction generally hydrolyze the chain from the nonreducing end.

GLYCOSIDE HYDROLASE FAMILY 13 ENZYMES

This family contains a variety of enzymes capable of hydrolyzing the α-1,4 and/or α-1,6 linkages in starch and is generally referred to as the "α-amylase" family. These enzymes are α-amylases, maltogenic and other maltooligosaccharide-producing amylases, and the debranching enzymes pullulanase (see above), and isoamylase.

α-Amylases (EC 3.2.1.1), which are typical endoamylases, more or less randomly hydrolyze the α-1,4 linkages of starch, yielding low molecular weight sugars and α-dextrins (Fig. 2.20). Sound, intact cereals have low levels of α-amylase. The enzyme is optimally active at about pH 5.3 and contains a calcium ion in its structure, which is necessary for it to have catalytic activity. Provided the starch has been gelatinized and pasted, α-amylases rapidly decrease the size of large starch molecules and thereby reduce the viscosity of a starch solution or slurry. However, given sufficient time, they also degrade granular starch, such as is observed during cereal germination. Upon germination, the level of α-amylase increases many times. This makes α-amylase activity a sensitive measure with which to detect sprouting of cereal grains. The level of sprouting is generally an important factor in the suitability of grain for food uses.

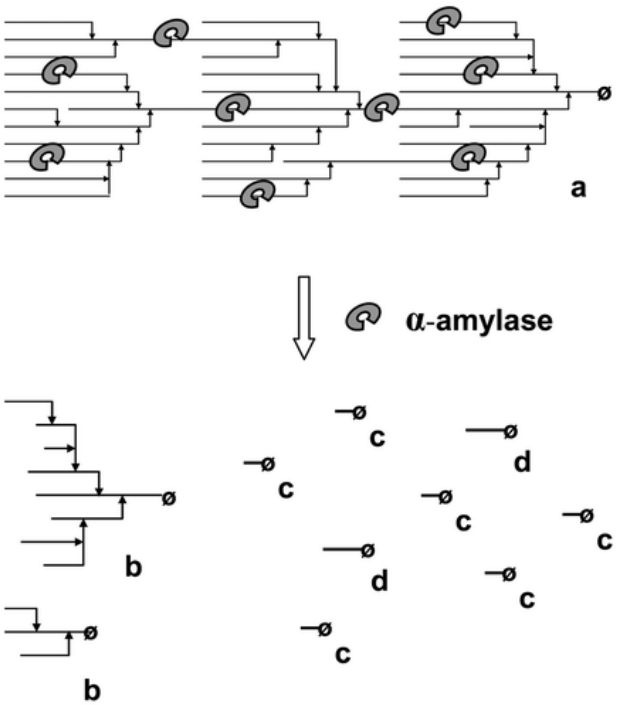


Fig. 2.20. Action of α-amylase on amylopectin (a), producing hydrolysis products of various sizes: α-limit dextrins (b), maltose (c), and maltotriose (d). The solid lines represent α-1,4-linked glucose units; arrows indicate α-1,6 linkages. Both amylopectin and α-limit dextrins have only one reducing end (ø). (Courtesy A. Bijttebier)

Because of the rapid effect of α-amylase on starch paste viscosity, viscosity measurements with the amylograph and Rapid Visco Analyser have been widely used as a secondary measure of α-amylase activity. In addition, the time needed for a standardized object to move through a starch paste (i.e., the falling number) has been taken as an indirect measure of activity. Several direct chemical and enzymatic tests have recently been developed to measure amylase activity.

Maltogenic amylase (EC 3.2.1.133) and other maltooligosaccharide-producing (e.g., EC 3.2.1.60, EC 3.2.1.98) amylases are mainly exoacting and, in essence, release maltose or other oligosaccharides (e.g., maltotetraose or maltohexaose) from starch. Recent work shows that, when the temperature of the system is increased to 70°C, the degree of endoaction of these enzymes increases.

Pullulanase (EC 3.2.1.41, see above) and isoamylase (EC 3.2.1.68) hydrolyze the α-1,6 bonds, thus removing the side-chains, but not the α-1,4 bonds. An important difference between these enzymes is that pullulanase debranches side chains of two or more glucose units, whereas isoamylase requires at least three glucose units.

GLYCOSIDE HYDROLASE FAMILY 14 ENZYME

β-Amylase (EC 3.2.1.2, see above) belongs to glycoside hydrolase family 14. Because β-amylase produces maltose, it is called the "saccharifying" (sugar-producing) enzyme. β-Amylase alone has practically no action on intact starch granules. Unlike α-amylase, β-amylase is found in sound, intact cereal grains. It is optimally active at a pH value of about 5.5. In general, the level does not increase much as a result of germination. Cereal β-amylase is more susceptible to heat inactivation than α-amylase (Fig. 2.21).

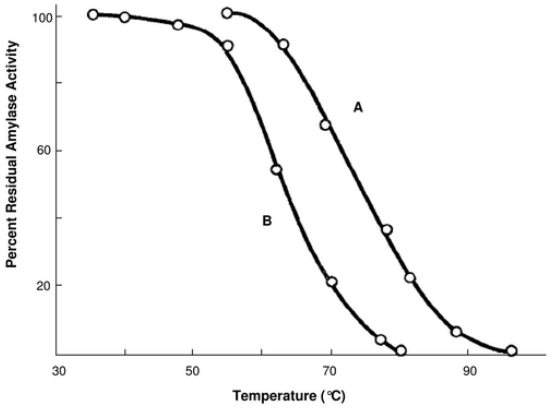


Fig. 2.21. Effect of temperature on the activities of α- (A) and β- (B) amylases. The graphs show the percentage of residual activity noted after a preincubation for a given time. (Reprinted from Reed and Thorn 1971)

During beer brewing (see Chapter 11), the combined activities of β-amylase and α-amylase (an enzyme formed during malting of barley for beer production) degrade starch quite rapidly and much faster and more completely than either alone. Each break that α-amylase makes in the starch polymer produces a new nonreducing end for β-amylase to attack. It follows that selective measurement of β-amylase activity is generally difficult, because its activity, as measured by maltose production, is strongly influenced by the level of α-amylase present. One approach to selectively measuring its activity in cereal extracts is to incubate such extracts with calcium-ion chelating agents, which destroy α-amylase activity, before performing an assay that measures maltose release.

However, a mixture of the two enzymes does not completely degrade starch, as neither enzyme can break the α-1,6 glucosidic bonds present in amylopectin. In fact, the rate at which α-1,4 bonds are broken close to an α-1,6 linkage is extremely low. In general, a combination of the two enzymes results in about 85% conversion of starch to sugar.

The α- and β-amylase activities in germinated wheat, barley, and rye appear to be much higher than those found for other cereal grains. The measurement of amylase activities in sorghum malts has been difficult because many of the enzymes are insoluble, and sorghum germination produces relatively low levels of α- and β-amylases.

GLYCOSIDE HYDROLASE FAMILY 15 ENZYME

Last, but not least, glucoamylase (EC 3.2.1.3) hydrolyzes the α-1,4 linkages at the nonreducing ends of the starch molecules and thus releases glucose. Although slower, glucoamylase also has activity on α-1,6 linkages. Theoretically, this enzyme can completely convert starch to β-D-glucose.

Modified Starches

Granular starches can be modified by chemical reaction to change their properties and functionality to better meet desired end uses. Starch gels can be produced with a wide range of properties by varying the source of starch as well as the degree and type of modification. One can use a mixture of unmodified, cross-linked, or substituted starches to achieve the desired viscosity, paste clarity, and freeze-thaw stability desired for a specific product. The more common modifications and how they modify starch properties are discussed in this section.

ACID-MODIFIED STARCHES

The oldest type of modification is treatment with acid to produce an acid-modified starch. The early work with acid modification was done in the late 1800s by Lintner and Naegeli. Acid-treated starches are today referred to as "lintnerized" or "Naegeli" starches. The industrial preparation of today's lintnerized starches consists of treatment of a fairly concentrated starch slurry with 1–3% hydrochloric acid at about 50°C for 12–14 h. After treatment, the slurry is neutralized and the starch recovered by filtration.

During the treatment, the acid freely penetrates the amorphous parts of the starch granule and hydrolyzes glucosidic bonds. The acid cannot attack the crystalline areas, perhaps because of their double helices, so they remain intact. The major effect of the acid is to reduce the molecular weight of the starch molecules while leaving the crystalline structure of the granule intact.

Upon heating in water, these modified granules fragment more and swell less. The gelatinization temperature range is increased, presumably because the amorphous chains cannot assist in the melting of the crystalline areas. Upon gelatinization, the starch becomes much more soluble than untreated starch does. As a result of acid treatment (hydrolysis of chains), the paste viscosity is much less than that for the native starch. Because the starch chains remaining after acid treatment are smaller (shorter in chain length), they tend to associate with each other more easily and thus form a rigid gel upon cooling. Common examples of such gels are jelly beans and other gum candies.

CROSS-LINKED STARCHES

Simply stated, cross-linking is the covalent bonding of two starch molecules to make a larger molecule. The linking is accomplished by forming a diester with phosphoric acid (in which case phosphorus oxychloride is the most common reagent) or by forming an ether bond (for which epichlorohydrin is a common reagent). The linkages are illustrated in Fig. 2.22. Although one generally considers the cross-link to occur between molecules, it could also occur within the large amylopectin molecule. However, such bonds within the molecule would not have a great effect on the starch's properties.

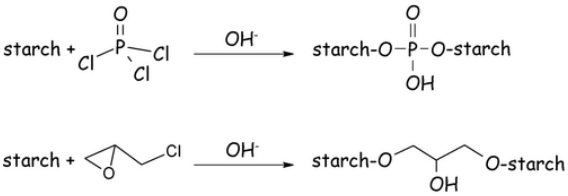


Fig. 2.22. Reactions used to cross-link native starch granules with phosphorous oxychloride (top) or epichlorohydrin (bottom). (Courtesy M. Verswyvel)

High levels of cross-linking increase the starch's gelatinization temperature. Highly cross-linked starches that do not develop viscosity when they are boiled in water or sterilized in an autoclave can be prepared. Such modified starches are useful as dusting starches for surgeon's gloves. The starch can be sterilized, works well to protect the surgeon's hands from sticking to the gloves, and, if accidently lost into the wound, is degraded with no ill effects.

Starch for use in food systems is generally cross-linked to a small extent. The extent of reaction is designated by the degree of substitution (DS) of the products obtained. A DS of 1 indicates that, on average, an anhydroglucose residue carries one substituent. Thus, the maximum DS is 3 for linear starch and slightly less for amylopectin. For food use, the DS is generally between 0.01 and 0.1.

Low levels of cross-linking do not significantly change the gelatinization temperature of the starch but do materially change its pasting properties. Cross-linked starch swells less and is less soluble than its unmodified counterpart (Fig. 2.23). Thus, cross-linked starch gives a lower viscosity upon pasting. One of the advantages of cross-linked starch is that it is more resistant to shear thinning than unmodified starch. Because the starch solubilizes less, it shears less and thus gives a more viscous paste after stirring or pumping.

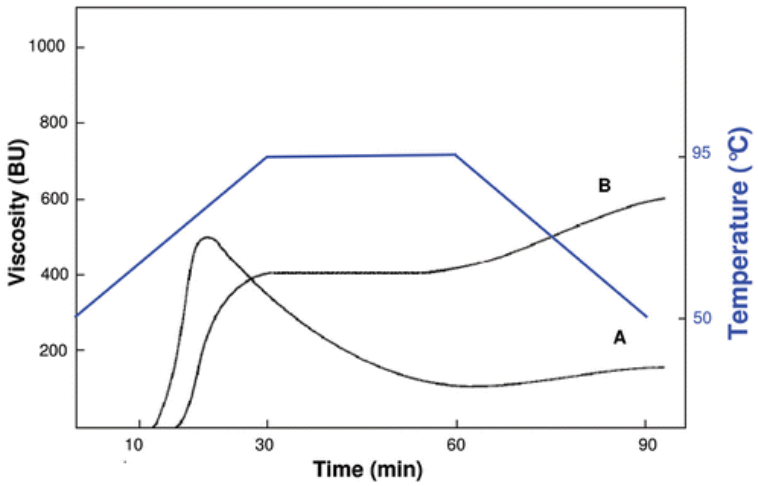


Fig. 2.23. Viscosity (in Brabender Units, BU) of native waxy maize starch (A) or cross-linked maize starch (B) suspensions at pH 6.5 in the presence of 1.0% salt. The temperature-time profile used is also indicated. (Courtesy T. LuAllen)

Another important use of cross-linked starch is to produce viscous systems in acidic media. An example is thickening a cherry pie filling. The acidity from the cherries is sufficient to speed hydrolysis of the α-1,4 glucosidic bonds in the starch during baking and thus produce a thin pie filling. Cross-linking does not stabilize the bonds in spite of the acid; however, with sufficient cross-linking, the starch swelling is greatly restricted, and, as the acid hydrolyzes the bonds, viscosity increases instead of decreasing. Therefore, if one starts with the right degree of cross-linking and obtains a constant amount of hydrolysis during baking, one can still end up with a thick pie filling. The change in viscosity as a function of pH is shown in Fig. 2.24.

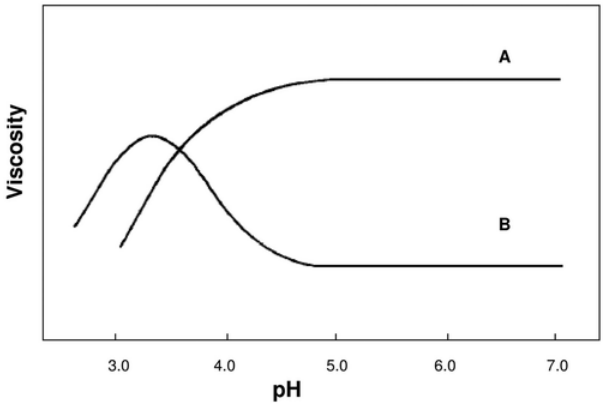


Fig. 2.24. Relative viscosity of starch gels made from either normal (A) or cross-linked (B) maize starch at different pH values. At neutral or slightly acidic conditions, no acid hydrolysis takes place, and constant relative viscosities are obtained for gels of both starches. As cross-linking reduces the swelling capacity of starches, the resultant gels are less viscous for cross-linked than for normal starch. When the starch gel from normal starch is produced under acidic conditions, acid hydrolysis takes place, and the resultant starch gel is less viscous than one prepared at neutral pH. However, when a gel from cross-linked starch is produced at acidic pH, the impact of cross-linking is partly overcome by the hydrolysis reactions, and a gel of higher relative viscosity is obtained. This principle finds applications in the production of, for instance, acidic pie fillings (pH about 3.0).

The texture of a starch paste is also affected by cross-linking. Starch pastes are classified as being either long or short. A short paste spoons well (cleanly), whereas a long paste tends to be stringy and does not spoon well. Figure 2.25 shows a convenient test for paste texture. A short paste gives a narrow deflection, and a long paste gives a broad deflection. Cross-linking of a starch makes its paste much shorter than the paste of the unmodified starch. Even low levels of cross-linking decrease the swelling and solubility of the starch. The more soluble the starch, the more entanglement and interactions occur, giving the paste its long character. In the cross-linked starch, more of the polymers remain in the remnants of the granules. This produces the short paste.

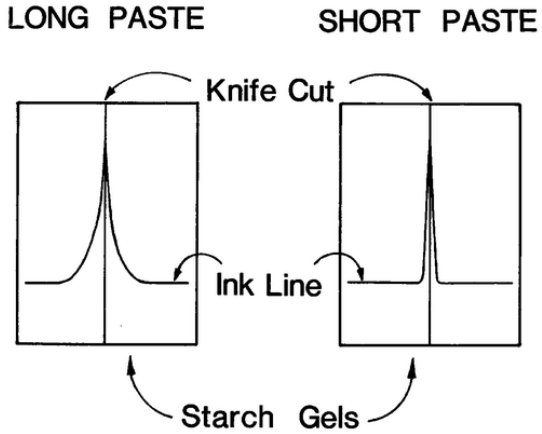


Fig. 2.25. Test for short and long pastes. Starch pastes are poured and allowed to cool. An ink line is drawn across the gel, and a knife is used to cut the gel at right angles to the ink line. With a long paste, the line is distorted further from the knife cut, showing the interaction of the molecules. In a short paste, the knife does not cause much distortion.

Many starch gels, particularly when stored under cool conditions, become opaque with time. The phenomenon is caused by starch crystallization. Crystallization is faster if the chains are smaller and more mobile. Therefore, cross-linking delays crystallization and retrogradation and thereby delays the time when the starch gel becomes opaque.

A similar phenomenon is found when gels are frozen and thawed. During freezing, the starch chains are rendered immobile, and ice crystals are formed. During storage, even at subfreezing temperatures, water migrates from small crystals to large ones. As a result, crystals are fewer but larger. Because the water is now concentrated into certain areas, the product also has voids. As the ice thaws, the first water produced supplies the starch chains with solvent and thus mobility. In unmodified starch, the chains rapidly interact with each other. The water released during additional melting cannot penetrate the interacting chains, and the product loses its gel consistency. The gel becomes opaque and watery and has a tough rubbery texture. Cross-linking holds the starch chains fixed in space so they cannot interact strongly. Therefore, the water produced during melting can again hydrate the starch chains, and the starch gel retains its properties. Cross-linked starch can withstand several freeze-thaw cycles.

SUBSTITUTED STARCHES

When a hydroxyl group of starch is converted into a monoester of phosphoric acid, the starch is "substituted" rather than cross-linked. It then carries a bulky as well as a charged group. Both of these facts make the starch chains repel each other. Thus, the granule tends to swell and solubilize more during gelatinization. This gives a starch paste with higher viscosity but with poorer resistance to shear thinning. Because the chains tend to repel each other, they do not interact or crystallize as easily as those in native starch. Thus, substitution stops retrogradation and opaqueness of starch gels and is helpful in giving improved freeze-thaw stability. High levels of substitution (about 0.7 phosphate groups per anhydroglucose residue) give starches that gelatinize at room temperature. This type of modified starch is useful in making instant pie fillings and puddings. Several chemical groups can be grafted onto starch to give a substituted starch.

STARCH-DERIVED FAT MIMETICS

Many ingredients used to produce no-fat or reduced-fat foods are based on starch. The role of fat in foods is complex and not well understood. Several of the important roles are to act as a plasticizer, to help incorporate air, to soften the mouthfeel of foods (often referred to as adding moistness), and to trap flavors. The above roles, except for trapping flavors and incorporation of air, can be compensated for by higher levels of water in the product.

Thus, we can visualize the role of the starch-based fat mimics as producing products with much higher water contents. To do this and still produce a reasonable product requires that the water be stabilized in some way. There are essentially three types of starch-based mimics. The first type comprises long-chain starch molecules. They control water in a way similar to that of the many gums that are used as fat mimics. The major problem with this type is that they interact with themselves to form strong gels or to crystallize. At higher concentrations, a second type (i.e., short-chain dextrins) also controls water and thus acts as a fat mimic. When the viscosity is not high enough, these also may crystallize. The third type, consisting of the microcrystalline particles produced from sheared, acid-hydrolyzed starch, also controls water and gives the desired product.

None of the starch-based mimics, by themselves, incorporate air or trap flavors. However, they have interesting properties and find many uses in foods, some of which have nothing to do with replacing fat.

OTHER MODIFIED STARCHES

Large quantities of oxidized starches (generally treated with hypochlorite) are produced. They are used, principally, in nonfood applications, i.e., as laundry starch and for paper manufacture. However, they are also used in breading formulations and are reported to give improved adhesion to meat products.

Although not strictly a modified starch (no covalent bond is formed), starch clathrates are also useful in modifying the properties of starch gels. The clathrate forms, presumably, with amylose and retards both the swelling and the solubility of starch. The reduced solubility results in a much shorter gel. An example is the use of monoacylglycerols to form a clathrate that gives a much fluffier instant mashed potato product.

Another modified starch that contains no new covalent bonds is cold-water-swelling starch. Such starch is produced by heating the native starch granules in an alcohol-water mixture. The starch crystallites are melted, but there is insufficient water to swell the starch granules. The solvent is then removed and the dried starch is stable. Addition of these granules to cold water results in their swelling. Thus, with these products, foods can be thickened without the use of heat except for that contained in the cold water.

Resistant Starches

It has long been assumed that all starch in our food is digested. However, it is now clear that some of the starch that we consume escapes digestion in the intestinal tract of healthy individuals. Such starch is now commonly referred to as "enzyme-resistant starch," or, more briefly, "resistant starch" (RS). It has some beneficial physiological effects that make it somewhat comparable to dietary fiber constituents. Four types can be discerned, i.e., RS I through RS IV.

RS I resists digestion because it is physically entrapped in its storage cell. Examples include those foods with whole or only partially milled cereal grains such as muesli.

RS II is native crystalline and hence ungelatinized starch. Potato starch is a typical example. Its crystalline polymers are only poorly degradable by human amylolytic enzymes.

RS III can, in a first approximation, be considered to be crystalline amylose. In practice, it has, by far, received most of the attention in the literature. Its production involves 1) starch gelatinization, 2) crystallization of the gelatinized starch molecules, and, if a concentrated form is desired, 3) amylolysis of the nonresistant starch residue.

RS IV is starch that has been chemically modified.

Conversion of Starch to Sweeteners

Because starch is composed essentially of glucose, hydrolysis produces glucose syrup. Large amounts of starch, especially maize and wheat starch, are commercially converted to syrups. Both the α-1,4 and α-1,6 bonds in starch are susceptible to acid hydrolysis. It would appear straightforward to cook starch with acid to produce such syrup. However, numerous side reactions can and do occur. From a practical standpoint, acid hydrolysis is effective only to thin the starch (reduce its viscosity) as it is being gelatinized.

Before continuing with a discussion of hydrolyzing starch to syrup, it is useful to discuss sweeteners and sweetness. The relative sweetness of several sugars is given in Table 2.2. Great variation exists in the way different people perceive sweetness. What is very sweet to one person may only be slightly sweet to the next one.

TABLE 2.2
Relative Sweetness of Several Common Sugars

Sugar	Relative Sweetness
Sucrose	100
Glucose	70
Maltose	30
Fructose	180
Invert syrup	130
High-fructose (42%) maize syrup	100

Also, the relationship between the concentration of sugar and the perceived sweetness is not linear. Sweetness perception is also affected by pH, as well as by other materials in the food. Thus, the values in the table are useful but not absolute. Sucrose is taken as the reference and given a value of 100. The table shows that its hydrolysis product, which consists of equimolar amounts of glucose and fructose and is generally referred to as "invert sugar," has a higher sweetness than the starting material. Glucose is only about 70% as sweet as

sucrose, and maltose is only 30% as sweet. Maltotriose and larger glucose oligomers are not sweet. Therefore, to produce sweet syrup from starch, much of the starch needs to be converted to glucose. It is also of interest to note the high relative sweetness of fructose.

Another concept important in understanding conversion of starch to syrups is that of dextrose equivalent (DE). *Dextrose* is the trivial name for glucose. The term is used extensively in the wet-milling industry. Glucose is a reducing sugar (i.e., it will reduce iodine to iodide) because it has a hemiacetal group at C-1. Thus, free glucose is a reducing sugar, whereas in maltose, one of the glucose molecules is reducing and the second one is not. In starch, there is only one reducing group in each starch molecule; all of the other glucose molecules are linked at the C-1 position. Therefore, with each hydrolytic cleavage of an α-1,4 or α-1,6 bond, one reducing group on a glucose molecule is freed. Dextrose equivalent is a measure of the percentage of glucosidic bonds that are hydrolyzed. Complete hydrolysis produces glucose. Thus, if one measures the reducing power of a solution obtained by complete hydrolysis of starch, expresses the reducing power as glucose, and divides the thus-estimated glucose content by the total weight of carbohydrate in the sample, that value is 100 DE. Measuring the reducing power of a glucose chain made up of 10 glucose units linked α-1,4 or α-1,6, expressing it as apparent glucose content, and dividing the resulting apparent glucose content by the weight of carbohydrate gives a DE value that is 10% of the value obtained with pure glucose (i.e., a DE of 10). Hydrolysis of one additional bond at any location in every chain doubles the reducing power while the amount of total carbohydrate stays the same. The DE is then 20. Thus, DE tells what percentage of the bonds is broken, but it does not tell the chemical composition of the resultant syrup.

To produce starch syrup, the starch is gelatinized in the presence of acid. This reduces the viscosity of the starch paste so that large amounts of water are not necessary to make it pumpable. Syrups can be made with acid hydrolysis alone; however, at about 40 DE, side reactions start to be important, and dark-colored (undesirable) syrups are obtained.

After acid thinning, several enzymes can be used to hydrolyze further, depending on the syrup desired. Low-DE syrups, called "dextrins," that are useful as viscosity builders and as humectants can be made with acid or a combination of acid and α-amylase. Solids having DE values varying from 10 to 35 are sold commercially. They are also useful as flavor diluents. Mixtures of α- and β-amylase are used after acid thinning to produce high-maltose syrup with a DE of about 42. An alternate path to high-maltose syrup is to use a debranching enzyme such as pullulanase together with β-amylase. This gives a higher percentage of maltose and a slightly higher DE. Note that a pure maltose solution has a DE of only 50.

Treatment of thinned starch with α- and β-amylase gives syrups with DE values of about 70 at complete reaction. The mixture of α- and β-amylase cannot break α-1,6 bonds; thus, a group of stubs containing α-1,6 bonds is left.

To produce high-DE syrups, glucoamylase must be used. This enzyme produces glucose from the nonreducing end of the starch chain and can hydrolyze both α-1,4 and α-1,6 bonds. Thus, it can theoretically produce a syrup of 100 DE. In commercial practice, values of 92–95 DE are more common. High-DE syrups do contain high levels of glucose and thus are relatively sweet. They are nearly completely fermentable by yeast and give solutions of high osmotic pressure.

To obtain higher sweetness, part of the glucose must be converted to fructose. This is accomplished with the enzyme glucose isomerase (EC 5.3.1.9). High-DE maize syrup treated with glucose isomerase to equilibrium typically analyzes as 50% glucose, 42% fructose, and 8% higher sugars. This is the classical high-fructose syrup of commerce, which, on a solids basis, is just as sweet as sucrose. This syrup has been very successful in competing with sucrose in many applications. Although it is as sweet as sucrose, it has a higher osmotic pressure and gives a lower water activity than does a sucrose solution. Both glucose and fructose are reducing sugars and therefore more subject to browning than is sucrose, which is not a reducing sugar.

Syrups with higher levels of fructose (60 and 90%) are now commonly available as well. These are produced by separating the fructose from the 42% mixture by ion exchange techniques.

CHAPTER 3: Proteins of Cereals

Cereal grains, like all biological materials, vary widely in their chemical composition. The variation is quite noticeable in the protein content. Wheat, for instance, varies from less than 6% to more than 27% in protein content, although most commercial samples are between 8 and 16% protein. The proteins in cereals are important from a nutritional point of view. In the case of wheat, the protein also has a drastic impact on functionality. This is undoubtedly the reason for the wheat storage protein, gluten, being the most-studied cereal protein. Gluten is believed to be mostly responsible for the breadmaking capabilities of wheat flour. We discuss this protein in more detail in this chapter.

Proteins are composed of amino acids linked together by peptide bonds. The structures of the common amino acids are given in Figure 3.1. As the name implies, all amino acids have an amino group along with an acid group, but they vary in the structure of the "R" group, or side chain (the part of the amino acid not involved in the peptide bond). Amino acids are commonly grouped according to their type of R group. Figue 3.1 shows the four common groups.

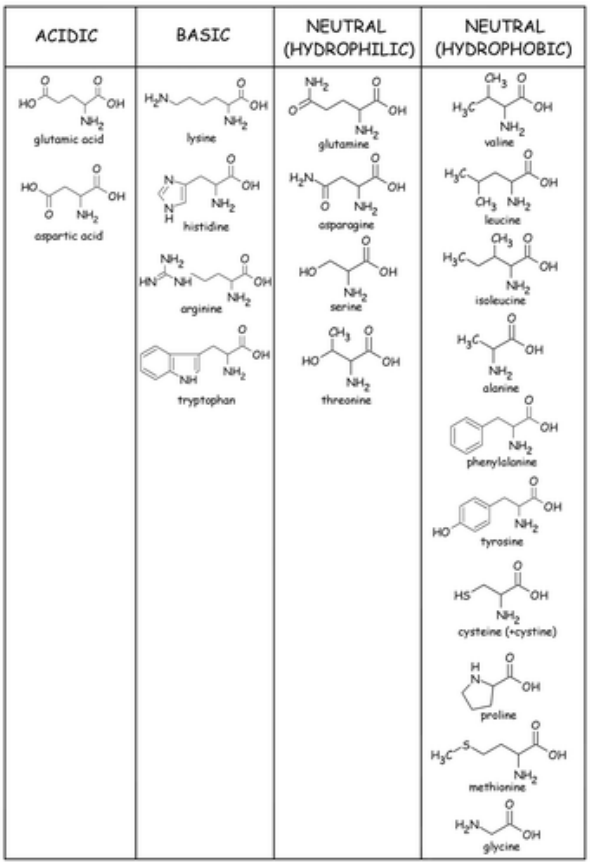


Fig. 3.1. Classification of amino acids as acidic, basic, neutral/hydrophilic, or neutral/hydrophobic. (Courtesy M. Verswyvel)

Proteins vary in molecular weight from a few thousand to several million. A protein of with a molecular weight of 100,000 would typically contain 850 amino acid residues. The acidic and amino groups of each amino acid are involved in the peptide bonds and form the backbone of the protein. The backbone structure of all proteins is essentially the same. The primary structure, i.e., the sequence of amino acids, is the first level of differentiation among proteins. However, for most of the functional differences in proteins, one must look to the secondary and tertiary structures. The peptide bonds that make up the backbone of the protein are flexible to a limited extent and can twist or curl the polypeptide into different forms. The sulfhydryl group (SH-) on the amino acid cysteine is an active group. It can react with another cysteine residue as a result of oxidation to form a disulfide bond (-S-S-). Such linkage is one factor that gives the protein its secondary structure. The two cysteine residues can be on the same protein chain (intramolecular bonding), forming a loop in the protein, or they can be on different protein chains (intermolecular bonding), linking two polypeptide chains together (Fig. 3.2).

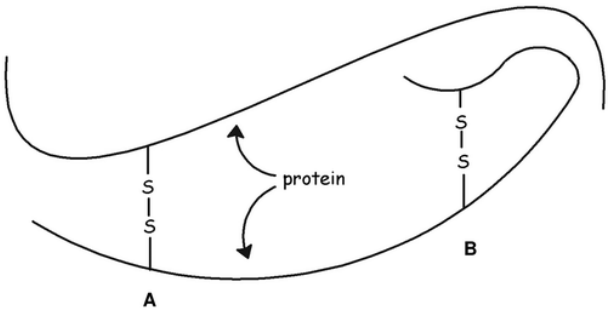


Fig. 3.2. Disulfide bonding between polypeptide chains (A) and within a single polypeptide chain (B). (Courtesy M. Verswyvel)

Several different types of noncovalent bonds are responsible for the tertiary structure of proteins. In most cases, the individual bonds are relatively weak, but their large number creates overall strength and stabilizes the structure.

Two examples of such bonds are ionic bonds (salt formation between an acidic and a basic group) and hydrogen bonds, which are very prevalent, with side chains containing uncharged oxygen, nitrogen, and hydrogen (Fig. 3.3). Another type of noncovalent bonding is hydrophobic bonding. While called "bonding," no actual bonds are formed; the term rather indicates a strong association of the protein chains. Such bonding arises when hydrophobic side chains associate closely with each other and, because of van der Waals and other forces, form a relatively strong "bond."

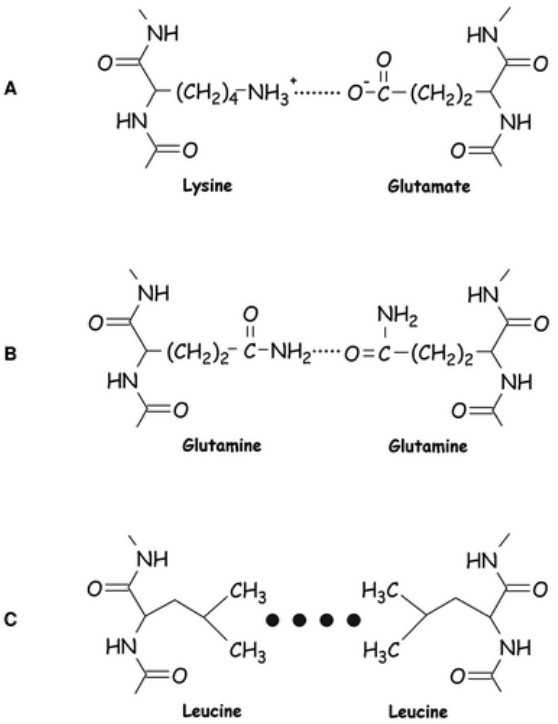


Fig. 3.3. Ionic bonds **(A),** hydrogen bonds **(B),** and hydrophobic bonds **(C)** between amino acid reesidues in protein chains. (Courtesy M. Verswyvel)

When a protein is placed in solution, several forces are active. For example, positive charges repel other positive charges and attract negative charges. Hydrophilic groups hydrogen-bond to water and/or to each other. Hydrophobic amino acid residues, for entropy reasons, tend to minimize their contact with water and hence associate together. The sum of all of this activity determines the tertiary structure of the protein.

It is the three-dimensional structure of the protein that determines its properties. Whether or not it is soluble in water depends on several factors, including its molecular weight (larger molecules are generally less soluble) and whether charges and hydrophilic groups are on the outside of the molecule where they can interact with water or are buried in the interior of the molecule. Whether or not the protein has enzymatic (i.e., catalytic) activity is determined by its three-dimensional structure and whether or how it binds a substrate molecule.

When the three-dimensional structure of the protein is altered or destroyed, the protein is said to be "denatured." Alteration of pH, increased temperatures, and treatment with various reagents may cause protein to be denatured. Denaturation may be reversible or irreversible. An example of a reversible denaturation is the loss of solubility of a protein when high concentrations of salt (e.g., ammonium sulfate) are added to a solution of the protein (i.e., the protein is "salted out"). The protein precipitates because the large amount of salt competes with the protein for the available water. However, when the salt is removed, the protein may regain its initial conformation and solubility; thus, the salt-induced denaturation process is reversible. A classic example of irreversible denaturation occurs when egg white protein is heated in water. The system's kinetic energy, which increases as the temperature is increased, breaks hydrogen bonds, and the protein goes from its original conformation to a more random one. In the particular case of egg white, the process is accompanied by disulfide bond formation, and the denaturation is irreversible. Needless to say, denaturation changes the physical properties of the protein. In many instances, it becomes less soluble, and, in the particular case of enzymes, denaturation often results in loss of activity.

Heat-induced protein denaturation in general can be monitored by differential scanning calorimetry (DSC), as it gives rise to a heat denaturation peak. Interestingly, DSC thermograms for wheat gluten fail to show a definite denaturation peak (Fig. 3.4). The small peaks seen are apparently the result of contaminating starch granules or contaminating soluble proteins. The lack of a denaturation peak would suggest that the gluten is in a random conformation.

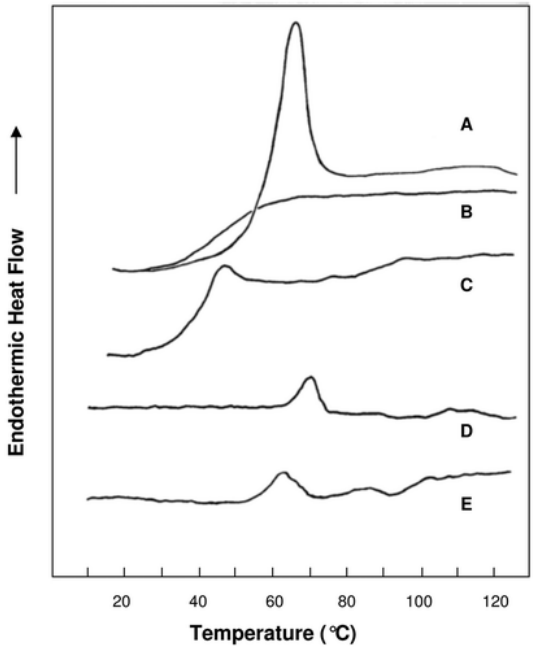


Fig. 3.4. Differential scanning calorimeter thermograms run at 10°C/min. A, commercial wheat gluten (11.3% moisture); B, sample A cooled and reheated; C, hand-washed gluten (11.4% moisture); D, hand-washed gluten, excess solvent (30% glycerol); E, hand-washed gluten, excess water. (Reprinted from Hoseney et al 1986)

Proteins in solution are affected to a large extent by both the pH and the ionic strength of the medium. The effects are brought about by the charge on the protein molecule and by how much the charge is shielded. As the pH of the medium is changed, the net charge on the protein can change from positive to negative or vice versa, and also the intensity of the charge can change. Because of a change in the charges, the three-dimensional structure of the protein also can change. This is, in some instances, why a change in pH can change the activity of enzymes. Salt can shield the charges on a protein molecule by becoming ordered around the charge. Such action negates the charge's effect on the protein structure.

Classification of Cereal Proteins

Traditionally, proteins have been classified into four types according to their solubility. This classification is based on the classic work of Thomas Burr Osborne in the early 1900s.

Albumins are soluble in water, and their solubility is not affected by reasonable (low) salt concentrations. In addition, these proteins are coagulated by heat. The classic example of this type of protein is ovalbumin (i.e., egg white).

Globulins are insoluble in pure water but soluble in dilute salt solutions and insoluble at high salt concentrations. Globulins show the classical salting in (i.e., their solubility increases when low salt concentrations are added to water) and salting out (see above).

Prolamins are proteins soluble in aqueous 70% ethanol. The prolamin of wheat is named *gliadin,* those of maize, sorghum, oats, and barley are *zein, kafirin, avenin,*and *hordein,* respectively.

Glutelins are proteins soluble in dilute acids or bases. The glutelin of wheat is named*glutenin,* that of rice *oryzenin,* and that of barley *hordenin.*

This type of classification is still used today, as it has stood the test of time. It gives reproducible results that provide useful information about cereal proteins. However, the fractions obtained show much complexity and are mutually contaminated. For example, prolamins have limited solubility in water, particularly at low ionic strength. In general, each group has subgroups and certainly none of the groups consists of a single pure protein.

In addition, some proteins do not appear to fall into any of the four solubility groups. Wheat, barley, and rye contain glycoproteins (i.e., proteins covalently bound to a carbohydrate), which are soluble in water but not coagulated by heat. Wheat, maize, sorghum, and rice have proteins not solubilized by dilute acids or bases. Clearly, better classification schemes and methods are required. However, most schemes suggested to date are so complicated that they quickly become useless. Therefore, it appears better to use solubility as the first classification scheme and rely on more-elaborate analytical separating techniques to further identify proteins.

Properties of the Osborne Protein Groups

Most of the enzymes (also referred to as "biocatalysts") are found in the albumin or globulin groups. From the germination of the seed to grain ripeness, an essentially unlimited number of enzymes is undoubtedly present in the grain, at least part of the time. When viewed from that perspective, essentially all plant metabolic enzymes are present. The albumins and globulins are concentrated in the aleurone cells, bran, and germ, with somewhat lower concentrations in the endosperm. Nutritionally, the albumins and globulins have a very good amino acid balance. They are relatively high in lysine, tryptophan, and methionine, three essential amino acids that occur in relatively low concentrations in cereals.

The prolamins and glutelins are the storage proteins in cereals. The plant stores these proteins for use by the seedling during germination. These proteins are found only in the endosperm in cereals and are not found in the pericarp or germ. The prolamins of all cereals are low in the nutritionally important amino acids lysine, tryptophan, and methionine. The glutelins appear to be more variable in amino acid composition. In wheat, the composition of the glutelins is similar to that of the prolamins. However, this is not true in maize. The glutelins of maize have a much higher lysine content than do the prolamins. In maize, at least, and probably in the other cereals, the ratio of the various protein groups is under genetic control. Certain varieties of maize have different ratios of protein. For example, high-lysine maize mutants have two to three times as much albumin and globulin, one third as much prolamin, and much higher levels of glutelins than normal maize does. Because the prolamins are low in lysine, the net result of these differences is maize cultivars with much higher lysine contents.

Finally, the relative proportions of the various protein groups change with the protein content of a cereal grain. At low protein content (Fig. 3.5), the proportion of albumins and globulins, expressed as a percentage of the total protein in the sample, is much higher than at higher protein content. Thus, at higher protein contents, the proportion of the storage proteins glutelin and prolamin are much higher than at low total-protein contents. This appears logical if one remembers that the albumins and globulins have physiological functions as enzymes and the prolamin and glutelin as storage proteins. As the plant produces more protein, less is required for enzyme functions and more can be stored as storage protein.

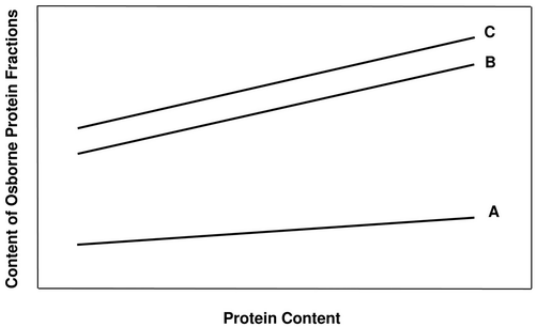


Fig. 3.5. Conceptualized graph showing the levels of protein in the sum of albumin and globulin (A), gliadin (B), and glutenin (C) Osborne protein groups as a function of the protein content of wheat. (Courtesy A. Bijttebier)

In this context, it is of note that certain cultivars of any given cereal consistently produce grain of higher protein content than others. Therefore, cereal protein content is, to a certain degree, affected by the genotype, and plant breeding can therefore be directed toward either higher or lower protein contents. However, the overall protein content in a sample is affected more strongly by the environment than by the genotype. The wide variation is thus the result of both environmental and genetic effects.

While protein is synthesized throughout the fruiting period of the plant, starch synthesis starts later during fruiting and accelerates as maturity approaches. Thus, good growing conditions providing adequate moisture and nutrients late in the fruiting period lead to good yields of starch and grain, but protein contents are relatively low. Of major importance, of course, is the availability of nitrogen throughout the growing period. An excess of nitrogen early in the growth cycle produces an increase in yield, whereas an excess of nitrogen later in the cycle (after flowering) results in increased protein content. Other environmental factors that might result in high protein are drought, frost damage, and certain diseases. Both the frost and the diseases can stop the normal deposition of starch and other constituents, including protein. However, since starch synthesis predominates later in the growing period, the net result is a higher protein content.

Wheat Proteins

White wheat flour typically contains 1% less protein than the wheat from which it was milled. Considering that the flour makes up slightly more than 70% of the total milling product, this shows that the nonflour part, or mill-feed, has a considerably higher protein concentration than the milled endosperm. The proteins in the pericarp and aleurone, which are the major components of mill-feed, do not contain any gluten proteins. Table 3.1 lists the amino acid composition of wheat and flour. The flour is higher in glutamic acid and proline, while wheat is higher in lysine, arginine, and aspartic acid and hence has a better nutritional profile.

TABLE 3.1
Amino Acid Composition[a] (g/100 g of protein) for Wheat, Flour, and Water- and Salt-Soluble Proteins from Wheat

Amino Acid	Wheat	Flour	Albumins	Globulins
Lysine	2.8	2.0	4.8	5.1
Histidine	2.4	2.1	2.2	3.1
Arginine	4.4	3.2	5.2	10.7
Aspartic acid	4.9	3.8	7.7	8.0
Threonine	2.8	2.6	3.8	3.8
Serine	4.5	4.5	4.0	4.5
Glutamic acid	32.3	35.4	24.6	19.2
Proline	10.6	11.7	9.4	4.8
Glycine	4.0	3.4	4.2	4.8
Alanine	3.5	2.9	5.1	5.4
Cysteine	2.4	2.5	2.8	5.2
Valine	4.2	4.1	6.1	6.5
Methionine	1.2	1.2	1.9	2.0
Isoleucine	3.4	3.6	3.3	3.9
Leucine	6.7	6.7	7.2	7.4
Tyrosine	1.7	1.4	2.6	3.2
Phenylalanine	4.6	4.8	4.9	4.6
Ammonia	3.6	4.0	...	...

[a] Data from Shoup et al (1966).

GLUTEN AND NONGLUTEN PROTEINS

Among the cereal flours, only wheat flour, when mixed with the appropriate amount of water, has the ability to form a strong, cohesive dough that retains gas and produces a light, aerated baked product. This property can be ascribed to the wheat storage proteins glutenin and gliadin, which together form gluten. Gluten is relatively easy to isolate from wheat flour dough because it is insoluble in water. Indeed, the starch and the water solubles can be removed from the gluten by gently washing dough under a small stream of water. After the washing, a rubbery ball of gluten is left. Gluten was first isolated by this method by Beccari in Italy in 1728. It was the first protein isolated from plant material. Before that time, proteins were thought to come only from animal sources. As isolated from flour, gluten contains (on a dry basis) about 80% protein and 8% lipids, with the remainder being minerals and carbohydrate.

Gliadin and glutenin can be conveniently separated by solubilizing the gluten in dilute acid, adding ethyl alcohol to a final concentration of 70% alcohol, and then adding sufficient base to neutralize the acid. After the mixture stands overnight at 4°C, the glutenins precipitate, leaving the gliadins in solution.

Gliadin is extremely sticky when hydrated (Fig. 3.6). It has little or no resistance to extension and appears to be responsible for the dough's cohesiveness. In contrast, glutenin is resilient and rubbery but prone to rupture. The glutenin apparently gives dough its property of resistance to extension, i.e., its elasticity.

Fig. 3.6. Physical properties of gluten **(left)** and its components: gliadin **(center)** and glutenin**(right).** (Reprinted, with permission, from Dimler 1963)

While the predominant proteins in wheat flour are the gluten proteins, about 15% of the total protein of flour is made up of soluble proteins (albumins and globulins).

GLUTEN SYNTHESIS

Gliadins and glutenin subunits (GS) are gene products. A posttranslational process forms the glutenin polymer, which is found in the wheat endosperm. Gluten has been reported in the endosperm as early as six days after anthesis (flowering). Protein bodies, the site of gluten deposition in the endosperm, have been reported as soon as 12 days after anthesis. The protein bodies increase in size, up to 20 μm in diameter, as the endosperm develops. When the grain is mature and the kernel starts to desiccate, the protein bodies are distorted by the starch granules and completely lose their identity in the mature seed. Protein bodies from immature seeds have been shown to contain gluten, both gliadin and glutenin, and essentially no albumins and globulins.

AMINO ACID COMPOSITION OF WHEAT PROTEIN

The amino acid composition of the soluble proteins (Table 3.1) is much different than that of the total flour proteins. In general, the soluble proteins are lower in glutamic acid and proline and much higher in lysine, arginine, and aspartic acid. This is similar to the amino acid composition of the mill-feed proteins.

The glutamic and aspartic acid levels listed in Table 3.1 must be considered as the sums of these acids and their respective amidated forms glutamine and asparagine. This can be deduced from the high levels of ammonia that are also listed in the table and that result from the breakdown of glutamine to form glutamic acid during the acid hydrolysis. Essentially all of the glutamic acid occurs as glutamine in the native proteins. Because of the high nitrogen content caused by the high level of glutamine in wheat, wheat protein content is estimated as its nitrogen (N) content times a factor of 5.7, rather than the factor of 6.25 used with most other cereals.

The amino acid composition in Table 3.2 shows that gluten proteins are unique in terms of glutamine, proline, and hydrophobic and basic amino acid contents. Gluten is very high in glutamine (about 35% of the total protein). Stated another way, one in every three amino acids in gluten is glutamine. As discussed above, glutamine is analyzed as glutamic acid.

TABLE 3.2
Amino Acid Composition of Wheat Gluten, Gliadin, and Glutenin (mol/10^5 g of protein)[a]

Amino Acid	Gluten	Gliadin	Glutenin
Arginine	20	15	20
Histidine	15	15	13
Lysine	9	5	13
Threonine	21	18	26
Serine	40	38	50
Aspartic acid	22	20	23
Glutamic acid	290	317	278
Glycine	47	25	78
Alanine	30	25	34
Valine	45	43	41
Leucine	59	62	57
Isoleucine	33	37	28
Proline	137	148	114
Tyrosine	20	16	25
Phenylalanine	32	38	27
Tryptophan	6	5	8
Cysteine	14	10	10
Methionine	12	12	12
Ammonia	298	301	240

[a] Source: Kasarda et al (1971).

The next most notable point about gluten's amino acid composition is the high level of proline, about 14% of the protein or about one in seven residues. Because proline's amino group is involved in a ring structure, peptide bonds of proline are not flexible. Thus, there is a rigid kink in the protein chain wherever proline occurs, and the protein cannot readily form into an α-helix. Measurements of helical structure in gluten have generally given low values. This does not necessarily mean that the gluten proteins have no ordered structure. It implies only that the ordered structure, if any, is not the α-helix with which we are familiar.

The amino acid composition of gluten proteins also shows that about 35% of the total amino acids have hydrophobic side chains. It has been suggested that, at levels above 28% hydrophobic side chains, the apolar residues are not accommodated in a hydrophobic core of the protein. Thus, the amount of surface hydrophobicity on the protein increases, encouraging hydrophobic interactions. Therefore, it is believed that hydrophobic interactions between gluten proteins play an important role in stabilizing gluten structure and in determining the rheological and baking properties of flour. Further evidence of the gluten proteins' hydrophobic nature is their effectiveness in binding lipids. Wheat flour contains about 0.8% lipids extractable with petroleum ether. However, after the flour is wetted and mixed into a dough, only about 0.3% of the lipids are extractable from the lyophilized dough. Presumably, under such conditions, the remaining 0.5% has been hydrophobically bound to the proteins.

The gluten proteins are also notably low in the basic amino acids. The low level of lysine is well known. Thus, the gluten proteins have essentially no potential negative charges (glutamic acid and aspartic acid occur as their amides) and only low levels of potential positive charges. The conclusion from these facts must be that the gluten proteins have a low charge density. That low level of charges means that the repulsion forces within the protein are low and, thus, the protein chains can interact with each other quite readily, a condition that appears to be necessary for dough formation (see Chapter 12).

The low level of lysine makes it the limiting amino acid when wheat is used in animal diets. If protein is limited in the diet, addition of other proteins with high lysine contents or addition of the free amino acid lysine greatly improves protein utilization. However, in Western diets, the average person eats many times his or her daily requirement for protein, and, therefore, the amino acid balance and the lysine content of the protein are of little or no importance.

GLUTENIN

Wheat glutenin is a heterogeneous mixture of disulfide-linked polymers of glutenin subunits (e.g., GS-S-S-GS) that can be liberated upon treatment with reagents that promote thiol-disulfide exchange reactions. An example is the reaction with cysteine (Cys-SH):

$$\text{GS-S-S-GS} + \text{Cys-SH} \rightarrow \text{GS-S-S-Cys} + \text{GS-SH}$$

The number of GS found in wheat cultivars as well as their relative amounts appear to be determined mainly by the genotype. In other words, it is the genetics of the wheat variety that determines which GS are present and in what amounts. Interestingly, the environment appears to have relatively little effect on the number or the relative amount of individual proteins (gliadin or GS) in a wheat sample. This fact has allowed methods to be developed to identify wheat cultivars by their electrophoretic patterns.

Since the properties of a polymer such as glutenin depend on those of its building blocks (i.e., GS in this case), much effort has been devoted to characterizing the latter. Two types of GS constitute the building blocks of the polymer. These are high molecular weight GS (HMW-GS) and low molecular weight GS (LMW-GS).

More than 20 different HMW-GS have so far been detected in wheat varieties, and new HMW-GS are still being found. In general, two types of HMW-GS, a higher-MW x-type and a lower-MW y-type, can be distinguished. The total number of different HMW-GS found in common wheat varieties varies from three to five. In rare cases, however, six HMW-GS can occur. The molecular weight of HMW-GS varies from about 65,000 to about 90,000. Both x-type and y-type HMW-GS have a typical three-domain structure consisting of relatively small N- and C-terminal domains flanking a major central domain (Fig. 3.7). While the C-terminal domain has a constant size (42 amino acid residues), and the N-terminal domain varies only slightly in length (about 80–90 amino acid residues for x-type HMW-GS and 104 amino acid residues for y-type HMW-GS), the length of the central domain is much more variable (750–850 amino acid residues for x-type HMW-GS and 600–700 amino acid residues for y-type HMW-GS). All cysteine residues are located near the ends of the HMW-GS (Fig. 3.7). The secondary structure of the N- and C-terminal domains is predominantly α-helix, and the central domain consists of repetitive sequences that are rich in proline, glutamine and glycine. The latter are believed to produce a series of overlapping β-reverse-turns that may form a "β-spiral" super-secondary structure.

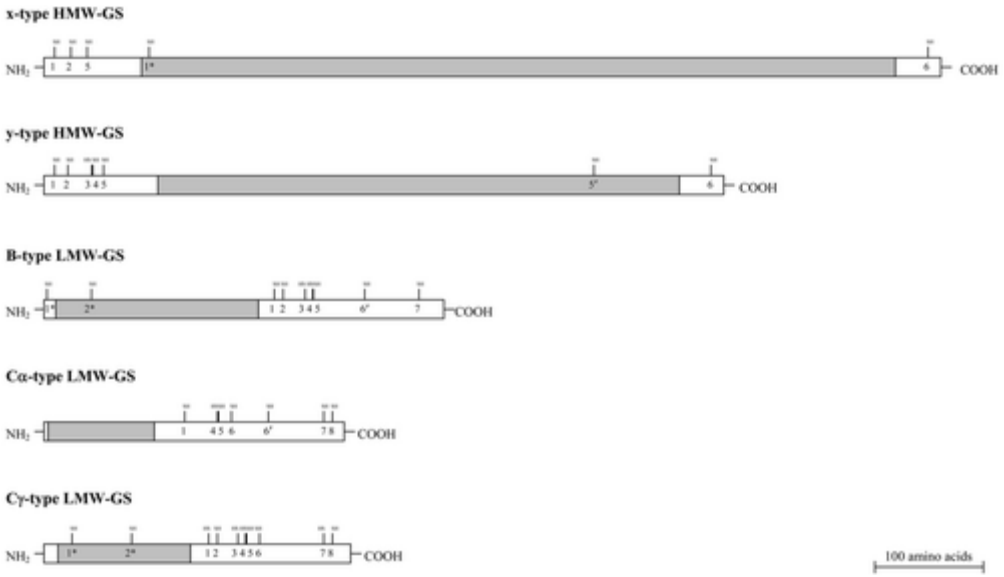


Fig. 3.7. Schematic representation of the structure of the main classes of wheat high molecular weight (HMW) and low molecular weight (LMW) glutenenin subunits (GS). (D-type LMW-GS have been omitted.) Comparative lengths of the repetitive (in gray) and nonrepetitive (in white) domains are shown, and positions of the conserved and unconserved cysteine residues found in all representatives of the GS class sequenced thus far are indicated by Arabic numerals and Arabic numerals with a prime, respectively. Unconserved cysteine residues that are not present in all representatives of the GS class are indicated by Arabic numerals with an asterisk. SH = sulfhydryl group, HSSH = two adjacent sulfhydryl groups. (Adapted from Veraverbeke and Delcour 2002)

LMW-GS represents a more heterogeneous and less well-characterized group of GS than HMW-GS. The estimated number of different LMW-GS in a single wheat variety varies from seven to 16. There are B-, C- and D-LMW-GS, and, taken as a group, their molecular weight varies between 30,000 and 60,000.

Weight ratios of HMW-GS to LMW-GS varying between 0.18 and 0.74 have been reported for wheat glutenin. This suggests that, on a weight basis, the LMW-GS content (55–85%) may vary from only slightly higher to almost sixfold higher than the HMW-GS content (15–45%). Based on the size difference of HMW-GS and LMW-GS, one can expect the molar excess of LMW-GS over HMW-GS to be about double the weight excess.

GLUTENIN STRUCTURE

The final glutenin as found in the wheat kernel is formed by a posttranslational process. The nature of the process is not fully understood. Environmental effects are known to affect the process. The result is a polydisperse protein that has essentially a linear character. Such a protein would be expected to behave much as synthetic linear polymers do. The physical properties of these polymers depend on their molecular weight. Small polymers result in a viscous liquid. As the molecular weight increases, the polymer becomes an elastomer (i.e., it possesses elastic properties) with low strength and high extensibility. Above a molecular weight of about 10^5, the polymers are subject to molecular entanglements and show rubbery properties. This explains the elastic properties of glutenin and therefore gluten. It is also true that the larger the polymer, the greater the elastic property.

Nearly all sulfhydryl groups of glutenin are involved in disulfide bonds. One of the first questions one can ask about the structure of glutenin polymers is whether HMW-GS and LMW-GS occur in separate polymers and/or whether mixed polymers are formed. However, while evidence was found for polymers consisting solely of LMW-GS and while polymers consisting solely of HMW-GS clearly are a possibility, it is generally assumed that most glutenin polymers are a mixture of both. The detection with two-dimensional sodium dodecyl sulfate–polyacrylamide gel electrophoresis of oligomers containing both HMW-GS and LMW-GS after partial reduction of dough supports the existence of such mixed polymers.

However, several studies suggest that GS are not randomly associated. Indications for a nonrandom association of GS initially came from partial reduction of glutenin. Glutenin fragments solubilized by low concentrations of reducing agent do not have the average GS composition of the native polymers.

However, the hypothesis that glutenin has a highly ordered structure can be criticized from the viewpoint of biosynthesis. Biosynthesis of such glutenin structure would require a very complex mechanism. It seems illogical that natural selection would have led to a very structurally complex molecule that functions only as a storage protein. Nevertheless, some degree of order in the structure of glutenin may arise simply because of difference in the timing of biosynthesis of structurally different GS. For example, even when HMW-GS do not react preferentially with each other, a glutenin structure consisting of a backbone of solely HMW-GS with branches consisting of solely LMW-GS could be the result of HMW-GS being biosynthesized before LMW-GS.

GLIADIN

The number of gliadin proteins in wheat cultivars as well as their relative amounts appear to be determined by the genotype, as is the case for the GS. Gliadins represent a highly heterogeneous mixture of monomeric gluten proteins. Three structurally distinct groups of gliadins (i.e., α-, γ-, and ω-types) can be distinguished. Comparison of amino acid sequences revealed that α-type and γ-type gliadins are both related to the LMW-GS (see above). Cysteine residues in α-type (six cysteine residues) and γ-type (eight cysteine residues) gliadins are all involved in conserved intrachain disulfide bonds. This probably explains why, at ambient temperatures, they are not involved in polymerization reactions such as clearly occur with GS. In contrast to the other gliadin types, ω-type gliadins lack cysteine residues and also have a very low level of methionine. These gliadins are classified separately as sulfur-poor prolamins.

Proteins in Other Cereals

The proteins of cereal grains other than wheat do not have dough-forming properties. Rye and triticale may come closer than the others but still do not form a viscoelastic dough. In many parts of the world, the so-called "coarse" grains (maize, sorghum, and pearl millet) are used to make dough-type products, such as the tortilla of Central and South America or the roti or chapatti of India. The dough produced is quite different from wheat flour dough. The major cohesive force appears to be that created by the surface tension of water rather than by the cereals' proteins (see Chapter 16).

MAIZE PROTEIN

Maize protein occurs in the endosperm as discrete protein bodies and as a matrix protein (see Chapter 1). The protein bodies are composed mainly of a prolamin called "zein." The endosperm contains about 5% albumins plus globulins, about 44% zein, and about 28% glutelins. The remaining protein is mainly a zein fraction (about 17%) cross-linked by disulfide bonds that is soluble in alcoholic media containing mercaptoethanol (a disulfide-bond-breaking agent) or a similar solvent.

Table 3.3 lists the amino acid composition of maize endosperm. Maize proteins have a high level of glutamic acid but only about half the level found in wheat. The low level of ammonia nitrogen shows that the glutamic acid is present as the acid and not as the amide.

TABLE 3.3
Amino Acid Composition (g/100 g of protein) of Maize and Sorghum Endosperm Proteins

Amino Acid	Maize Endosperm[a]	Sorghum Endosperm[b]
Lysine	2.0	2.8
Histidine	2.8	2.3
Ammonia	3.3	...
Arginine	3.8	4.5
Aspartic acid	6.2	7.7
Glutamic acid	21.3	22.8
Threonine	3.5	3.3
Serine	5.2	4.2
Proline	9.7	7.7
Glycine	3.2	3.3
Alanine	8.1	9.2
Valine	4.7	5.1
Cystine	1.8	1.3
Methionine	2.8	1.7
Isoleucine	3.8	4.0
Leucine	14.3	13.2
Tyrosine	5.3	4.3
Phenylalanine	5.3	5.1

[a] Data from Mertz et al (1966).
[b] Adapted from Wall and Paulis (1978); data from Pomeranz et al (1973).

Of particular interest in the amino acid composition is the high level of leucine. This amino acid has been implicated in the incidence of pellagra (a B-vitamin deficiency disease). Both the water- and salt-soluble fractions and the glutelin fraction appear to have a reasonably good amino acid balance (Table 3.4). The zein and cross-linked zein fractions are low in lysine and high in leucine. Also of interest is the high level (18%) of proline in the cross-linked zein fraction. Maize, like sorghum and pearl millet, has both vitreous and opaque parts to its endosperm (see Chapter 1), and both the distribution of protein fractions and their amino acid composition differ in these two types of endosperm.

TABLE 3.4
Amino Acid Composition (g/100 g of protein) of Maize Proteins Extracted with Certain Solvents[a]

Amino Acid	Albumin and Globulins	Zein	Cross-Linked Zein	Glutelins
Lysine	4.18	0.46	0.57	4.38
Histidine	2.38	1.28	6.77	2.52
Ammonia	2.36	2.72	2.23	1.68
Arginine	7.35	2.16	3.46	4.49
Aspartic acid	10.06	5.12	1.73	7.90
Threonine	4.60	2.93	3.86	4.04
Serine	5.23	5.11	4.03	5.15
Glutamic acid	14.70	22.18	23.61	16.70
Proline	5.06	9.84	17.83	6.95
Glycine	6.69	2.02	4.72	4.12
Alanine	7.10	9.01	4.92	7.49
Cysteine/2	3.73	2.27	0.87	0.64
Valine	5.28	3.43	6.07	5.27
Methionine	1.72	0.94	1.63	2.86
Isoleucine	4.25	3.53	2.23	3.97
Leucine	6.50	17.49	10.23	12.09
Tyrosine	3.25	4.54	2.52	4.72
Phenylalanine	3.57	6.11	2.56	5.31

[a] Data from Robutti et al (1974).

SORGHUM PROTEIN

In many ways, the proteins of sorghum are similar to those of maize. The prolamin from sorghum, kafirin, resembles zein in amino acid composition, and the total amino acid compositions of sorghum and maize are similar (Table 3.3). The major difference between the two grains appears to be in the solubility of their prolamins and in the amount of cross-linked prolamins. Kafirin is not soluble in 70% ethanol at room temperature, but it is soluble in this solvent at 60°C. It is also soluble in 60% *t*-butyl alcohol at room temperature.

The level of cross-linked kafirin in sorghum is about 31%, compared to about 17% cross-linked zein in maize. The difference is partly made up by the prolamin fractions: 17% kafirin in sorghum and 44% zein in maize. As in maize, the prolamins (kafirin and cross-linked kafirin) are very low in lysine.

PEARL MILLET PROTEIN

Pearl millet, like sorghum and maize, is a coarse grain, and the three grains are similar in many respects. The amino acid composition of pearl millet varies quite widely, which may reflect the fact that the grain has not been bred extensively. The distribution of protein in pearl millet endosperm appears to be more similar to that of maize than to that of sorghum. Pearl millet also has a high leucine content, but the ratio of leucine to isoleucine is much lower than in sorghum. The ratio is thought to be important in the vitamin deficiency disease pellagra.

OAT PROTEIN

Oats are unique among the cereals in that their amino acid balance is quite good from a nutritional standpoint (Table 3.5). It compares favorably with the standard protein established by the Food and Agriculture Organization of the United Nations. In addition, the protein content of oat groats is, in general, much higher than that found in other cereals. The relatively good amino acid balance is stable even at higher protein content, also in contrast to the case with other cereals. So, in many respects, oats are clearly superior to the other cereals in nutritional content.

TABLE 3.5
Amino Acid Composition (as % of protein) of Oats and Certain of Its Fractions[a]

Amino Acid	Total Oats	Groats	Endosperm	FAO[b] Scoring Pattern
Lysine	4.2	4.2	3.7	5.5
Histidine	2.4	2.2	2.2	...
Ammonia	3.3	2.7	2.9	...
Arginine	6.4	6.9	6.6	...
Aspartic acid	9.2	8.9	8.5	...
Threonine	3.3	3.3	3.3	...
Serine	4.0	4.2	4.6	...
Glutamic acid	21.6	23.9	23.6	...
Cysteine	1.7	1.6	2.2	...
Methionine	2.3	2.5	2.4	3.5
Glycine	5.1	4.9	4.7	...
Alanine	5.1	5.0	4.5	...
Valine	5.8	5.3	5.5	5.0
Proline	5.7	4.7	4.6	...
Isoleucine	4.2	3.9	4.2	4.0
Leucine	7.5	7.4	7.8	7.0
Tyrosine	2.6	3.1	3.3	...
Phenylalanine	5.4	5.3	5.6	6.0

[a] Adapted from Youngs et al (1982).
[b] Food and Agriculture Organization of the United Nations.

As suggested by the above, the distribution of protein in oats is different than in the other cereals. The dilute alcohol-soluble prolamins of oats, i.e., the avenins, constitute only 10–15% of the total protein. The predominant class appears to be the globulins (about 55%), with glutelins making up about 20–25%.

RICE PROTEIN

In general, the protein content of rice is lower than that of the other cereals. It averages about 7% and is calculated as N × 5.95. This is lower than the factor employed for other cereals but higher than that for wheat. The amino acid composition is relatively well-balanced, with lysine constituting about 3.5% of the total protein. Lysine is still the first limiting amino acid, followed by threonine. The reason why feeding trials show threonine to be limiting is not clear, as analysis shows adequate levels. The level of glutamic acid is relatively low (less than 20%).

The rice endosperm proteins occur mainly (up to 95%) as protein bodies varying in size from 1 to 4 μm. A small proportion of the rice protein is associated with the starch granules. In rice, much as in maize, protein bodies remain as discrete entities in the mature grain. This is unlike the case in other cereals, including wheat, barley, and rye, where all or most of the protein bodies collapse during the later stages of development of the grain. Rice has two types of protein bodies. The first is a spherical body. It contains most of the prolamin and accounts for about 20% of the total protein content of the rice endosperm. The second has an irregular form. It consists mainly of glutelins and contains about 60–65% of the rice endosperm proteins. The subaleurone layer of the endosperm contains both types of protein bodies, whereas the central endosperm contains only the spherical type.

The classical Osborne fractionation of the proteins shows that the glutelin (i.e., oryzenin) is the major fraction, being about 80% of the total protein, and that the prolamin fraction accounts for only 3–5% of the total protein.

It is difficult to study the rice glutelins, as they are soluble only at pH values lower than 3.0 and higher than 10.0. Extraction media other than sodium hydroxide solutions, including those containing sulfite or mercaptoethanol, are less effective. Rice glutelins are homologous to the dilute, salt-soluble 11S globulins of the leguminosae. They consist of two groups of subunits: a basic and an acidic polypeptide with molecular weights of about 22,000 and 38,000, respectively. These two groups are formed by cleavage of precursor with a molecular weight of about 57,000. Despite the similarity to the 11S globulins, these proteins are classified as glutelins because posttranslational modifications result in mature proteins that are insoluble in dilute salt solutions. Although the reason for the low solubility is not completely clear, it has been attributed to extensive subunit aggregation and glycosylation. The prolamin group contains polypeptides of mol wt 10,000, 13,000, and 16,000.

RYE PROTEIN

The amino acid composition of rye proteins is slightly better from a nutritional standpoint than those of most of the other cereals, oats being a notable exception. The lysine content is higher in rye than in wheat or most other cereals (about 3.5% of the protein). Tryptophan is the first limiting amino acid. The glutamic acid content is about 25%, and the leucine content is notably low (about 6%).

The reason for this well-balanced amino acid composition is the relatively high levels of albumins and globulins in rye. The albumins are about 35% of the total protein and the globulins about 10%. Rye prolamins, i.e., the secalins, are about 20% of the total. The glutelins, soluble in dilute acid, are only about 10% of the total. However, about 20% of the protein is not solubilized by the normal Osborne scheme.

TRITICALE PROTEIN

Triticale has a protein distribution similar to that of rye. In general, the levels of the water- and dilute-salt-soluble proteins are slightly lower than for rye, while those of the prolamin are slightly higher.

BARLEY PROTEIN

Most barley is harvested with the hull (lemma and palea) intact. The hull makes up about 10% of the total kernel. In general, the hull is low in protein, but its proteins are relatively high in lysine. The germ proteins are also high in lysine, and the endosperm proteins are lower (about 3.2%) but still higher than in many cereals. The endosperm is relatively high in glutamic acid (about 35%) and proline (about 12%). The glutamic acid is present as the free acid and not as the amide. The prolamin of barley, i.e., hordein, makes up about 40% of

the barley protein and is very low in lysine. The glutelins (hordenin) and especially the albumins and globulins are relatively high in lysine.

Enzymes Hydrolyzing Protein

Enzymes that hydrolyze proteins are called "proteases." They invariably attack the peptide bond between the amino end of one amino acid residue and the carboxyl end of the adjacent amino acid residue in a protein (Fig. 3.8).

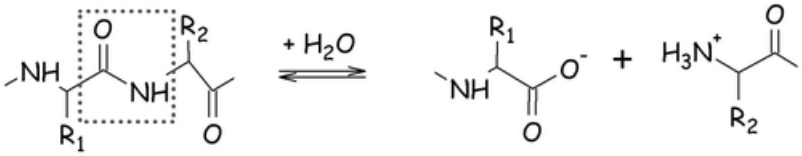


Fig. 3.8. Hydrolysis of a peptide bond (in the dotted box) by proteolytic enzymes. (Courtesy M. Verswyvel)

There are both endo- and exoproteases. Endoproteases (or proteinases) hydrolyze peptide bonds somewhere along the protein chain and result in two peptides being formed. The exoproteases, which attack the ends of the protein chain and remove one amino acid at a time, are called "carboxypeptidases" when acting from the carboxy terminus or "aminopeptidases" when acting from the amino terminus. In general, proteolytic enzymes can be classified on the basis of their catalytic mechanism as serine, metallo-, aspartic, and thiol or cysteine proteases.

SERINE PROTEASES

Serine proteases (EC 3.4.21) require a hydroxyl function at the active site in order to function properly. Optimal activity tends to be in the alkaline pH range, usually between about 7.5 and 10.5. Trypsin and chymotrypsin are the classic examples of this type of proteinase. Serine proteinases are responsible for almost all of the proteolytic activity during the early stages of wheat grain development, and their impact decreases at later stages. The localization of serine proteases in developing and germinating embryos suggests that their physiological role is in protein metabolism (processing or turnover) rather than in storage protein degradation.

METALLOPROTEASES

Metalloproteases (EC 3.4.24) require the presence of a metal ion such as zinc in their active site. These proteases are present during the later stages of wheat grain development.

ASPARTIC PROTEASES

Aspartic proteases (EC 3.4.23), earlier named "acid" or "carboxyl" proteases, are a widely distributed class of proteases present in animals, microbes, viruses, and plants. All aspartic proteinases contain two aspartic acid residues in their active site, are active at acidic pH, and have specificities for peptide bonds located between amino acid residues with large hydrophobic side chains. The best-known members of this group are pepsin, chymosin, rennin, cathepsin D, and yeast proteinase A. Both wheat and barley seeds contain prominent aspartic proteinase activity.

CYSTEINE PROTEASES

Proteases in which the nucleophile (electron donor) is the sulfhydryl group of a cysteine residue are known as "cysteine-type" peptidases (EC 3.4.22). The catalytic mechanism is similar to that of the serine-type proteases in that a nucleophile and a proton donor or general base are required, and the proton donor in all cysteine proteases in which it has been identified is a histidine residue, as in the majority of the serine-type proteases. The pH range in which these enzymes function is usually rather broad, with greater activity below pH 7.0. Germinated wheat and barley contain cysteine proteinase activity.

Protease Inhibitors

Protease inhibitors in plant tissues with a protein structure are believed to be involved in the regulation of some endogenous proteolytic activities as well as in the defense of plant tissues from insects by inhibition of the proteinases present in insect alimentary tracts. Wheat contains aspartic-protease-inhibiting activity, and barley, wheat, and rice contain cysteine-protease-inhibiting activity.

CHAPTER 4: Minor Constituents

Starch and the (storage) protein are quantitatively the most important (and hence the major) constituents of cereals. In addition to these major constituents, cereals also contain a whole array of minor constituents. Some of these, such as phytic acid, vitamins, and the nonstarch polysaccharides, are important from a nutritional point of view. In addition, constituents such as nonstarch polysaccharides and lipids have a great impact on the functional properties of cereal-based products. We here focus on some of the minor cereal constituents as well as on the enzyme systems that have particular impacts on nonstarch polysaccharides, phytic acid, and lipids. The starch-degrading enzymes, α- and β-amylase, which are also important biocatalysts, were described in Chapter 2.

Nonstarch Polysaccharides

In cereal science, the term *nonstarch polysaccharides* is generic for cellulose, arabinoxylan, β-D-glucan, and arabinogalactan. These polysaccharides differ from starch in that they are not found in an insoluble granule. They also differ from the starch components amylose and amylopectin by the nature of their constituent monosaccharides and/or by the nature of their linkages. They are dietary fiber constituents, and health-promoting effects have been ascribed to some of them. The noncellulose part of the cereal nonstarch polysaccharides is sometimes referred to as "hemicellulose." Hemicelluloses can either be water-extractable or water-unextractable.

CELLULOSE

Cellulose is the major structural polysaccharide of plants. It has a quite simple structure, as it is composed of β-1,4-linked D-glucose units (Fig. 4.1). It is a large polymer, its chain length apparently being determined by its source. Because it is subject to degradation during isolation, samples from the same source can vary widely in size. Because it is unbranched and has essentially a linear configuration, it associates strongly with itself and is very insoluble. In its native state, cellulose is partially crystalline. The high degree of order and insolubility, together with its β linkage, make the polymer resistant to many organisms. Humans, for instance, do not have the cellulase enzymes necessary to degrade cellulose. In plant material, cellulose is usually found associated with other nonstarch polysaccharides and lignin in cell walls.

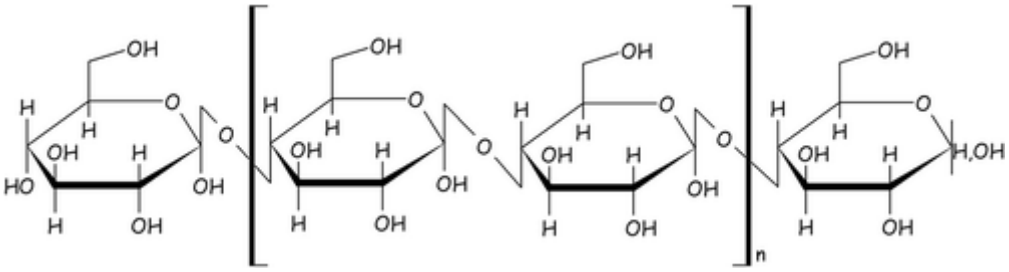


Fig. 4.1. Basic structure of cellulose, showing β-1,4-linked glucose units. The number of repetitive glucose units is represented by n. (Courtesy M. Verswyvel)

Cellulose is a major component of straw, fodder, and hulls. It may make up 40–50% of such plant parts. Thus, kernels that are harvested with their hulls (rice, barley, and oats) contain more cellulose than other kernels. The pericarp of cereals also is quite rich in cellulose (up to 30%).

Cereal endosperm tissue contains little, if any, cellulose. Reported values are usually 0.3% or less. Given the difficultly of determining cellulose quantitatively, this low value probably means that there is no cellulose in the endosperm.

CEREAL HEMICELLULOSES IN GENERAL

Taken together, hemicelluloses encompass the nonstarch, noncellulosic plant polysaccharides. They are widely distributed in the plant kingdom and, in general, are thought to make up the cell walls and the cementing material that holds cells together (Fig. 4.2). Chemically, they are quite diverse, varying in composition from a single sugar, such as is found in β-D-glucans, to polymers that may contain pentoses, hexoses, and phenolics. D-Xylose, L-arabinose, D-galactose, D-glucose, D-glucuronic acid, and 4-*O*-methyl-D-glucuronic acid are some of the more common building blocks of cereal hemicelluloses. Some of these polymers also contain ferulic acid (see below).

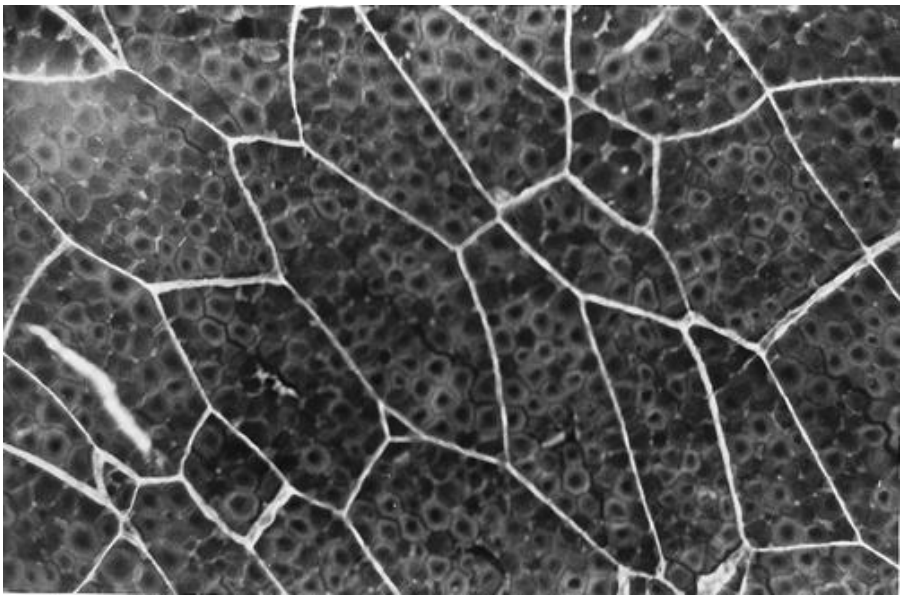


Fig. 4.2. Photomicrograph showing the walls of cells in the endosperm of a sorghum kernel. (Courtesy J. Faubion)

Much of the confusion concerning the structure of the hemicelluloses stems from difficulty in obtaining a pure chemical entity to study. An additional problem is the lack of definitive tests to show whether one has a pure entity. Hemicelluloses come in many sizes and with many different chemical compositions.

WHEAT HEMICELLULOSES

The predominant wheat hemicellulose is arabinoxylan. Wheat typically contains about 6–7% arabinoxylan. It also contains small levels of an arabinogalactan peptide. All of the wheat nonstarch polysaccharides are sometimes referred to by the generic term*pentosan.* However, it seems more appropriate to refer to these constituents by their respective names. The different subgroups of pentosans have different physicochemical properties, and they are not in all cases built up exclusively from pentose monosaccharides.

Arabinoxylan and Glucuronoarabinoxylan

Wheat endosperm contains between 1.5 and 2.5% arabinoxylan, which is the predominant component of the endosperm cell walls, as it makes up about two-thirds of the cell wall dry matter. In addition, wheat endosperm cell walls typically contain about 20% β-D-glucan (see below). In contrast to what might be expected for a structural component of the cell wall, 25–33% of the 1.5–2.5% arabinoxylan found in wheat flour endosperm is water-extractable.

While both water-extractable and water-unextractable arabinoxylan exist, they have one general structure, and it therefore seems logical that the water-extractable arabinoxylan is a building block or precursor of the water-unextractable material. Arabinoxylan is made up of β-1,4-linked D-xylopyranosyl residues, with monomeric α-L-arabinofuranose substituted at the C(O)-3 and/or the C(O)-2 position. Ferulic acid can be coupled to the C(O)-5 position of arabinose through an ester linkage (Fig. 4.3). An important parameter of arabinoxylan is the arabinose-to-xylose ratio, with a typical average value of 0.5–0.6 for the wheat endosperm arabinoxylan population. When increasing levels of alcohol are added to solutions of such arabinoxylan, subfractions of increasing arabinose-xylose ratio precipitate, showing the heterogeneity of the arabinoxylan population.

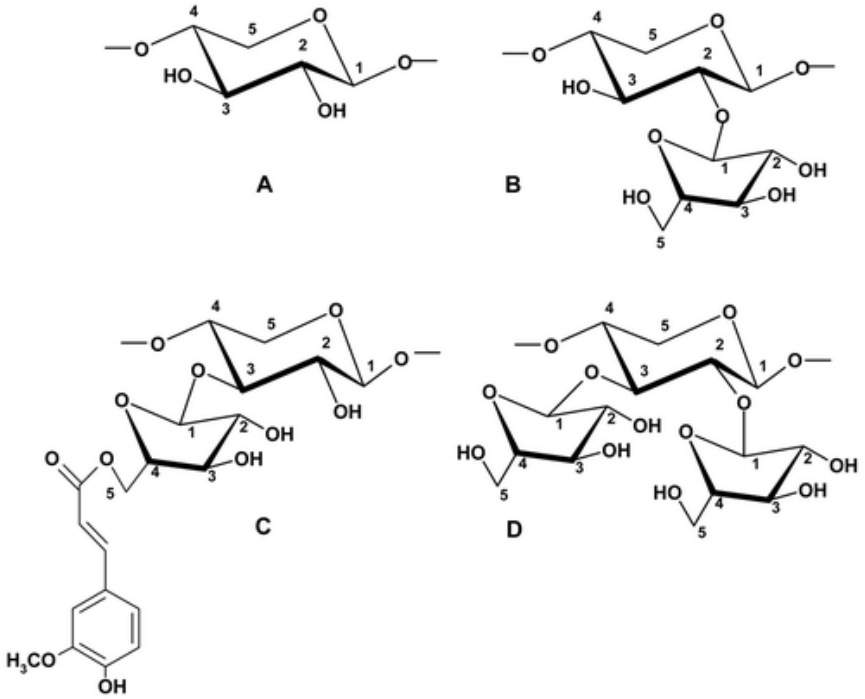


Fig. 4.3. Structural elements of arabinoxylan. **A,** nonsubstituted D-xylopyranosyl residue; **B,** D-xylopyranosyl residue substituted at C(O)-2 with an L-arabinofuranosyl residue; **C,** D-xylopyranosyl residue substituted at C(O)-3 with an L-arabinofuranosyl residue; **D,** D-xylopyranosyl residue substituted at C(O)-2 and C(O)-3 with L-arabinofuranosyl residues. Structure C shows the link of ferulic acid to C(O)-5 of an L-arabinofuranosyl residue. (Courtesy C. Vinkx)

The reason for the unextractability of a large proportion of the arabinoxylan resides is the high molecular weight of arabinoxylan, which apparently results from cross-links between arabinoxylan molecules. Such cross-links are formed by ferulic acid residues and can be removed by alkaline saponification. This step greatly increases the solubility of arabinoxylan.

Water-extractable arabinoxylan can form highly viscous solutions, the viscosity of which depends on arabinoxylan chain length, substitution degree, substitution pattern, and degree of cross-linking. Approximately two thirds of the intrinsic viscosity of flour extracts is attributable to water-extractable arabinoxylan.

Under certain oxidizing conditions, water-extractable arabinoxylan can cross-link by covalent coupling of ferulic acid residues. This results in a strong increase in the viscosity of the solution or, at high arabinoxylan concentrations, the formation of a gel. Such oxidative gelation is apparently a unique property of certain cereal flour arabinoxylans and has therefore been studied rather extensively. The loss of ultraviolet absorbance at 320 nm (ferulic acid absorbs at this wavelength) shows that ferulic acid oxidation is involved in the gelation. Several oxidants are effective in causing oxidative gelation. The one that has been studied the most is hydrogen peroxide in the presence of peroxidase, an enzyme native to flour. Whether oxidative gelation phenomena are important in breadmaking remains unclear at present. However, it is possible that oxidative gelation is responsible for the dough drying, dough strengthening, and loaf improvement that result from fermentation. Its importance in other cereal processes is even less clear.

Water-unextractable arabinoxylan has a high water-holding capacity. When flour is suspended in water and the suspension is stirred (compare Chapter 9), the gluten agglomerates and can be removed by hand from the suspension containing water-extractables, starch, and the water-unextractable arabinoxylan. The remaining slurry can be centrifuged to give the water-extractable and water-unextractable fractions. The water-unextractable fraction can be divided into two layers or fractions, based on density. The bottom, denser layer is the prime starch. On top of this is a gelatinous layer, which is referred to in the literature by a number of names, including*squeegee, sludge,* or *tailings starch* (compare Chapter 9). This fraction is made up of starch, both small-granule and damaged, and water-unextractable arabinoxylan, along with small levels of protein and ash. Both the water-extractable and water-unextractable arabinoxylan greatly affect the functionality of wheat in biotechnological processes such as breadmaking and gluten starch separation, as well as animal feeding.

Approximately 30% of wheat bran consists of a variant of arabinoxylan, i.e., glucuronoarabinoxylan, which almost exclusively occurs as water-unextractable material. Its structure is very similar to that of wheat endosperm arabinoxylan, apart from the fact that (methylated) glucuronic acid is incorporated into the arabinoxylan structure.

Arabinogalactan Peptide

Wheat arabinogalactan peptide molecules have molecular weights of approximately 23,500. They occur in wheat in concentrations of approximately 0.3%. Their function is not known. The carbohydrate part consists of a β-1,6-linked D-galactopyranosyl backbone with a single α-L-arabinofuranosyl or a single β-D-galactopyranosyl residue substituted at the C(O)3 position. The latter can also have the substitution of a single α-L-arabinofuranosyl residue in its C(O)3 position. The peptide has 15 amino acids, including three highly conserved hydroxyprolines, each linked to a carbohydrate chain. Homology with the N-terminal part of grain-softness-protein precursors indicates that the peptide is a processing product of grain-softness-protein synthesis.

RYE HEMICELLULOSE

The hemicelluloses of rye are quite comparable to those of wheat; i.e., they consist mainly of arabinoxylan. However, rye contains higher levels of arabinoxylan than wheat. Total levels in the whole grain vary between 6.5 and 12.2%. Rye flour typically contains 2% water-extractable and 3% water-unextractable arabinoxylan, which have been strongly implicated in determining its breadmaking quality. Rye also contains an arabinogalactan peptide.

BARLEY HEMICELLULOSE

The cell walls of barley endosperm contain 70% β-D-glucan and 20% arabinoxylan, the remainder being protein and a small amount of mannan. The total β-D-glucan content in barley grain is 3–11%, compared to only 0.5–1.0% in wheat grain. Because of the function of the cell walls in both malting and brewing, these nonstarch polysaccharides of barley have been studied in detail.

β-D-Glucans are either water-extractable or water-unextractable. In barley, on average, about 50% of the β-D-glucan is water-extractable at 38°C. β-D-Glucans are a heterogeneous group of polymers with a general structure consisting of long, linear chains of β-1,4- and β-1,3-linked D-glucopyranosyl residues (Fig. 4.4). On average, about 30% of the glucose residues are connected by β-1,3 and 70% by β-1,4 bonds. The β-D-glucan chain is mainly (about 90%) made up of blocks of cellotriosyl and cellotetraosyl units, separated by single β-1,3 linkages. The ratio of cellotriosyl to cellotetraosyl units is 2.8 to 3.3, and approximately 10% of the chain consists of blocks of 4–15 consecutive β-1,4-linked glucose residues. The β-1,3 linkages interrupt the extended, ribbonlike shape of β-1,4-linked glucose molecules, inducing kinks in the chain. This makes the β-D-glucan chains more flexible, more soluble, and less inert than those of cellulose. Indeed, the solubility of β-D-glucan increases as the chain structure becomes more irregular.

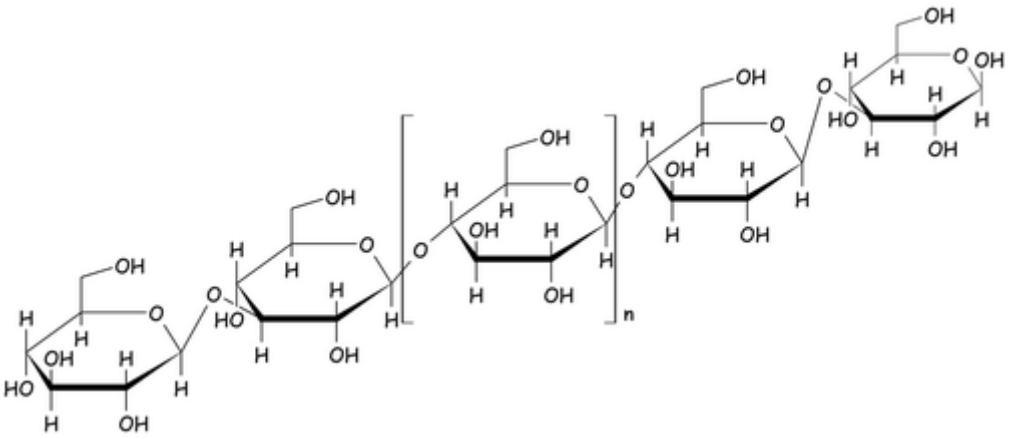


Fig. 4.4. Schematic representation of the structure of β-D-glucan Units in which *n* = 1 or 2 constitute about 90%; those in which *n* = 3–13 constitute about 10%. (Courtesy P. Åman)

β-D-Glucans have a high viscosity-forming potential and can form gels. This is probably due to their asymmetric configuration and the intermolecular interactions between long regions of β-1,4-linked glucose residues of different β-D-glucan chains. Gel formation occurs most readily with chains of structural regularity.

OAT HEMICELLULOSE

About 70–85% of the hemicellulose in oats is β-D-glucan. Typical levels are 4–6%, and its structure is comparable to that of barley β-D-glucan. There has been much interest in this nonstarch polysaccharide because of its reported ability to lower cholesterol levels. In 1997, the United States Food and Drug

Administration (FDA) allowed a health claim that β-D-glucan may lower risk of heart disease. Later, such a claim was also allowed for barley β-D-glucan.

HEMICELLULOSES OF OTHER CEREALS

When viewed with the scanning electron microscope, the cell walls of the so-called "coarse" cereals (maize, sorghum, and millets) appear much thinner than the cell walls of wheat or rye. Figure 1.13 clearly shows maize starch granules through the endosperm cell walls, illustrating that the cell wall is thin. The hemicelluloses of these cereals do not result in the viscous, slimy mixtures that are common with rye and oats. They contain arabinose, xylose, and glucose as constituent monosaccharides.

Rice endosperm also is low in hemicellulose and has thin cell walls. Rice endosperm hemicellulose contains arabinose, xylose, and galactose, as well as a high level of uronic acids.

Cereal Nonstarch-Polysaccharide-Hydrolyzing Enzymes and Their Inhibitors

Many enzyme systems can degrade cereal nonstarch polysaccharides. We here focus on those enzyme systems that significantly affect cereal functionality in biotechnological systems.

ARABINOXYLAN-DEGRADING ENZYMES

Because of the complex nature of arabinoxylans, their hydrolysis to monosaccharides is possible only with a mixture of enzymes.

Endo-1,4-β-Xylanases

Endo-1,4-β-xylanases (EC 3.2.1.8), mostly referred to as "endoxylanases," hydrolyze arabinoxylan internally to generate fragments such as arabinoxylan oligosaccharides, xylobiose, and xylose. Their action strongly changes the properties and functionality of arabinoxylan.

Most endoxylanases can be classified into two major glycoside hydrolase families, i.e., glycoside hydrolase families 10 and 11 (compare Chapter 2). However, some enzymes with endoxylanase activity belong to other families (glycoside hydrolase famiies 5, 8, and 43). Glycoside hydrolase family 10 endoxylanases have a higher molecular weight and more complex structure and produce smaller oligosaccharides than their family 11 counterparts. They also require less unsubstituted consecutive xylose residues in the main chain for hydrolysis and have greater catalytic versatility than family 11 endoxylanases. Many microorganisms produce both types of endoxylanases. In cereals, all endogenous endoxylanases described to date belong to glycoside hydrolase family 10. They are important during germination since they degrade the endosperm cell walls and make starch and protein more available for amylases and proteases.

Other Arabinoxylan-Degrading Enzymes

β-D-xylosidases (EC 3.2.1.37) degrade arabinoxylan oligomers generated by endoxylanase action by removing xylose residues from the nonreducing end.

α-L-Arabinofuranosidases (EC 3.2.1.55) release arabinose substituents from the xylose backbone of arabinoxylan, resulting in the formation of less-substituted arabinoxylan.

Ferulic acid esterified to the arabinose residues can be released by feruloyl esterases (EC 3.1.1.73).

ENDOXYLANASE INHIBITORS

In wheat, two structurally different endoxylanase inhibitors have been identified, i.e.,*Triticum aestivum* endoxylanase inhibitor (TAXI) and endoxylanase-inhibiting protein (XIP). While TAXI inhibits family 11 endoxylanases, XIP has a bias for fungal family 10 and 11 endoxylanases. Inhibitor concentrations in wheat flour are typically in the range of 150 mg/kg or higher for both TAXI and XIP and can vary two-to threefold depending on cultivar. These endogenous inhibitor levels in wheat flour are clearly often in excess of what is theoretically needed to stop all of the activity of the endoxylanase added for bread-improving purposes. Such levels result in a significant reduction of the activity of the inhibition-sensitive endoxylanases used in breadmaking. In the dough phase, inhibition kinetics determine to a large extent the impact of the inhibitors. A mutant *Bacillus subtilis* endoxylanase that is insensitive to wheat endoxylanase inhibitors and has improved breadmaking functionality has been developed by molecular engineering and has reached the market.

β-D-GLUCAN-DEGRADING ENZYMES

Because the D-glucopyranosyl units of β-glucan are connected with two types of linkages, different hydrolysis methods produce partial hydrolysates with different primary structures. Hydrolysis with lichenase (endo-1,3–1,4-β-D-glucan-4-glucanohydrolase from *B. subtilis,* EC 3.2.1.73) cleaves only β-1,4 glucosidic linkages of a triple-substituted unit. Cellulase (endo-1,4-β-D-glucan-4-glucanohydrolase from*Trichoderma* sp., EC 3.2.1.4) requires two adjacent β-1,4 glucosidic linkages. Neither enzyme cleaves the β-1,3 glucosidic linkage. Acid can cause hydrolysis of all of the linkages, but it is unknown whether it cleaves the β-1,3 and β-1,4 glucosidic linkages at the same rate.

Mono-, Di-, and Oligosaccharides

IN WHEAT

Sound wheat contains about 2.8% mono-, di-, and oligosaccharides. These include small levels of glucose (Glu, 0.09%) and fructose (Fru, 0.06%), somewhat higher levels of sucrose (Glu-Fru, 0.84%) and the galactose (Gal)-containing raffinose (Gal-Glu-Fru, 0.33%), and much higher levels of glucofructosans (1.45%).

Glucofructosans occur mainly in wheat endosperm and are absent in germ and bran. The smallest member of the series is sucrose (Glu-Fru); the next largest is glucodifructose (Glu-Fru-Fru). Half of the wheat glucofructosan is made up of saccharides with a DP that does not exceed 5. A similar material is found in chicory root inulin. It is almost exclusively made up of β-1,2 linkages, while wheat glucofructosan also contains significant proportion of β-2,6 linkages. The molecular weight of wheat glucofructosan may be as high as 2,000.

Wheat germ contains about 25% mono-, di-, and oligosaccharides, which appear to consist mainly of sucrose and raffinose, with sucrose making up about 60% of the total.

Wheat bran contains about 4–6% mono-, di-, and oligosaccharides. Sucrose and raffinose are the predominant sugars in the bran.

IN OTHER CEREALS

Neither sorghum, pearl millet, oats, nor rice appear to contain appreciable levels of glucofructosans.

In sorghum, the total sugar content may vary from 1 to 6%, the higher sugar levels being in specific cultivars grown for sugar. In those cultivars, sucrose is the major sugar. The trisaccharide raffinose and the tetrasaccharide stachyose (Gal-Gal-Glu-Fru) are found at low levels.

Values reported for pearl millet are somewhat lower than those for sorghum, ranging from 2.6 to 2.8%. Sucrose accounts for about two thirds of the total.

Oats contain about the same levels of sugars as the other cereals. In the starchy endosperm, sucrose and raffinose are the major sugars.

Brown rice contains about 1.3% sugars. The major sugar is sucrose, with minor levels of glucose, fructose, and raffinose also reported. White rice, which no longer contains the pericarp or germ, contains only about 0.5% sugars, and, once again, sucrose is the major sugar.

Phytic Acid and Phytase

The majority (about 70–75%) of the phosphorus in cereals occurs as phytic acid. Phytic acid is inositol hexaphosphoric acid (Fig. 4.5). It chelates divalent cations, such as calcium, and keeps them from being absorbed in the intestinal tract.

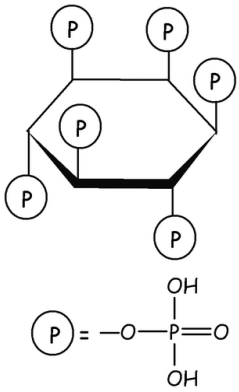


Fig. 4.5. Structure of phytic acid. (Courtesy M. Verswyvel)

Phytase (EC 3.1.3.26) is an esterase that hydrolyzes phytic acid to inositol and free phosphoric acid. Thus, this enzyme's activity converts a detrimental entity into inositol (a vitamin) and phosphoric acid (a nutrient). In breadmaking, at least part of the phytic acid in wheat flour is hydrolyzed during fermentation. The solubility of the substrate appears to be the factor limiting hydrolysis. When used as an additive in animal feed applications, phytase leads to higher utilization of phosphate in the feed, thereby increasing its nutritional value and reducing the detrimental effect of phosphorous run-off into the environment.

Lipids

CEREAL LIPIDS

Lipids are defined as materials soluble in organic solvents. In the cereal literature, lipids are often defined as free or bound. This distinction is based upon extractability. If the lipid is extractable in a nonpolar solvent such as petroleum ether, it is considered free. If, on the other hand, it requires a polar solvent for extraction, it is considered bound. Another important distinction is that of polar and nonpolar lipids. Nonpolar lipid is that material that can be eluted from a silica column with chloroform. By this definition, free fatty acids and triacylglycerols are nonpolar lipids. The polar lipids are the materials eluted from the column with methanol. This fraction includes the phospholipids and glycolipids.

It follows from the above that the lipid population in cereals is quite complex. It consists of a large number of chemical classes and a much larger number of individual compounds. The distribution of the classes and compounds is different not only in the various cereals but also in the various anatomical parts of each cereal. Another confusing factor is the fact that lipids can be bound to various other constituents in the cereal, and thus the same chemical entity can exhibit differences in extractability.

About the only way to quantify the lipids is to extract the lipid, make sure the extract does not contain nonlipid species, remove the lipid from the extract, and determine the levels gravimetrically. The problems with such a scheme are many. Some lipids may require a very polar solvent to become extractable. However, polar solvents, such as the various alcohols, also extract considerable levels of nonlipid material. Thus, the lipids must be redissolved in a nonpolar solvent such as chloroform or petroleum ether before they are weighed. Other lipid entities may be covalently bound to nonlipid materials and must be hydrolyzed before they can be extracted and quantified. Although acid hydrolysis usually gives the highest values for lipids and is generally considered to give the best results, it also poses problems. For example, triacylglycerols contain the polar entity glycerol, which is released by acid hydrolysis but is not soluble in lipid solvent and is, therefore, not a lipid by the previous definition. So, although acid hydrolysis may give the largest value, it does not measure all the lipid material that was in the original sample.

If wheat flour is extracted with petroleum ether, a value of about 1.9% extractable lipid is obtained. No purification is necessary, as a relatively nonpolar lipid solvent is used. Extraction with a highly polar solvent such as water-saturated butanol and purification of the extract by dissolving it in a lipid solvent to remove nonlipid material soluble in the water-saturated butanol gives higher values, in the range of 2.2%. Acid hydrolysis gives an even higher value (about 2.5%), of even though some lipid material is converted into

nonlipid material. The only way to obtain a good view of the lipids in cereals is to use a series of solvents, e.g., petroleum ether followed by water-saturated butanol and then by acid hydrolysis. Of course, one can make finer fractionations in lipids by using a series of solvents that differ in their polarity.

WHEAT LIPIDS

The distribution of the crude fat lipids within the wheat kernel varies widely (Table 4.1). Whole-wheat lipids contain about 70% nonpolar lipids, 20% glycolipids, and 10% phospholipids. Glycolipids (Fig. 4.6) were not identified until 1956. The germ has the highest level of lipids. These are mainly nonpolar triacylglycerols. The polar lipids in the germ have the highest percentage of phospholipids (Fig. 4.7) when compared to the polar lipids from the rest of the kernel. The polar lipids of bran contain more phospholipids than glycolipids, whereas the endosperm lipids contain more glycolipids than phospholipids.

TABLE 4.1
Distribution of Crude Fats in Wheat Kernels[a]

Kernel Fraction	Proportion of Kernel (%)	Crude Fat (%)
Whole grain	100	3.0
Bran	15	5.4
Pericarp	7	1.0
Aleurone	6	8.0
Endosperm	82	1.5
Germ	2.5	28.5

[a] Adapted from Morrison (1978).

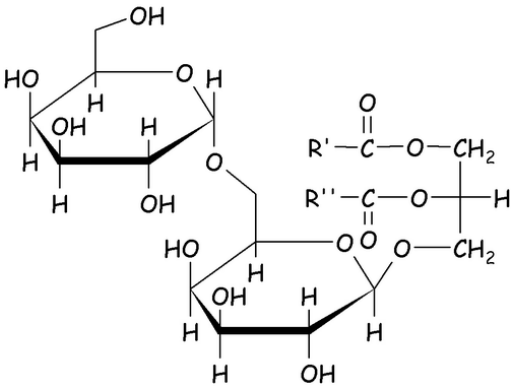


Fig. 4.6. Structure of digalactosyl diacylglycerol from wheat flour. (Courtesy M. Verswyvel)

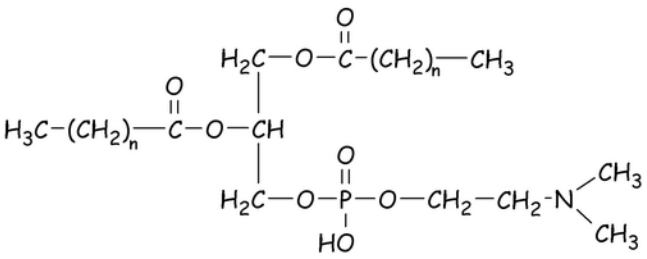


Fig. 4.7. Structure of a phospholipid. (Courtesy M. Verswyvel)

Vitamin E is one of the lipids present in wheat wholemeal (about 3.9 mg/100 g). Wheat lipid contains about 200 mg of total tocopherols per 100 g of wheat oil. The starchy endosperm contains only about 15% of the total tocopherols. Tocopherols are phenolic structures that display antioxidant activity.

In flour from the starchy endosperm, the lipid content can be divided into lipids associated with starch granules and nonstarch lipids (see above, Chapter 2). The nonstarch lipids, representing a large number of classes, can

be divided into about 60% nonpolar lipids, 25% glycolipids, and 15% phospholipids. The starch-associated lipids also represent a large number of classes but with the following general breakdown: 9% nonpolar lipids, 5% glycolipids, and 86% phospholipids. Clearly, phospholipids make up most of the starch lipid; lysophosphatidylcholine makes up a large percentage (85%) of the phospholipids in starch.

Another variable found in lipids is their fatty acid composition. In general, this is determined more by the species of grain than by the anatomical part of the seed or the lipid type. However, the starch lipids appear to be an exception to the above rule.Table 4.2 shows the distribution of fatty acids in wheat and its fractions.

TABLE 4.2
Fatty Acid Composition of Wheat Lipids[a]

	Fatty Acid[b] (%)					
Wheat Fraction	**16:0**	**16:1**	**18:0**	**18:1**	**18:2**	**18:3**
Whole wheat						
Total	20	1	1	15	57	4
Nonpolar	20	...	...	22	53	3
Polar	18	...	...	15	62	4
Bran	19	1	2	20	50	4
Germ	21	<1	2	13	55	6
Flour						
Nonstarch	19	...	<2	12	63	4
Starch	40	...	<2	11	48	2

[a] Adapted from Morrison (1978).
[b] 16:0 indicates 16 carbons and 0 double bond, etc.

LIPIDS IN OTHER CEREALS

The oil content of maize varies widely. The germ makes up a relatively large percentage of the total kernel, about 12% compared to 3% for wheat or barley, and it generally contains about 30% lipids. Both the proportion of germ in the kernel and the percentage of oil in the germ vary, and both appear to be under genetic control. In most cultivars, free lipids are about 4.5% and bound lipids somewhat below 1%. The fatty acid composition of maize lipids is similar to that found in sorghum and pearl millet (Table 4.3). Maize germ, a by-product of industrial maize starch production, is used commercially for the production of oil (see Chapter 9).

TABLE 4.3
Fatty Acid Composition of Cereal Lipids[a]

	Fatty Acid (%)				
Cereal	**16:0**	**18:0**	**18:1**	**18:2**	**18:3**
Maize	13	<4	35	50	<3
Sorghum	12	1	35	49	3
Pearl millet	20	5	25	48	3
Rice	22	<3	39	36	4
Oats	20	2	37	37	4
Rye	18	1	25	46	4
Barley	22	<2	12	57	5
Wheat	21	2	15	58	4

[a] Adapted from Morrison (1978).

Sorghum contains from 2.1 to about 5.0% lipids. The lipids are 90% nonpolar lipids, 6% glycolipids, and 4% phospholipids. About 75% of the lipids are in the germ, with the remainder split about evenly between the bran and the endosperm. Sorghum lipids contain about 0.5% wax, which resembles carnauba wax in composition. The fatty acid composition of sorghum lipids (Table 4.3) is similar to that of pearl millet.

The oil content of pearl millet ranges generally from 3 to 8%. Reports on the lipid content, like much of the other literature dealing with pearl millet, are confused by the many species of millets and the number of scientific names that pearl millet has had in recent times. The fatty acids of pearl millet free lipids are higher in oleic acid (18:1) than are those of wheat or most other cereals, oats being an exception. The quality of pearl millet quickly deteriorates after it has been ground into meal, and the lipid components are generally considered to be responsible for this deterioration. While the mechanism of this deterioration is not clear, it is not a classical lipid oxidative rancidity.

The lipid content of oats is generally higher than that of the other cereals but also varies quite widely. Values as low as 3% and as high as 12% have been reported. Most lines contain 5–9% lipids. Oats are also unique in that most of the groat lipid (80%) is in the endosperm instead of the germ and bran. Oat lipids have more 18:1 acid than most other cereals. The fatty acids found in oat lipids extracted from the various groat fractions do not differ much. Oats contain only about 2.3 mg of tocopherols per 100 g of grain, somewhat lower than the levels in wheat and barley. In spite of these lower levels, oats are known for their antioxidant activity. This appears to be the result of a series of phenolic compounds, mainly caffeic and ferulic acid esters of C_{26} and C_{28} 1-alkanols.

Rice contains about 3% lipids, in line with most other cereals. Because the lipid is concentrated in the peripheral parts of the grain, the lipid content decreases when brown rice is converted into white rice by rice milling (see Chapter 10). In fact, fat content has been used as a measure of the degree of rice milling, i.e., the operation of removing the rice's pericarp tissue. Milled rice may contain only 0.3–0.5% lipids. Brown rice contains more nonpolar lipids and less glycolipids and phospholipids than do such cereals as barley, wheat, and rye. The fatty acid composition of brown rice is similar to that found in other cereals (Table 4.3). Rice oil also contains a phenolic antioxidant (oryzanol), an ester of ferulic acid, and triterpene alcohols.

Rye has a lipid content of about 3%, in line with the levels in barley and wheat. The lipids consist of 71% nonpolar lipids, 20% glycolipids, and 9% phospholipids. Rye germ contains about 12% lipid and thus less than does barley or wheat germ. Rye starch contains about half the level of lipids found in wheat, barley, and oat starches. Lysophosphatidylcholine is the major starch lipid in rye, as in other cereals. Rye contains significantly less linoleic (18:2) fatty acid than does wheat but significantly more palmitic (16:0), stearic (18:0), and linolenic (18:3) fatty acids. The high level of 18:3 acid may be responsible for the susceptibility of rye to oxidative deterioration.

Triticale has a lipid content and composition similar to those of its parent species. The lipids in barley are reported to constitute about 3.3% of the kernel. About one-third of the lipid is in the germ. Because the germ is only about 3% of the total kernel weight, this suggests a lipid content of about 30%. Lipids of the whole barley kernel can be broken down into nonpolar lipids (72%), glycolipids (10%), and phospholipids (21%). Barley also contains tocopherols on the order of 5.0 mg/100 g. The starch-associated lipids in barley are similar to those reported in other cereals. The fatty acids of barley lipids are slightly more saturated than those of wheat.

Enzymes Affecting Lipids

Various enzyme systems affect cereal lipids and hence may affect their functionality in cereal-based biotechnological processes.

LIPASE AND PHOSPHOLIPASE

Lipases (EC 3.1.1.3) hydrolyze the ester bonds of (mainly) the triacylglycerols, yielding mono- and diacylglycerols and free fatty acids. Although one generally thinks of lipase as an enzyme releasing fatty acids from triacylglycerols, it is difficult to separate that activity from the activity of other esterases. All cereals have lipase activity, but the activity varies widely among cereals, with oats and pearl millet having relatively high activity compared with that of wheat or barley. Lipase activity is important because a free fatty acid is more susceptible to oxidative rancidity than is the same fatty acid in a triacylglycerol. Indeed, part of the released polyunsaturated fatty acids are oxidized by the wheat lipoxygenase (see below). In addition, free fatty acids in a product often give it a soapy taste.

Phospholipase A (EC 3.1.1.4) liberates fatty acids from phospholipids.

LIPOXYGENASE

Lipoxygenase (EC 1.13.11.34) catalyzes the peroxidation of polyunsaturated fatty acids by oxygen. The preferred substrate has methylene-interrupted double bonds, with both double bonds in the cis configuration. The enzyme is rather widespread in nature. It is in high concentration in soybeans but is also found in many cereals, although it has been reported to be absent in pearl millet. Two types of lipoxygenase exist. The type present in soybeans attacks the fatty acids in triacylglycerols as well as the free fatty acids. In its action, it can cooxidize carotenoids—hence the bleaching effect observed when enzyme-active soy flour is added to bread formulas. In contrast, wheat and durum wheat lipoxygenases are active only on free fatty acids. As, in many instances, limited levels of free fatty acids are available, wheat lipoxygenase can also exert limited effects on bread color. Likewise, if given a chance to be active (Chapter 14), durum wheat lipoxygenase can destroy pasta carotenoids.

A major effect of lipoxygenase is that it promotes the oxidative deterioration of carotenoids. When such enzymes catalyze the reaction of linoleic acid (LH) with molecular oxygen, linoleic acid peroxy radical (LOO°) is formed (reaction 1). This radical can then react with, for instance, a second LH, resulting in the formation of LOOH and a radical (L°) (reaction 2). Alternatively, when carotenoids (car-H) are present, LOO° can react with them, resulting in both LOOH and car° (reaction 3). The latter radical (car°) can then react with molecular oxygen, resulting in colorless products (reaction 4).

$$LH + O_2 \rightarrow LOO^\circ \quad (1)$$

$$LOO^\circ + LH \rightarrow LOOH + L^\circ \quad (2)$$

$$car\text{-}H + LOO^\circ \rightarrow car^\circ + LOOH \quad (3)$$

$$car^\circ + O_2 \rightarrow \text{colorless products} \quad (4)$$

Vitamins and Minerals

Most cereals are important sources of vitamins such as thiamin, niacin, riboflavin, pyridoxine, pantothenic acid, and tocopherol. In addition, they are good sources of a number of minerals. Table 4.4 lists the vitamin and mineral compositions of several cereals. In general, most of the minerals (61% of the total) are concentrated in the aleurone layer. Vitamins are concentrated in the aleurone or the scutellum or both.

TABLE 4.4
Vitamin and Mineral Composition (mg/100 g) for Several Cereal Grains[a]

	Wheat	Rye	Barley	Oats	Rice	Maize	Sorghum
Vitamins							
Thiamin	0.55	0.44	0.57	0.70	0.33	0.44	0.58
Riboflavin	0.13	0.18	0.22	0.18	0.09	0.13	0.17
Niacin	6.4	1.5	6.4	1.8	4.9	2.6	4.8
Pantothenic acid	1.36	0.77	0.73	1.4	1.2	0.70	1.0
Pyridoxine	0.53	0.33	0.33	0.13	0.79	0.57	0.60
Minerals							
Phosphorus (P)	410	380	470	340	285	310	405
Potassium (K)	580	520	630	460	340	330	400
Calcium (Ca)	60	70	90	95	68	30	20
Magnesium (Mg)	180	130	140	140	90	140	150
Iron (Fe)	6	9	6	7	...	2	6
Copper (Cu)	0.8	0.9	0.9	4	0.3	0.2	0.5
Manganese (Mn)	5.5	7.5	1.8	5	6	0.6	1.5

[a] Adapted from Simmonds and Campbell (1976) and Hoseney et al (1981).

CHAPTER 5: Rheology of Doughs and Batters

Doughs and batters are complex mixtures of many ingredients. Their complexity results not only from their chemical composition but also from their physical properties. These physical properties are extremely important, as they determine not only the processing properties of doughs and batters in both artisan and industrial environments but also the quality of the final products.

Attempts to describe the physical properties of doughs and batters have resulted in the design of many rheological devices. Some of these instruments were designed to determine, for instance, the amount of mixing that dough requires or the amount of water that should be added to the flour to obtain dough of the desired consistency. They are also used to characterize the various flours or other ingredients used and are especially important tools for developing flour specifications. Hence, it is appropriate to devote the present chapter to rheology, its application to doughs and batters, and the measurement of dough and batter rheological properties.

Rheology

Rheology is the study of how materials deform, flow, or fail when force is applied. The rheological properties of some materials can be described by a single value. For example, the flow of water is defined by its viscosity, and the deformability of a steel spring is defined by Hooke's constant, i.e., its modulus of elasticity.

However, most materials, and certainly doughs and batters, are not that simple in their properties or behaviors. Instead, they show more complex rheological behavior.

For example, if a material's viscosity is independent of shear rate (i.e., the rate of stirring or flowing through a pipe), the material displays Newtonian, or ideal, viscosity. Its flow behavior then can be defined by a single viscosity value. This is the case for water and dilute sugar or salt solutions. However, in many systems, including most flour-water systems, the viscosity decreases as the shear rate is increased. Such systems are said to display non-Newtonian behavior. They cannot be defined by a single viscosity value but must be characterized by a viscosity value at each shear rate. In addition, viscosity can also be affected by the time involved in making the measurement.

In rheology, the term *modulus* refers to the stiffness of the material. It is a proportionality constant relating the applied force per unit of area (i.e., the stress, see below) to the relative deformation (i.e., the strain, see below). In lay terms, it tells how much force is required to produce a specific deformation of the material under test.

A common rubber band is elastic. When the band is deformed and the force causing the deformation is removed, the band returns to its original size and shape essentially instantaneously. To exhibit these properties, the rubber must have a high molecular weight and be highly cross-linked. Natural rubber (i.e., that coming directly from the rubber tree) is of high molecular weight but is not cross-linked. In fact, it is a viscoelastic material (see below). A ball made from natural rubber, if left overnight, will flow to become a flat pool that can be rounded into a ball again. Rubber to make rubber bands (and, for that matter, essentially all rubber products) has been chemically cross-linked by adding sulfur to the rubber and heating the mixture, in a process called “vulcanization.”

Wheat Flour Dough: A Viscoelastic System

Wheat flour dough is a viscoelastic system. It exhibits both viscous flow and elastic recovery. *Viscous flow* means that the material flows under stress and does not recover immediately or at all when the stress is released. When a piece of dough is placed on a flat surface in a humid atmosphere such that it does not develop a skin, it flows. The amount of flow depends on the balance of viscous and elastic properties.

As mentioned above, dough, like natural rubber, has flow properties. However, because it is not highly cross-linked like vulcanized rubber, it is not truly elastic. When a piece of dough is stretched rapidly and the force is immediately released, it partially recovers its original shape. An example of this is when dough is stretched for French bread. When stretched to a certain length and then allowed to rest, the dough recoils elastically to a smaller size. Another way of illustrating the difference between dough and valcanized rubber is to stretch a piece of dough and hold it in the extended position for some period of time. When the force on the dough is released, it recoils little, if at all. The stress has relaxed during the time, and the dough no longer has elastic properties.

The explanation of the difference in behaviors of vulcanized rubber and dough is that the large polymers that make up rubber are cross-linked by covalent bonds. In dough, the cross-links between molecules are noncovalent bonds, which constantly break and reform. This allows the high molecular weight polymers of gluten to relax after being deformed.

Rheological Measurements on Wheat Flour Doughs

Many experimental techniques are available to measure rheological properties of doughs, and additional rheological measurement devices have become available over the past decade, leading to increased popularity of dough rheological evaluations. In the following sections, both classical equipment and more-recent dough rheological measurement techniques are described.

FARINOGRAPH AND MIXOGRAPH

The cereal chemistry literature shows many examples of rheological experiments with a farinograph or mixograph. Certainly, these instruments measure how doughs deform and flow. Therefore, they clearly fit our definition of rheological devices. The problem with the use of these instruments for rheological studies is that they do not allow the stress on the sample to be defined at any moment during the test. For example, in a mixograph bowl, only a small part of the dough is in contact with a pin at any given time, and the shape of the dough sample changes in very complicated and unpredictable ways. Thus, it is impossible to determine the stress on the dough as the geometry of the test piece changes. As a result, the measurements made using a farinograph or mixograph are valid only for these instruments.

The above limitations do not imply that the instruments are not useful. They have stood the test of time and can give much relevant information. They are particularly useful to characterize or "fingerprint" flour. For one thing, they can determine whether the mixing and water-absorption properties of different batches of flour are similar or different. However, this chapter does not concentrate on these types of rheological measurements but instead focuses on more fundamental rheological measurements. Fundamental measurements allow one to study the effects of various interactions and how the properties of the dough or batter change as a function of time or temperature. In addition, such measurements can often be made on complete dough or batter systems.

EXTENSIGRAPH

The extensigraph has been used widely in both quality control and research laboratories for studying flour quality and the effect of certain additives in breadmaking. This instrument was designed in the 1930s to provide empirical measures of stress-strain relationships in doughs. After mixing, dough is scaled, molded into cylindical shapes, and clamped at both ends in a special cradle. After a rest period, the dough is stretched through its midpoint with a hook that moves at a constant rate of speed until the dough ruptures. For this reason, it is classified as a load-extension instrument. The result is a load-resistance-versus-extension curve called an "extensigram" (Fig. 5.1). The interpretation of extensigraph measurements in terms of basic physical or rheological terms is difficult because the dough geometry and strain rate change constantly during the test. However, several useful measurements can be made.

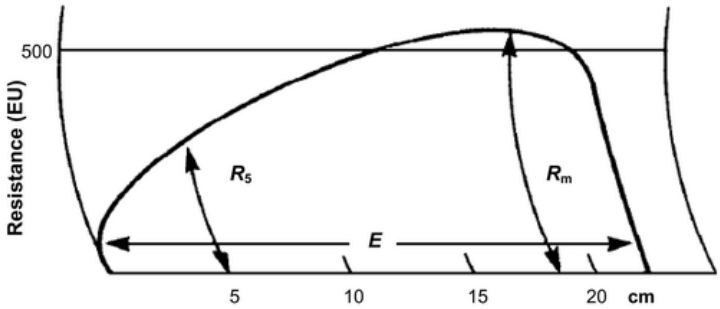


Fig. 5.1. Extensigram, showing extensibility (E), resistance to a constant extension of 5 cm (R_5), and maximum resistance (R_m). The resistance to extension is a measure of dough strength. A higher resistance to extension implies that more force is needed to stretch the dough. The extensibility indicates the ability of the dough to stretch without breaking. (Reprinted from Preston and Hoseney 1991)

The measurements most commonly obtained from extensigrams are the following: R_m, the maximum height of the curve; R_5, the resistance at an extension of 5 cm; and the total curve length in centimeters. The R values are often given in arbitrary units of resistance called Brabender units. Occasionally, one finds the total area under the curve reported in square centimeters. For most practical applications, the curve height and the area

under the curve are taken as measures of flour strength, with larger values indicating greater strength. The overall shape of the curve, or the ratio of curve height (*h*) to extensibility *(E),* gives an estimation of the dough's viscoelastic balance. Obviously, long, low curves produce low *h/E* ratios and a predominance of viscosity over elasticity.

Extensigrams are used to classify flours according to their strength: weak, medium, strong, and very strong (as illustrated in Figure 5.2). They are also quite useful in studying reagents that alter the strength of the dough. Examples of this are the actions of proteolytic enzymes and various oxidizing or reducing agents (see Chapters 3 and 12).

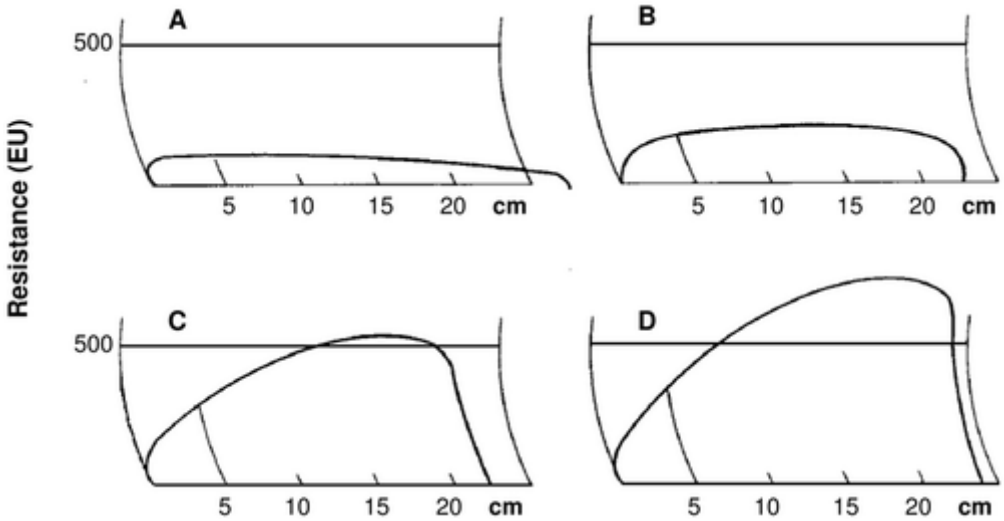


Fig. 5.2. Extensigrams of flours with weak **(A),** medium **(B),** strong **(C),** and very strong **(D)**dough properties. (Reprinted from Preston and Hoseney 1991)

The extensigraph has also been used to follow the structural relaxation of doughs. This involves measuring the R_5 or R_m as a function of time, whch clearly shows the relaxation of dough.

ALVEOGRAPH

The alveograph was developed in the 1920s as an empirical instrument to measure flour quality. The instrument inflates a bubble of dough and measures the pressure during the inflating operation. The dough is mixed, sheeted into a flat piece, rested, and secured in the instrument; then air pressure is used to blow the bubble. Presumably, the idea behind the test was that blowing a bubble is related to the expansion of bubbles (gas cells) in fermenting dough.

Figure 5.3 presents a typical alveogram of bread dough, indicating the measurements that are commonly made. At first glance, the alveogram appears to be a force-time or load-extension curve similar to that produced by an extensigraph or other similar instrument. However, this is not the case. While the extensigraph stretches the dough in a uniaxial mode, i.e., along a single axis, the alveograph stretches the dough sheet in a biaxial mode, i.e., using two directions at right angles to each other. Such biaxial stretching has advantages in terms of the relevance of the test to dough systems, as it is the type of expansion that actually occurs in fermenting dough.

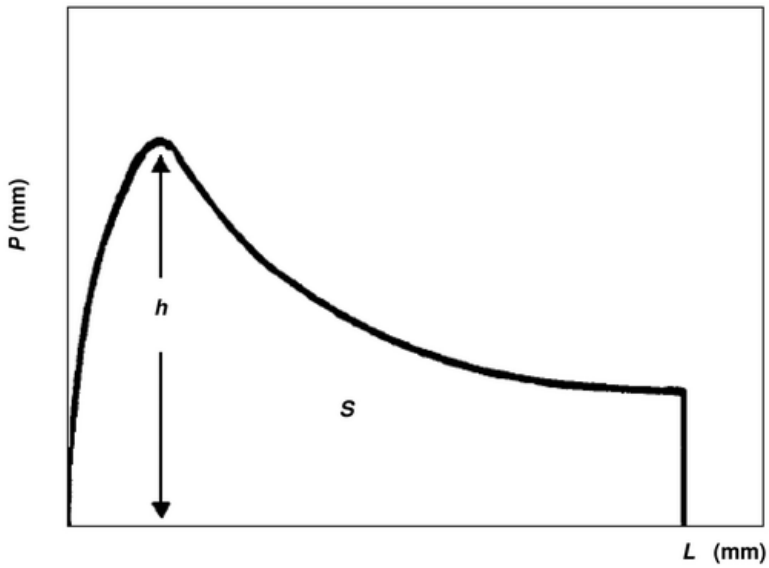


Fig. 5.3. A representative alveogram, showing overpressure (*P, P* = 1.1 × *h*, in mm), abscissa at rupture (*L*, in mm), maximum height (*h*, in mm), and area under the curve (*S*, in cm^2). The alveograph measures the strength of a dough. (Adapted from Faridi and Rasper 1987)

The commonly measured values from the alveogram are the height of the curve, its length (*L*), and the area under the curve. The *P* value (or overpressure) is the height of the curve multiplied by a constant. The overpressure, expressed in millimeters of water, gives the maximum pressure attained during inflation of the bubble. Although it is not totally clear exactly what property the maximum height of the alveogram curve measures, the height of the curve (or sometimes the overpressure) is widely used in interpretation of alveograms.

The average curve length to bubble rupture (*L*) is clearly a measure of the dough's extensibility. Other important parameters obtained from alveograms are the area under the curve and the deformation energy *(W).* The *W* value is calculated as

$$W = 1.32\ (V/L) \times S$$

where *V* is the volume of air (in milliliters) displaced, *L* is the length of the curve in millimeters, and *S* is the area under the curve in square centimeters. *W* is often considered to be a measure of the flour strength and, therefore, the most important value derived from the alveogram. The ratio *P/L* is also widely used and shows the balance of elastic and viscous properties of the dough.

Alveograms have been used to calculate fundamental rheological values of wheat flour dough. These calculations are tedious. The interested reader is referred to the discussion in the *Alveograph Handbook* listed at the end of this chapter for a more detailed discussion.

A texture analyzer equipped with a Kieffer rig can be used to obtain similar data.

LUBRICATED UNIAXIAL COMPRESSION

The rheological properties of fermenting doughs are particularly difficult to determine. In fact, most of the techniques discussed above do not give satisfactory results with fermenting doughs. Part of the problem is that such doughs not only contain gas, but the ratio of gas to dough continuously changes during fermentation. The use of a specific relaxation technique called "lubricated uniaxial compression" produces good results for fermenting or chemically leavened dough systems.

The test is conveniently run with a universal testing machine or textue analyzer. Its metal plate is coated with an adhesive-backed teflon sheet, while the dough sample is coated with a paraffin oil. The teflon and mineral oil eliminate any friction between the dough sample and the instrument. The sample is compressed at a predetermined rate to a predetermined relative deformation, i.e., a strain; the crosshead is then stopped, and the stress decays. The result is a stress relaxation curve (Fig. 5.4) from which the elongational viscosity can be determined.

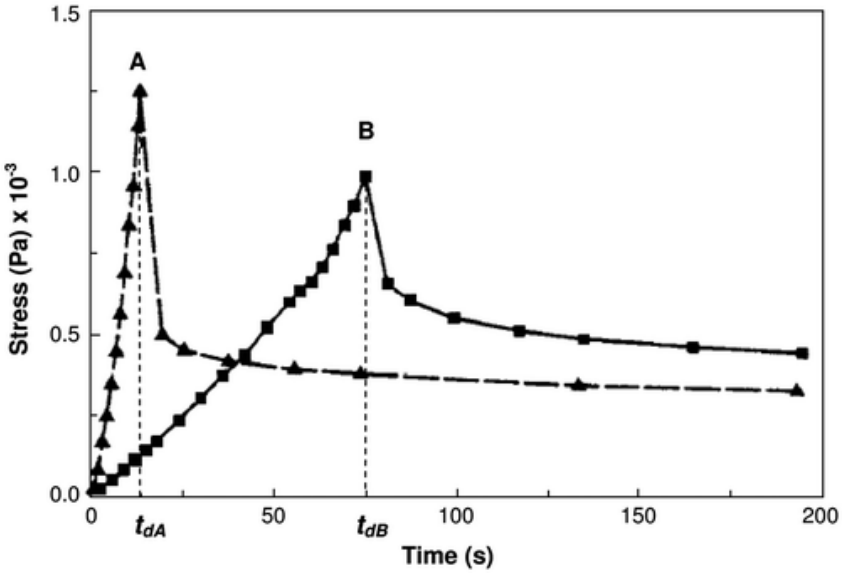


Fig. 5.4. Stress (Pa) versus time (s) for a chemically leavened dough in lubricated uniaxial compression. Deformation rates: 5.0 cm/min (A) and 1.0 cm/min (B). After deformation to 70% in time T_{dA} or T_{dB}, deformation is held constant and stress relaxation occurs. (Reprinted from Bagley and Christianson 1986)

DYNAMIC RHEOLOGICAL MEASUREMENTS OF DOUGH

The type and geometry of a dynamic rheometer can vary widely, but the basic measuring principles are independent of the testing geometry. Figure 5.5 illustrates them in a parallel-plate testing mode in which one plate is fixed to a force transducer and the other plate oscillates in a back-and-forth motion such that its amplitude versus time is sinusoidal and creates simple shear.

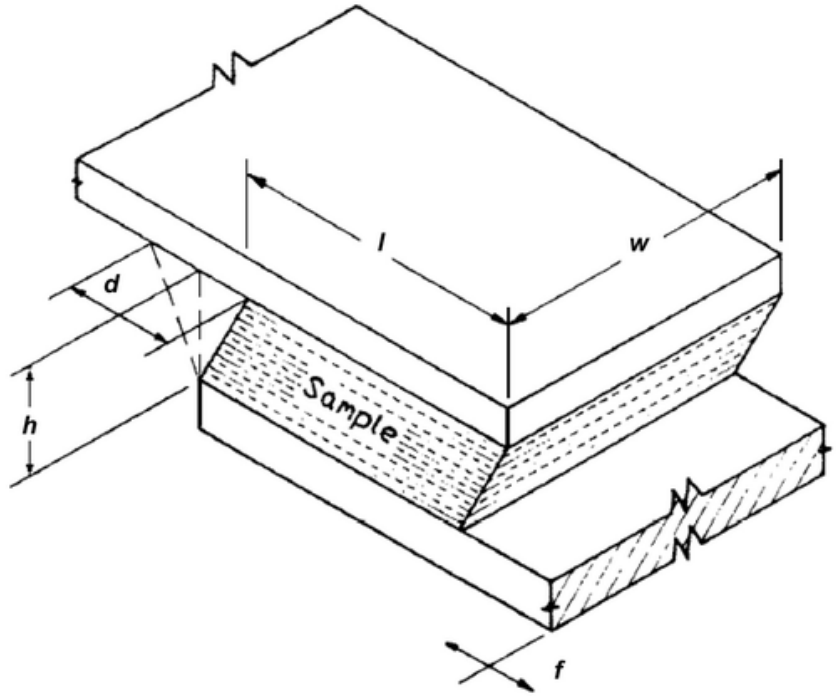


Fig. 5.5. Parallel-plate geometry for dynamic testing, showing deformation (*d*), force transmitted through the sample (*f*), sample height (*h*), sample length (*l*), and sample width (*w*). (Reprinted from Faubion et al 1985)

As the top plate is moved, a force is applied to the dough sample between the plates over the entire contact area. Stress is defined as force acting over a unit area. It is commonly expressed in Pascals (N/m^2) and usually referred to by the symbol σ (sigma). When sufficient force is applied to the dough, it deforms. The deformation produces a strain in the dough. Here, the strain is the deformation divided by the height or thickness of the dough and expressed as a percentage. For example, if the deformation is 1% of the thickness of the dough, the dough is under a 1% strain. Strain is usually referred to by the symbol γ (gamma).

To make the measurement, the dough sample is placed between the plates, contacting both plates in such a way that there is no slippage at either surface (Fig. 5.5). The top plate is then made to oscillate back and forth at some frequency ω (radians per time unit) and with an amplitude (*d*) measured in millimeters. The bottom plate remains stationary and is attached to a force transducer. If no slippage occurs at either plate, a deformation gradient (*h*) is created across the thickness of the sample. The force transducer measures the force transmitted through the sample in Newtons (N). The force is distributed over the sample area (l × *w*) and is uniform over the sample thickness.

Figure 5.6 shows the output data of such a dynamic rheometer. The γ curve is from the moving (dynamic) plate and is a measure of the amplitude, or the shear strain. The τ (tau) curve is the output of the force transducer and represents the shear stress. Deviation from the sinusoidal behavior would indicate that slippage had occurred. For completely elastic materials, the two curves are in phase (peak together), while, for completely viscous materials, the two curves are out of phase by 90°. The phase angle ϕ (phi), in radians, gives a measure of how much the system is out of phase.

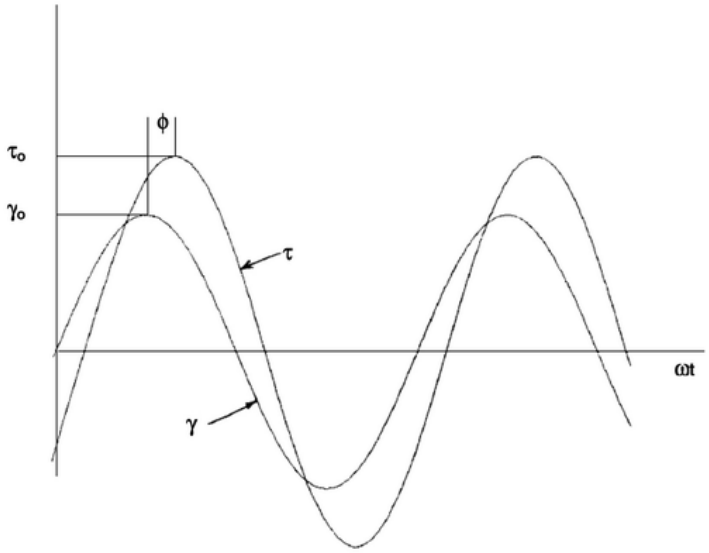


Fig. 5.6. Sinusoidal signal output from force and deformation transducers, showing shear stress amplitude (τ_o), shear strain amplitude (γ_o), phase angle (ϕ), and radians × s (ωt). (Reprinted from Faubion et al 1985)

Two moduli can be calculated from these curves: the storage modulus *G*′ and the loss modulus *G*″:

$$G' = (\tau_o/\gamma_o) \times \cos \varphi$$
$$G'' = (\tau_o/\gamma_o) \times \sin \varphi$$

In lay terms, *G*′ is the part of the energy that is stored during a cycle of oscillation (reflecting its elastic behavior), and *G*″ is the part that is lost (reflecting its viscous behavior). A term that is often used is tan ϕ, which is the ratio *G*″/*G*′. This is a simple index of the relative elastic or viscous nature of the material under test. Finally, the complex modulus (*G**) is made up of the storage modulus (*G*′) and the loss modulus (*G*″) and is calculated as

$$\tau_o/\gamma_o$$

Rheology of Batters

Like doughs, cake batters are very complex mixtures of interacting ingredients. The first step in producing a batter is mixing, during which the soluble components of both the flour and added ingredients (e.g., sugar) dissolve, and the insoluble components (e.g., starch and gluten) hydrate. Another important factor at this point is the incorporation of air into the batter. After the batter is mixed, no new air cells can form during the subsequent leavening and baking. On the other hand, air cells can be lost from the batter either by rising to the surface and thereby being lost or by two cells coalescing into one.

While basically an aqueous system, the batter contains several dispersed phases. The fat, air, and starch granules are all dispersed phases in the aqueous system. When the viscosity of the batter is too low, these phases separate readily, leading to final products with a tough, rubbery layer formed by the gelatinized starch at the bottom of the pan and a light, open cell structure caused by the air at the top. While proper viscosity prevents this separation within the time frame necessary to make the product, it does not, in itself, ensure a good-quality cake. Nevertheless, it is still important to be able to measure the viscosity of the batter and the way it changes with temperature.

Rheological Measurements on Batters

Because of the many dispersed phases in a batter, it is difficult to obtain a true measure of the batter viscosity. Most procedures to measure batter viscosity call for the batter to undergo severe shearing by being stirred or poured. Because the batter is a non-Newtonian material, its viscosity changes as a consequence of the measurement being made. Thus, the risk of measuring how the batter changes as it is sheared is real. This is, usually, not what is desired. In the following section, the use of the oscillatory probe rheometer is described. A problem in studying the effect of temperature on batter rheology is that it is difficult to obtain a constant temperature throughout the batter. Generally, large temperature gradients are produced in the batter as it is heated. One solution to this problem is to heat the batter by electrical resistance heating (ohmic heating). This is described below as well.

OSCILLATORY PROBE RHEOMETER

With an oscillatory probe rheometer, the probe is immersed in the batter sample to a standardized depth (Fig. 5.7). The probe oscillates at a high frequency but with very small amplitude. The sample provides a surface load on the probe and, thus, more power is required to maintain its amplitude and frequency of oscillation than in the absence of sample. The power required is related to the complex viscosity of the sample. Some instruments allow one to change the oscillation frequency and hence the calculation of the rheological parameters *G′, G″*, and tan ϕ with the appropriate equations. Figure 5.8 shows that the apparent viscosity of the batter does not change as a function of the measurement time.

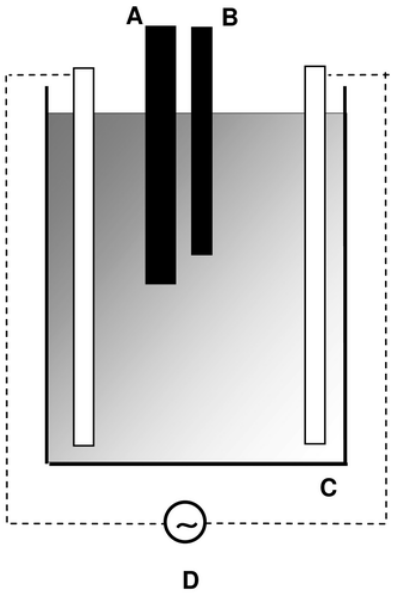


Fig. 5.7. Schematic diagram of the oscillatory viscometer and electrical resistance oven combination, showing viscometer probe (A), temperature probe (B), electrical resistance oven (C), and auto transformer (D). (Adapted from Shelke et al 1990)

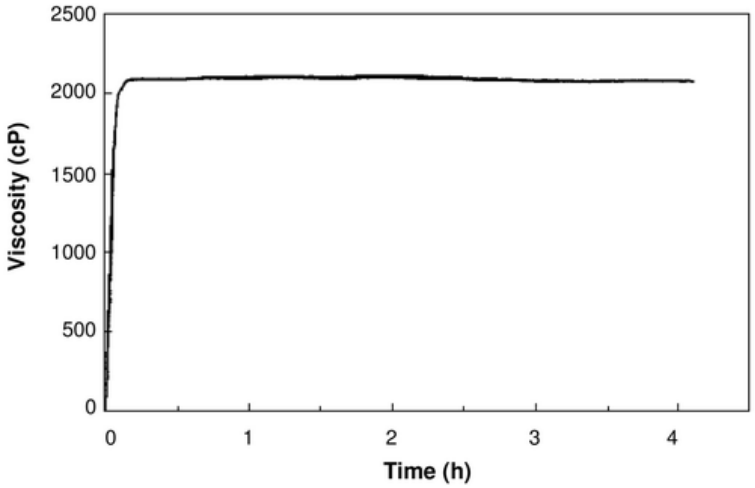


Fig. 5.8. Cake batter viscosity measured using the oscillatory rod viscometer at ambient temperature over a 4-h testing period. (Reprinted from Shelke et al 1990)

ELECTRICAL RESISTANCE HEATING

In an electrical resistance oven, batter is introduced between two metal plates as a conductor material. As a result of an electrical potential applied, the batter is heated in a fashion that produces no temperature gradient. Coupling resistance heating with an oscillatory probe viscometer allows one to measure the change in viscosity as a function of temperature. As is well known empirically and shown in Figure 5.9, as the temperature is increased, the viscosity of the batter decreases. This continues until the starch in the batter begins to gelatinize, at which point the viscosity increases rapidly.

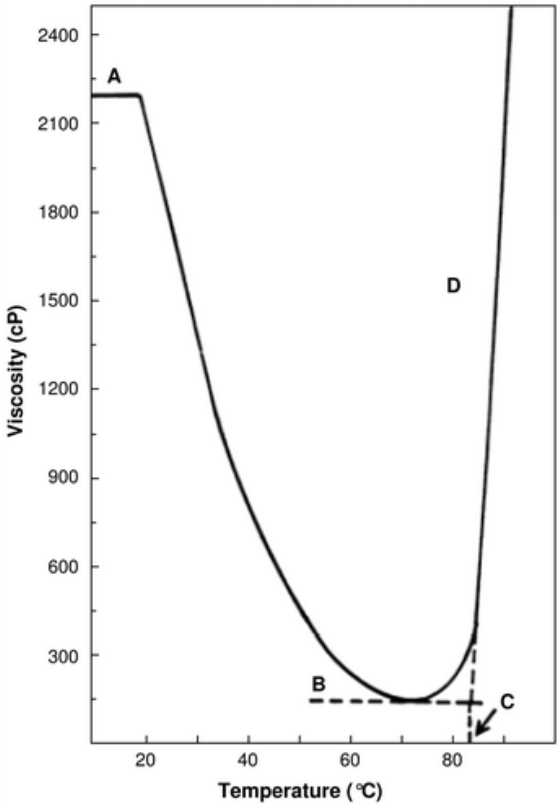


Fig. 5.9. Viscosity-temperature profile of the AACC International cake formula during heating. Viscosity at ambient temperature (A), minimum viscosity of heated batter (B), temperature of onset of rapid viscosity increase (C), and rapid viscosity increase (D) are shown. (Reprinted, with permission, from Shelke et al 1990)

CHAPTER 6: Glass Transition and Its Role in Cereals

When crisp cookies are kept in a moist environment, they loose their crispiness and become pliable. When breakfast cereals are left in milk for too long, they become soggy. To prevent bread from firming, one can store it in a household freezer at −18°C (0°F). These examples of changes in properties of cereal foods have to do with a phenomenon known as "glass transition." While glass transition has been known for a long time as a phenomenon of synthetic polymers, scientists have understood for only about two decades that proteins and polysaccharides, as natural polymers, are also subject to glass transition. In the following sections, the phenomenon of glass transition and its significance for cereal-based food systems are described.

Glass Transitions

The above examples show that the cereal systems described can be present in two major forms. In the first, they behave as a rigid and, perhaps, fragile or brittle material, while, in the second, they are rubbery and flexible. The transition between the two states is the glass transition.

To reconsider the earlier examples, the dry, crisp cookies and breakfast cereals before milk are in the glassy state; following water uptake, they are in the rubbery state. They thus have undergone a glass transition. It follows that water uptake can mediate the glass transition. Bread at room temperature is in a flexible and rubbery state. Once frozen, it loses its flexibility and is then to be considered a glassy system. In this case, it is the temperature change that is responsible for the glass transition. Below its glass transition temperature (most often designated as T_g), the system is in a glassy state, while, above such temperature, it is in a rubbery state.

The T_g affects many of the physical properties of a material. Much can be learned from the generalized plot in Figure 6.1. It relates the rheological properties (see Chapter 5) of a polymer to temperature. When the temperature is raised above that of the glass transition, the modulus decreases. The physical properties of the polymer go from glassy to rubbery. This temperature region is called the rubbery "plateau," and, as the name implies, it extends over a temperature range. The length of the rubbery plateau varies depending upon several factors, the most important of which is whether or not the polymer is cross-linked. Noncross-linked polymers flow as the temperature is raised. Cross-linked polymers remain rubbery as the temperature is raised. Increasing the temperature even higher causes thermal degradation.

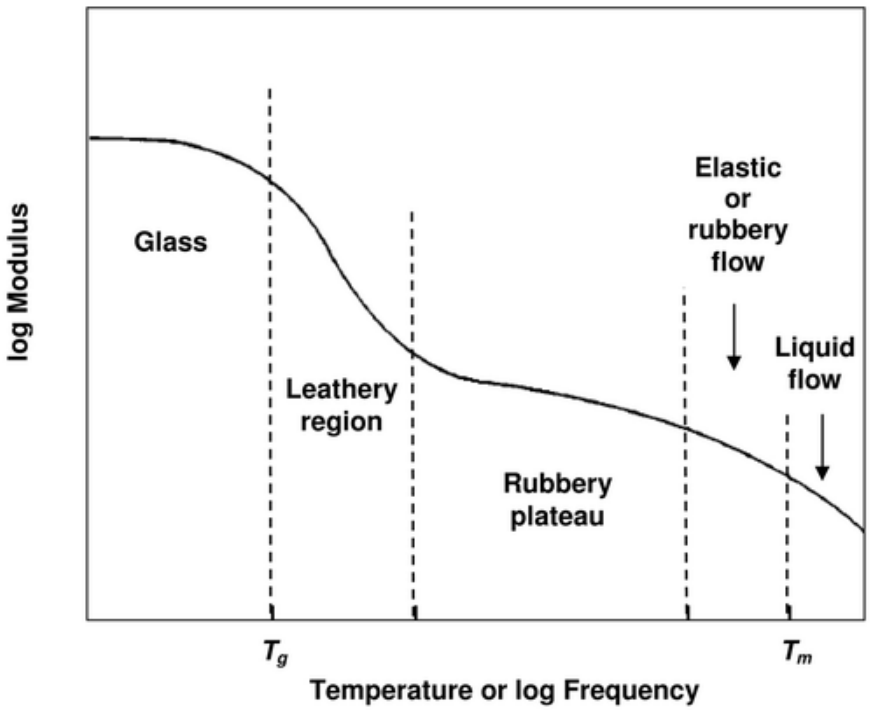


Fig. 6.1. Master curve of the modulus as a function of temperature or frequency, illustrating the five regions of viscoelastic behavior of a partially crystalline polymer. Below the glass transition temperature (T_g), the partially crystalline polymer is in a glassy state; above the melting temperature (T_m), it is characterized by liquid flow behavior. An amorphous polymer would show a similar curve, except that T_m would be missing. (Reprinted, with permission, from Levine and Slade 1990

GLASS TRANSITIONS

Stated in very simple terms, T_g (or, more accurately, the T_g range) is the temperature (or temperature range) at which an amorphous material or the amorphous component of a partially crystalline material undergoes a large change in its modulus. The classic example is glass itself. When the glass blower heats a piece of rigid, brittle glass, it softens and eventually flows. If this flexible material is allowed to cool, it again becomes rigid and brittle. The phenomena during the cooling phase are described as "vitrification" (from the Latin word *vitrum* or glass). The change in modulus (see definition in Chapter 5) at the glass transition for most pure polymers is amazingly uniform, typically five orders of magnitude over a relatively narrow temperature range.

The midpoint of the modulus change is often taken as T_g. However, the glass transition is a secondary transition. This means that measurement of the T_g is not as reproducible as that of a primary transition such as a melting point. T_g is further affected by the history of the sample and thus, among other factors, by how long it has been stored, the rate of cooling or heating, etc.

In contrast to partially crystalline materials, fully crystalline materials do not show aT_g. However, many polymers, such as native starch, are partially crystalline, and their amorphous portion undergoes the glass transition.

CAUSES OF GLASS TRANSITIONS

Picture a polymer system consisting of relatively high molecular weight polymers that are highly entangled. A ball of cooked spaghetti strings, worms, or snakes is a good analogy. At moderate temperatures, the kinetic energy in the system is such that each polymer chain undergoes a number of motions. An important molecular motion in polymers is the segmental motion of the chain backbone. This long-range motion involves the cooperative motion along the backbone chain. It can be visualized as a snake crawling. This motion of the chain defines the free volume of the polymer. The polymer chain requires this amount of space and, by its motion, keeps other chains from invading its space. In addition, in polymers with side chains, one can imagine such chains spinning.

As the temperature of the system (and hence its kinetic energy) is lowered, the motion of the chains slows down. As their motion slows, the individual polymer chains are less able to keep other chains from invading their space. The result is a net reduction in the volume of the system and an increase in the interaction of the polymer segments with each other. As the polymer segments of the various polymers interact with each other, the complex viscosity of the system increases rapidly. At some point, i.e., when the material is cooled to below T_g, the viscosity increase becomes so large that the chains no longer have segmental motion. Now, the kinetic energy of the system is no longer enough to overcome the friction of the chains interfering with each other. The system is now vitrified and described as glassy. As the sample is heated, the process is reversed. The kinetic energy of the chains then increases to a point where it overcomes the friction of their rubbing against each other. The volume increases, and the physical properties go from glassy to leathery to rubbery and finally have viscous flow properties. All of this occurs over a relatively narrow temperature range.

There are other explanations for the glass transition phenomenon that are not based on the free volume. However, they are beyond the scope of this book. Whatever be the case, the explanation given here requires the volume of the system to change as the system goes through the glass transition. Note also that the glass transition does not require the stopping of other motions in the polymer system. For example, the spinning of the side chain may continue even though the material is glassy.

FACTORS THAT AFFECT THE GLASS TRANSITION TEMPERATURE

A number of factors affect the T_g of a polymer. Most of them are intuitively obvious when one reasons in terms of the free volume.

In general, the T_g of a polymer increases with its molecular weight. To explain this, one should consider that the motion of the ends of a polymer are less restricted than its interior section and thus can increase the free volume as a result of their motions. As molecules become larger, the effect that their ends have becomes proportionally less important. As there are proportionally fewer moving polymer ends, they are less able to keep other chains from invading "their" space. This results in a net reduction in free volume and increased interaction of the polymer segments with one another. As a result, T_g increases with molecular weight.

Chemical cross-linking of polymers increases their molecular weight, impairs the free movement of the chains, and also increases T_g. Partial crystallization of the polymer can act as a form of cross-linking, and it increases T_g as well. However, there are also instances in which crystallized polymers show a lower T_g than their noncrystalline counterparts.

In addition, the number, size, and rigidity of the side chains on the polymer chain affect the glass transition. An increase in the number or size of rigid side chains increases T_g, as it restricts the overall motion of the polymer chain. Flexible side chains, in contrast, may act as a plasticizer and thereby lower T_g.

High pressure decreases T_g because it decreases the free volume. However, the pressures required for a significant effect are large and typically of the order of up to hundreds of MPa. In cereal polymer systems, water is generally a very effective plasticizer, as it reduces the level of friction between polymer chains and thus reduces their T_g. As outlined above, at T_g, the kinetic energy of a given polymer system is no longer enough to overcome the friction of the chains interfering with each other. It follows that addition of plasticizer to such a system decreases the temperature and thus the kinetic energy content at which the glass transition occurs.

Thus, when a polymer is glassy at room temperature and a plasticizer is introduced into the polymer matrix, the polymer can go through the glass transition with no change in temperature. If so, it has been plasticized and the T_g of the plasticized system is lower than that of the starting material. As long as the polymer is glassy, the rate of diffusion of small molecules through the polymer is slow. Thus, adding a low molecular weight plasticizer to a glassy system in many instances does not immediately plasticize it. In addition, not all materials added to the system act as plasticizers. Materials that increase the friction between the polymer chains (rather than decrease it) act as antiplasticizers, and, of course, they increase T_g.

MEASUREMENT OF GLASS TRANSITIONS

In principle, several techniques can be used to measure the glass transition. As mentioned above, the volume of the polymer material changes as it goes through a glass transition, and the measurement of the volume change, in principle, is a first way to determine T_g. When an amorphous (noncrystalline) or partially amorphous (and thus at the same time partially crystalline) material is heated, the volume of the polymer increases with temperature in a linear fashion until T_g is approached. At that point, the volume increases at a much faster rate. Once the transition has occurred, the slower linear increase again resumes. This is in contrast to a crystalline material, for which the increase in volume occurs sharply as the melting point is reached (Fig. 6.2).

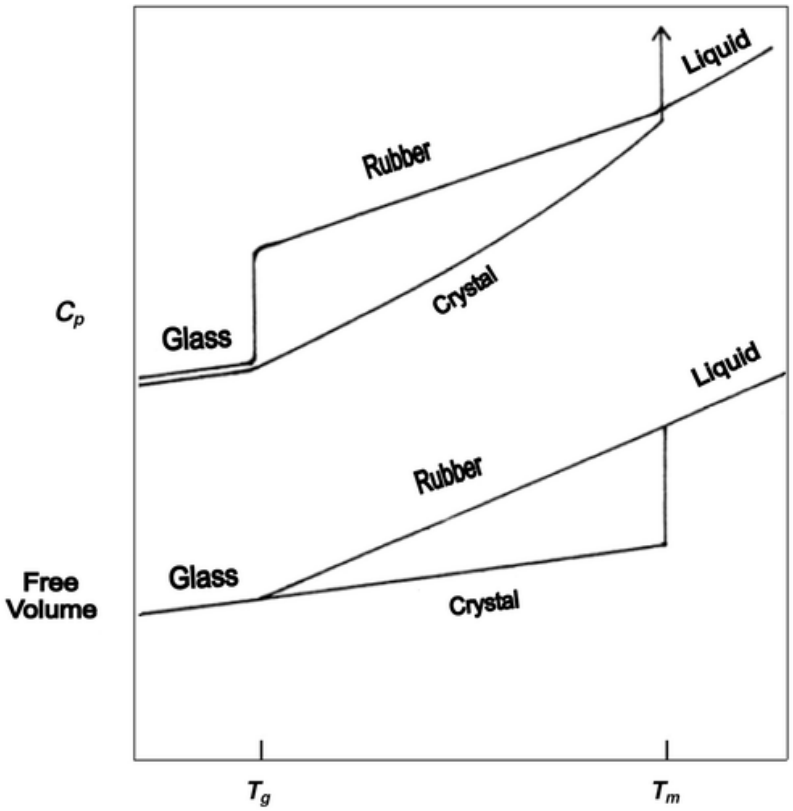


Fig. 6.2. Plot of heat capacity (C_p, top curves) and free volume (bottom curves) as a function of temperature for various polymers. An amorphous glassy polymer goes from glassy to rubbery to liquid. This leads to changes in both its heat capacity and its free volume. Its C_p changes rapidly at the glass transition temperature (T_g) and then gradually changes with increasing temperature. Its free volume does not show a steep increase at T_g but gradually increases with increasing temperature above T_g. For a crystalline polymer, there is a steep change in both C_p and free volume when the crystal melting temperature (T_m) is reached. For a partially crystalline (and therefore partially amorphous) polymer, both changes in C_p and free volume of amorphous and crystalline polymers can be observed. (Adapted from Slade and Levine 1991)

As outlined above, the increase in volume at T_g can be used to determine the transition. An instrument such as a thermal mechanical analyzer (TMA) measures the change in dimension as the material is heated. However, such an instrument does not differentiate between volume changes caused by glass transition, gas expansion, or solvent vaporization. Therefore, in many instances, a TMA is not the first choice.

Another method for measuring glass transitions is with a differential scanning calorimeter (DSC). As a polymer becomes mobile by going through T_g, its heat capacity increases. This change in heat capacity can often be measured calorimetrically (Fig. 6.2). Because the glass transition is reversible, the change in heat capacity can be measured in either direction (heating or cooling). Differential scanning calorimetry works relatively well with pure materials. However, when other materials dilute the polymer system to be analyzed, the small change in heat capacity may be too small to be detected.

There are also rheological and electrical methods to measure glass transitions. In general, they have not been used with cereal systems and thus are outside the scope of this book.

Glass Transitions in Cereals

The major polymers in cereal grains are starch, proteins, and small levels of nonstarch polysaccharides in the endosperm and nonstarch polysaccharides (including cellulose) and protein in the pericarp. Starch and cellulose are partially crystalline, while the proteins and the other nonstarch polysaccharides are amorphous. Glass transitions are undoubtedly important to the properties and behavior of all these polymers.

Examination of a mature wheat kernel at normal safe-storage moisture contents (below 14% for wheat, see Chapter 7) shows the pericarp to be friable and the endosperm to be hard and brittle. If the kernel is soaked in water, striking changes result. The pericarp becomes leathery and tough and the endosperm soft and rubbery. These are classic examples of behaviors that result from going through a glass transition from glass to rubbery. In the above cases, the polymers in the kernel have gone through the transition with no change in temperature.

PROTEINS

The continuous phase within the cells of the wheat kernel consists of amorphous gluten proteins (see Chapter 1). Because of this, the changes noted above in the wheat endosperm as a result of water uptake are likely the result of changes in the gluten proteins.

When gluten is heated in a DSC under low moisture conditions (about 13%), a glass transition is clearly detected (Fig. 3.4). As would be expected, its T_g decreases rapidly as more water is added to the gluten. Figure 6.3 shows that it approaches room temperature (23°C) at about 16% moisture. Thus, such temperature and moisture conditions produce a leathery protein.

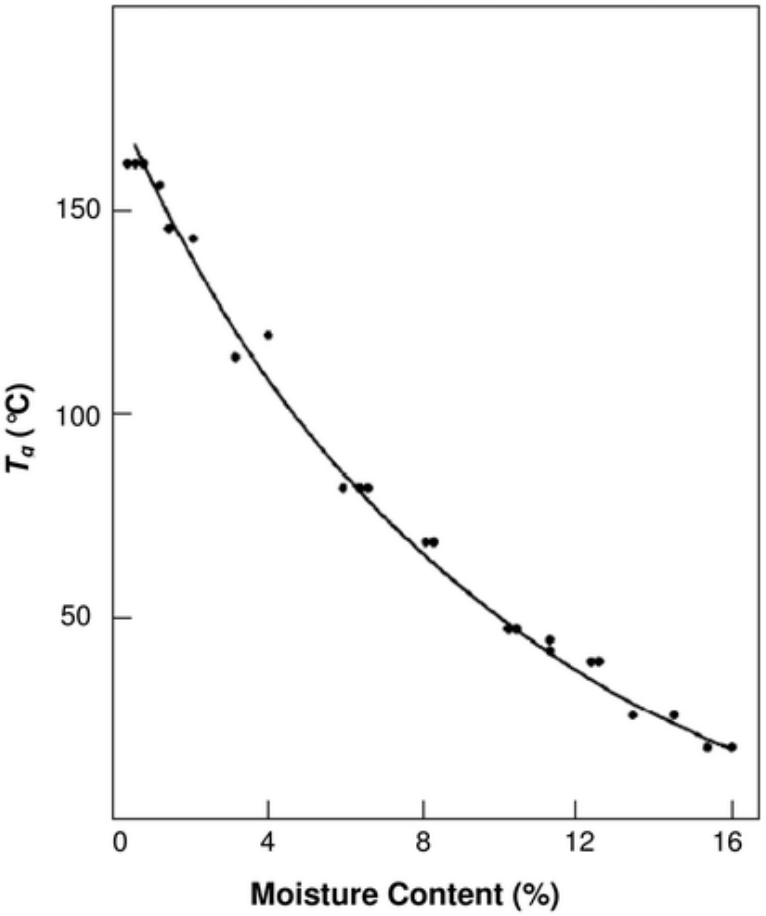


Fig. 6.3. Glass transition temperature (T_g) of both hand-washed and commercial gluten as a function of moisture content. (Reprinted from Hoseney et al 1986)

If either moisture or temperature is increased further, the protein becomes rubbery. Thus, no specific configuration of the protein is needed to produce the partially elastic properties of gluten but only the correct moisture and temperature conditions.

It is often stated that the gluten proteins are unique in many ways, especially in their ability to form viscoelastic dough when hydrated. While much has been written about the reasons for this unique ability (see Chapter 3), from a polymer science viewpoint, to have a rubbery material, all that is needed is a large polymer that has a glass transition at the correct temperature. In the case of gluten, the T_g at 16% water is room temperature. Addition of more water at that temperature moves the polymer into the leathery and finally into the rubbery region. From the above, one must conclude that the uniqueness of wheat gluten is that it undergoes a glass transition at the "correct" temperature.

In contrast to wheat, maize (corn) endosperm does not change appreciably when it is soaked in water. The endosperm hydrates but does not swell appreciably and retains its hard, gritty nature. These phenomena can be explained by the fact that the maize matrix protein is highly cross-linked and thus does not absorb large amounts of water. A second factor is that the glass transition in maize protein (Fig. 6.4) occurs well above room temperature. Mixing the maize protein (zein) and starch at elevated temperatures (above zein's T_g) gives a cohesive dough, as shown by a farinograph (Fig. 6.5).

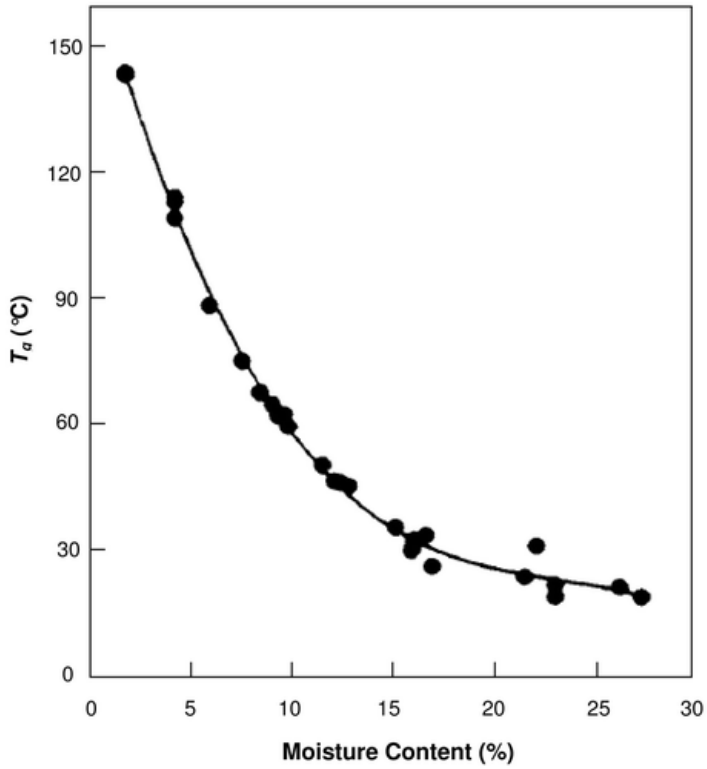


Fig. 6.4. Glass transition temperature (T_g) of zein protein as a function of moisture. (Reprinted from Lawton 1990)

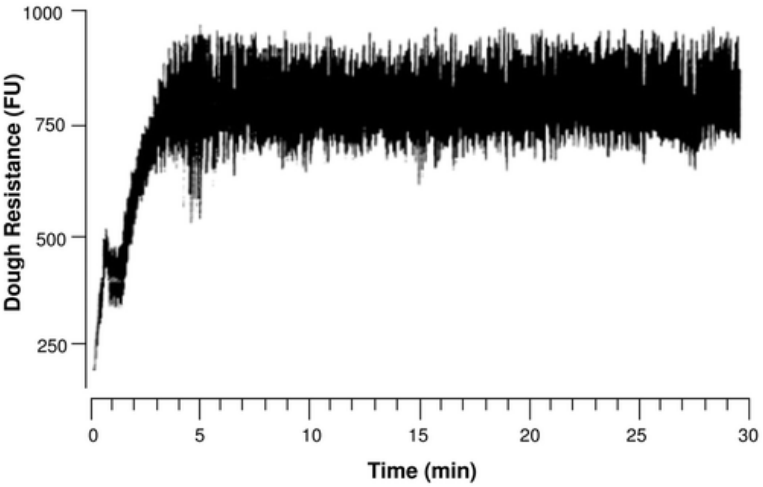


Fig. 6.5. Farinogram of a zein-starch dough mixed at 35°C. The resistance of the dough against the rotating blades of the farinograph instrument is measured as torque, expressed in farinograph units (FU), and recorded and plotted on-line as a function of time. (Reprinted from Lawton 1990)

STARCH

Starch, as it occurs in nature, is a partially crystalline polymer system (see Chapter 2). As such, it should go through a glass transition. The granules take up only about 30% water at room temperature. Figure 6.6 shows its T_g as a function of moisture content. When gelatinized, all the crystals are melted, and the resulting starch freely hydrates and swells in water. With excess water, the T_g of gelatinized starch has been shown to be about −7°C. When the T_g levels of native and pregelatinized starches are compared as a function of moisture content, under limited moisture contents, the T_g of the native starch is always higher than that of the pregelatinized starch. One way to explain this difference is to consider the native, partially crystalline starch as a form of cross-linked (see above) starch, in which the free movement of the chains is restricted and which therefore has a higher T_g than its gelatinized counterpart. However, Figure 6.6 is not universally accepted. Other workers have suggested that the glass transition of native starch occurs at higher temperatures. A thorough discussion of the arguments is beyond the scope of this book.

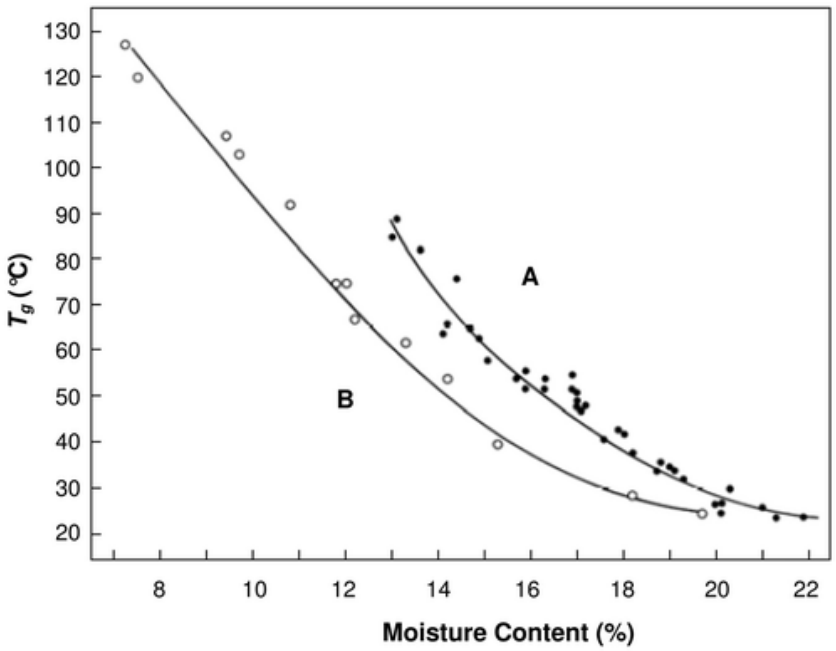


Fig. 6.6. Glass transition temperature (T_g) of native (A) and pregelatinized (B) wheat starches as a function of moisture content. (Reprinted from Zeleznak and Hoseney 1987)

OTHER POLYMERS IN CEREALS

Little is known about glass transitions in cellulose or other nonstarch polysaccharides in cereals. However, they may well be important in cereal processing.

Importance of Glass Transitions in Cereal Products

As already outlined in the introduction to this chapter, there are many examples of glass transitions in cereal products. Corn (maize) chips are crisp and glassy but lose much of their desirability if the moisture content increases and the product changes from glassy to leathery. Breakfast cereals become soggy in milk before they are consumed. Pizza crust becomes soggy due to moisture migration. Popcorn left to pick up moisture becomes quite tough and less palatable. Saltine crackers get much of their characteristic delightful texture from the fact that they are glassy at room temperature, with the moisture content below about 2%. Breading and batter products that are used to coat fish, chicken, or other products are other common examples of crispness that is related to the presence of the glassy state.

Bread characteristics can change as a result of glass transitions. A loaf of bread comes from the oven with a hard, crisp crust that is fragile and truly delightful. Coming from the oven, the crust is very dry. It typically contains only 2% moisture. With time, the moisture from the crumb migrates to the crust, as it tries to establish equilibrium. At the same time, moisture is lost to the atmosphere and the crust's property is preserved. However, if the bread is placed in a plastic bag, as essentially all North American bread is (and European bread, too, in some instances), the loss of water from the crust is slowed. As a result, the moisture content of the crust increases, and it becomes tough and leathery within a very short time because the moisture migration has caused the polymers in the crust to go from glassy to leathery even though the temperature has remained constant. Toasting bread with a leathery crust drives the moisture out, restoring the glassy state to the crust and, if sufficient moisture is removed, to the rest of the bread.

Another good example of the occurrence of glass transition in cereal products is what happens during high-temperature short-time cooker-extruder processing. Maize or other cereals in the glassy state are fed into the extruder, and the moisture and temperature are both raised to cause the cereal material not only to go through a glass transition but also to become a flowable mass, often called a "melt." As the material leaves the extruder, some of the moisture is lost, and the plastic material cools to again form a glassy product.

The physical properties of cereals and many other materials can be summarized in the generalized "state diagram" given in Figure 6.7. Thus, if the material starts at point A in the glass region and its temperature is raised, it first becomes leathery, then rubbery, and eventually flows in most cases. If the temperature remains constant and the moisture content is raised, the product properties can change from glassy to leathery and rubbery.

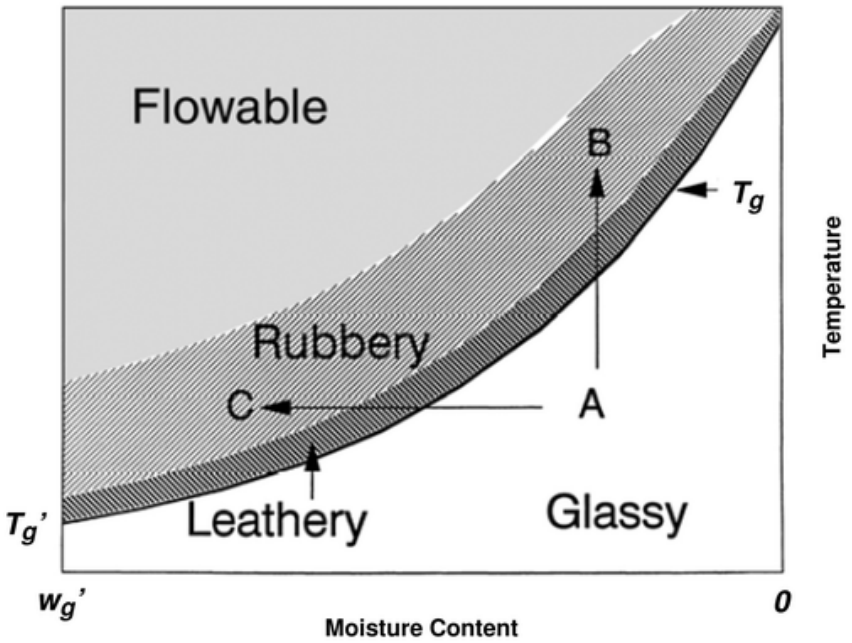


Fig. 6.7. Conceptual state diagram of a cereal material as a function of temperature and moisture. $T_g$is the glass transition at 0 moisture content, and $T_{g'}$ is the glass transition at the moisture content at which free (freezable) water starts to appear as a separate phase ($W_{g'}$). The system goes from glassy to rubbery when the temperature is increased from A to B or when the moisture content is increased from A to C The transitions from glassy to leathery to rubbery to flowable with increasing temperature are also shown in Figure 6.1. (Courtesy D. Ortiz)

Glass Transitions of Sugar Solutions

Although we usually think of polymers when we think of glass transitions, it is also true that smaller molecules can undergo glass transitions. Sugar solutions used with cereal products are a good example. Sugar coatings for some of the ready-to-eat breakfast cereals are a sugar glass. The glassy material makes diffusion of water very slow and thus provides a barrier to moisture reaching the cereal product. Therefore, the cereal product has a much longer shelf life under adverse conditions. A similar sugar glass is used to protect popcorn in popcorn balls.

CHAPTER 7: Storage of Cereals

Although grain is generally harvested once or, in some areas of the tropics, twice a year, it is consumed throughout the year. Therefore, practically all grain must be stored. The cereal grains are, in general, amenable to storage for relatively long periods of time. They are usually harvested at relatively low moisture content and, when stored out of the weather and protected from insects and rodents, easily keep for several years. Under ideal storage conditions (low temperature, inert atmosphere, etc.), safe storage may be measured in decades.

Throughout history, the cereal grains have given humans a buffer against crop failure and starvation. In comparison with such foods as dairy products, meats, and fresh vegetables, cereals are relatively easy to store. However, they can go "out of condition" if storage conditions are not proper. In the past, and indeed, even today in some parts of the world, such loss of cereal stores has led to starvation. We here focus on the main aspects that should be taken into account when storing cereal grains.

Basic Types of Storage

Storage can vary from the simple expedient of pouring the grain onto the ground to storage in large concrete structures. We here describe different practices of grain storage.

SIMPLE METHODS

Generally, grain is piled on the ground only during the harvest season when transportation equipment is in short supply. In fact, such storage is not as bad as it sounds. A pile of grain sheds water quite well, and typically, only the top 5 cm or so (inch or two) is damaged with short-term storage. Of course, as storage time increases, the loss increases, as the grain accepts more water from rain and is also exposed to birds, insects, and rodents. In some countries, however, grain is covered and stored on the ground for long periods.

In some parts of the world, grain is stored underground. Underground storage offers a number of advantages. For example, it protects the grain from daily and seasonal variations in temperature; the construction is relatively simple; and it protects grain from insects and molds because of the low oxygen and high carbon dioxide content of the interseed air. Of course, the site for underground storage must be picked to give a dry environment.

Bagged grain can be stored in almost any shelter that protects the bags from the weather and from predators. Bags can be handled without any equipment. However, they are relatively expensive, and handling them is expensive unless labor is very cheap.

BULK STORAGE IN BINS

Bulk storage in bins is the most widely used type of storage today. The size of the bin may vary from a few tons for an on-farm storage bin to thousands of tons for a bin in a terminal elevator. On-farm bins are today mostly constructed of steel, and, depending on the part of the world, the larger elevators are now practically all constructed of either steel or concrete.

When grain is poured into a bin, it forms an angle from the horizontal that is called the "angle of repose" (Fig. 7.1). With most grains, this angle is about 27°. Damp grain or very small grain gives a slightly flatter slope. The outflow hopper at the bottom of a bin must be cone-shaped and have a slope greater than the angle of repose, or the grain will not flow out. Smaller bins require a steeper slope because of the greater friction on the sides of the hopper.

Fig. 7.1. Pile of grain, showing angle of repose.

The pressure that grain exerts on the bin floor is not proportional to the height of the grain. Because much of the grain's weight is supported by the bin's walls, grain follows the laws of semifluids rather than of fluids. Each kernel rests on several kernels below it, so part of the weight is distributed laterally until it reaches a wall. The lateral pressure of the grain on bin walls is about 30–60% of the vertical pressure, and the vertical pressure increases very little after a depth of about three times the bin diameter.

Grain settles or packs during storage. Light-density grain such as oats may pack to lose as much as 28% of its volume. However, heavier grains may pack only slightly. When grain is poured into a bin, the heavier grain falls faster and straighter. The lighter particles such as chaff accumulate toward the bin walls. However, when the stream of grain hits other grains, small particles are trapped between the larger kernels. Those particles ("fines"), consisting of weed seeds, broken kernels, or heavy dust particles remain at the pile's center, where the incoming stream hits the grain pile. The whole-grain kernels flow away down the slope (angle of repose). Because the space between kernels may account for 30% of the space in the pile, there may be 30% fines in the area where the grain was introduced. This is called the "spoutline."

When a bin is opened, a column of grain directly above the opening flows out first. The column widens as it reaches further from the opening, giving an inverted cone. The grain in the center flows faster, producing a cone-shaped depression on the surface. The grain at the surface flows into the depression and down to the draw-off.

Unless unusual steps are taken or abnormal conditions occur, all cereal grains contain some moisture, and a difference in moisture content of 1% for any cereal grain can be translated into roughly a difference of 1% in the value of that grain. However, the moisture content is not only of direct economic importance but also of importance for the stability and safe storage of any cereal. Of course, apart from moisture content, temperature and time (duration of storage) are also important variables that can influence the rate of fungal growth. Grains, like most other foods, store better at lower temperatures. However, in practice, moisture control is of paramount importance for ensuring safe storage.

In this respect, it has long been known that different cereals have different maximum moisture levels for safe storage. For the major grains, these levels are 12–13% for rice; 13% for barley, maize, oats, and sorghum; and 14% for wheat. However, like all general rules, this one does not always hold; the maximum moisture varies depending upon the temperature, uniformity of moisture in the mass, and other factors. Above the maximum levels quoted above, fungal growth begins. Between these maximum levels and about 20% moisture, a small increase in the moisture level greatly increases the rate of fungal growth and also changes the number and type of species that develop. Of course, it becomes clear that it is not the moisture content *per se,*but the water activity, that controls the onset of fungal growth.

GRAIN WATER ACTIVITY

In layman's terms, water activity is a measure of the availability of water, and it is such availability of water that determines whether fungi develop on cereals. The moisture in grain is in equilibrium with the air surrounding the grain. The equilibrium moisture content is defined as the moisture content at equilibrium with an atmosphere at a certain relative humidity. Water activity (a_w) is defined (and hence measured) as

$$a_w = p/p_o$$

where p is the vapor pressure of water in a given system (e.g., interseed air), and $p_o$is the vapor pressure of pure water at the temperature of the system.

It follows that, as more water is bound to the cereal constituents and the solutes become more concentrated, the vapor pressure and the water activity become lower even though the moisture content stays the same. As moisture content increases, in general, the water becomes more and more available to contribute to the vapor pressure, and the water activity increases.

When grain is in storage, the grain and the moisture content of the associated air come into equilibrium. One of the most damaging factors in grain storage is the growth of molds. Generally molds do not grow on grain in equilibrium with air of less than about 70% relative humidity (i.e., on grain at water activities below 0.70). Their spores germinate at water activities of about 0.75. Bacterial growth is generally not a problem with cereals as it would require water activities approaching 0.90, and, hence, much higher moisture contents.

However, different lots of grain, even of the same type of cereal, may have different moisture contents at a given water activity (Fig. 7.2). In addition, grains of the same lot may have different moisture contents, depending on the history of the grain.Figure 7.3 illustrates this phenomenon, which is called "hysteresis." The exact reason for the hysteresis effect is not known. However, one can readily imagine that, when a cereal has been dried excessively and subsequently rehydrated to the same moisture content it had originally, a higher water activity results, as the rehydrated grain is now less efficient in binding water.

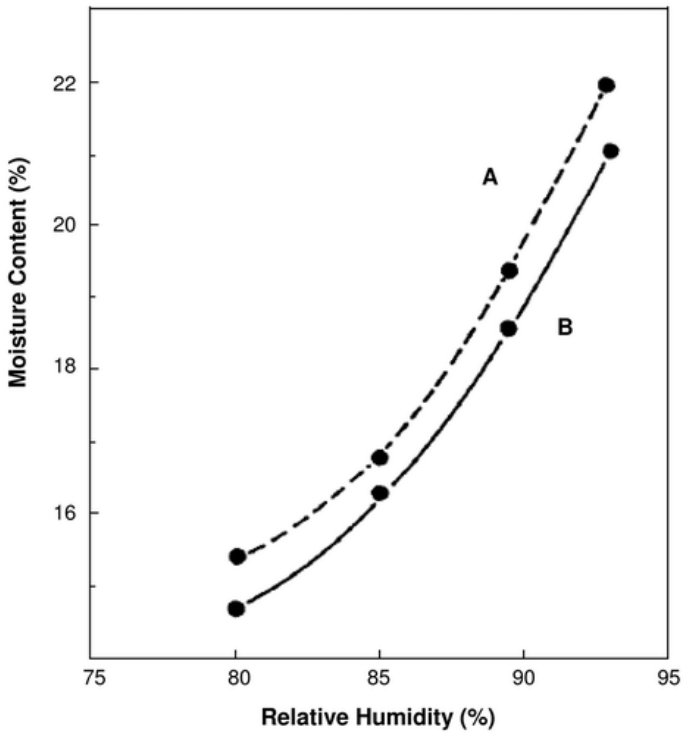


Fig. 7.2. Moisture content as a function of relative humidity for two maize samples (A and B). (Reprinted, with permission, from Sauer and Burroughs 1980)

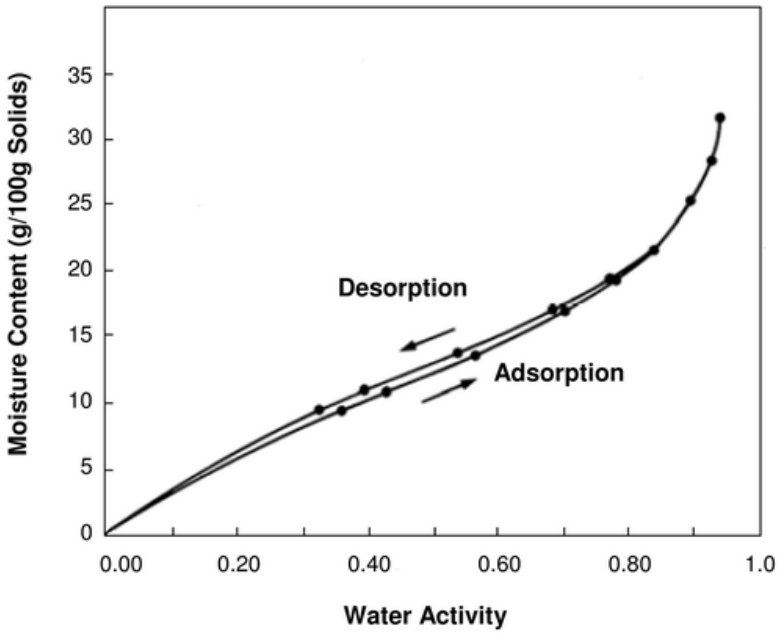


Fig. 7.3. Wheat drying (moisture desorption) and wetting (moisture adsorption) curves, illustrating the phenomenon of hysteresis. When wet grain is dried excessively and subsequently rehydrated to its original moisture content, the water activity is higher than the original water activity, as the rehydrated grain is now less efficient in binding water. (Reprinted, with permission, from Labuza 1984)

ANALYSIS OF GRAIN MOISTURE CONTENT

While it is true that water activity really dictates whether fungi can grow or not, it is common industrial practice to determine moisture content. The moisture content of the grain has a strong economic effect, as grain is bought and sold based on weight. However, for any given cereal, there is an established average relation between moisture content and water activity.

The measurement of moisture content is, at best, difficult. First of all, we need to consider the purpose of the analysis. A uniform or average sample may be important if we are buying or selling grain. It is, however, of

little, if any, value if we are interested in how a lot of grain will store. In this particular case, the important moisture level is not the average but the highest moisture found in the lot. Indeed, if the moisture content in one area in the grain exceeds a critical level, microorganisms will grow at that point, producing both moisture and heat as a result of their metabolism, which will then lead to even greater damage.

Therefore, if one is to store cereals for an extended period of time, it is important to know the moisture content in any given portion of the stored grain. A mass of grain in a bin indeed looks deceptively uniform. While one could easily assume that the moisture content is also uniform throughout the bin, this is seldom, if ever, the case. First, grain coming from a single field may vary quite widely in moisture content because of differences in the soil, stages of ripeness of the grain, and harvest time. In addition, even within a single head or ear of grain, the moisture can vary from kernel to kernel. Furthermore, if grain is obtained from several sources, the moisture will surely vary. Furthermore, while one would expect that, given sufficient time, the grain bulk would come to moisture equilibrium, in fact, this occurs only if the grain is stored under stable conditions. In practice, it does not readily occur, as illustrated in Figure 7.4. In addition, other forces, which are discussed later, often upset the equilibrium.

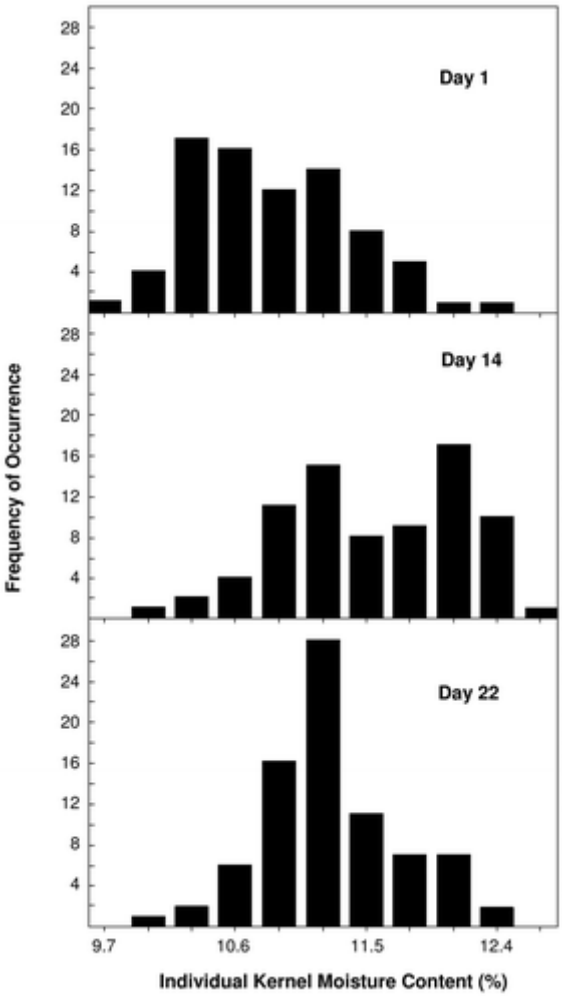


Fig. 7.4. Evolution of the distribution of the moisture content (over a 22-day period) of individual wheat kernels from a wheat sample stored at ambient conditions. (Courtesy A. A. Abdelrahman)

When one analyzes moisture content, this lack of homogeneity in moisture content of the grain in a particular bin makes sampling difficult. Furthermore, to be completely accurate, one must measure water, rather than other volatile substances, and therefore one cannot simply measure loss of weight. This would require the use of, for instance, the Karl Fischer reagent. Luckily, near-infrared (NIR) technologies, which can readily analyze large numbers of samples, are widely available today. If calibrated correctly, the NIR techniques give sufficient accuracy.

Because in many parts of the world, the weather conditions are rather unpredictable and the risk exists that the crop could be destroyed in the field, it is usually wise to harvest the crop early. In many instances, the small cereal grains dry rapidly in the field and thus have safe storage moisture contents when harvested. However, in wet harvest years, considerable quantities of small grains must be dried. Even in normal years, most of the harvested rice and part of the maize are dried. Both low and high temperature drying are in current use.

LOW-TEMPERATURE DRYING

Low-temperature drying (Fig. 7.5) uses air with no heating above ambient conditions. Because of its economic advantages, it is used wherever possible. In practice, air is forced through the grain mass. The only energy input required is that necessary to force the air through the grain. In many instances, drying also cools the grain, which also contributes to safe storage. Another major advantage of ambient drying is that the grain functionality is not damaged by high heat, as is too often the case with high-temperature drying. The major disadvantage is the relatively long time required to reduce the moisture content significantly and the need to use air of low relative humidity. In practice, low-temperature drying is used when the temperature is low enough so that moist grain can be safely stored long enough for the ambient drying to be effective.

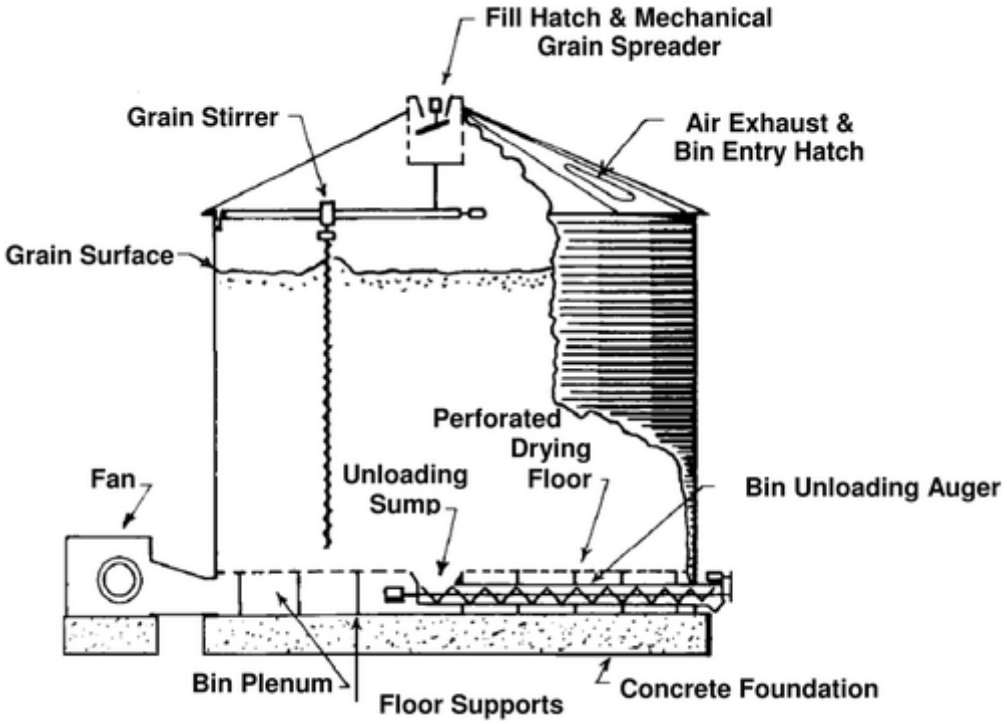


Fig. 7.5. Low-temperature drying bin. (Reprinted, with permission, from Foster 1982)

HIGH-TEMPERATURE DRYING

In high-temperature drying, the air used is heated to higher temperatures. This increases the capacity of the air to hold water and speeds the removal of the water from the grain. While the major advantage is saving time, the major disadvantages are the cost of energy for heating the air and the heat damage the grain may suffer. Such damage may include stress cracks, increased brittleness and susceptibility to breakage, bulk density changes, and discoloration. Less obvious heat-induced damages, which are seen when the grain undergoes processing, include loss of germination capacity of malting barley, loss of breadmaking capacity of wheat flour (Fig. 7.6), poor separation of starch and protein in maize wet milling, and reduced yields of high-value large grits in maize dry milling. However, because high temperature apparently does not change the feed value of maize, there is little concern about use of heat-damaged maize in animal feeding.

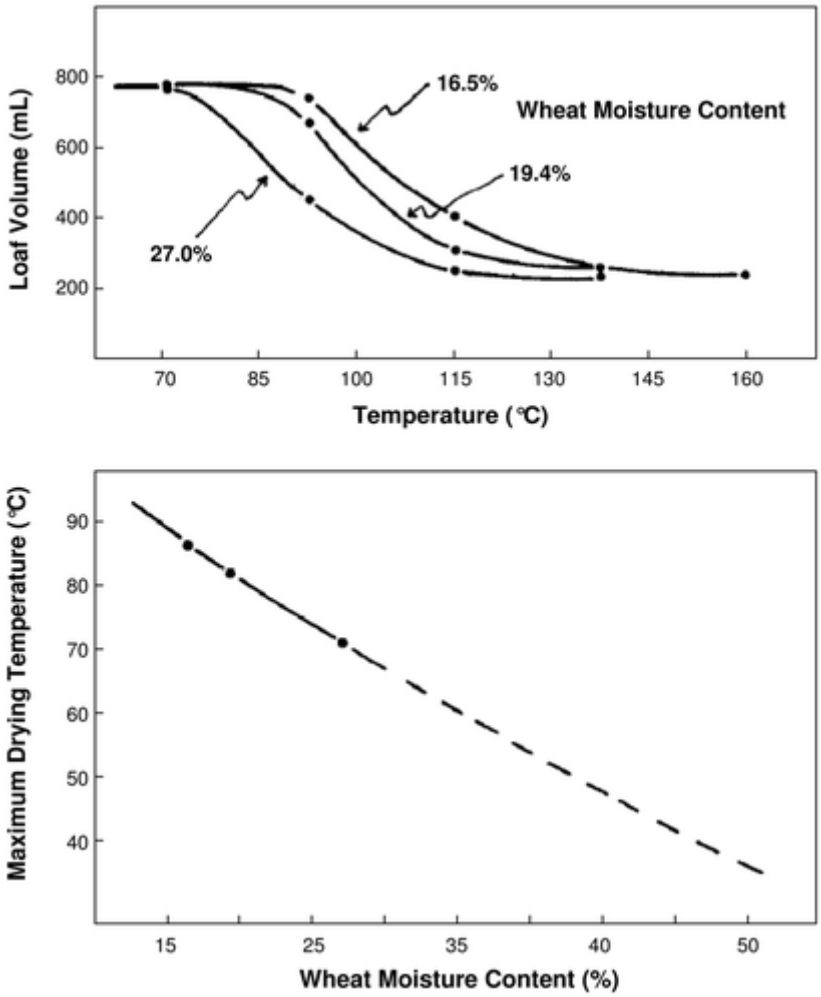


Fig. 7.6. Top, interrelations between bread loaf volume, drying temperature, and intitial wheat moisture content. The graph shows that, when wheat is to be used for milling into flour for breadmaking, the maximum drying temperature that can be employed without impairing the breadmaking capacity of the resultant wheat flour decreases with the wheat's initial moisture content.**Bottom,** maximum drying temperature that, for a given initial wheat moisture content, allows milling of dried wheat into breadmaking flour without impairing bread loaf volume and crumb grain. (Reprinted, with permission, from Finney et al 1962)

DRYING IN PRACTICE

Low-temperature drying often is done with a full-bin system. A bin of grain is dried by forcing air through the grain mass. An important consideration in this type of drying is the grain's resistance to airflow. Many factors affect this resistance. Some of them are the size, shape, and surface characteristics of the grain; the size distribution of the grain (which depends, in part, on the number of broken kernels); and the depth of the grain bed.

In general, if the amount of air passing through a mass of grain is doubled, the force required for the air to pass through the grain mass increases about threefold. If the grain layer is doubled in depth, the force required for the air to move through mass increases about 11-fold. The minimum heat required to dry grain is controlled by the amount of water to be removed and the latent heat of vaporization of that water. Other important factors are the amount of air used (as well as its initial temperature and its heat capacity), the temperature of the incoming grain and its heat capacity, and the temperature of the outgoing grain.

In drying practice, the loss of moisture (vaporization) occurs at the surface of the grain. After a short time, the moisture content at the surface of the grain is low, and the drying rate falls. The rate of drying then depends on the rate of diffusion of moisture to the surface. As drying continues, the distance the moisture must diffuse is greater and the rate of drying is slower. A system that accelerates drying is called "dryeration." It actually combines heated air drying and aeration cooling. The grain is heated during a high-temperature-drying phase, held at elevated temperatures to temper (i.e., to allow the moisture to equilibrate in the kernels), and then cooled and dried with unheated air. In a typical example, maize of 20–30% moisture content is dried at a temperature of 95°C to a moisture content of 16–18%. It is then held at high temperature for 4–10 h, and then

cooled, and finally dried with an airflow of typically 10–20 liters per second and per tonne (10–20 $L \cdot s^{-1} \cdot t^{-1}$) during typically another 10 h.

Rice, like most cereals, has a propensity to crack, fissure, or check if dried too rapidly. To minimize cracking and fissuring, paddy rice is generally dried with air heated to less than 65°C for only 15–30 min, which typically removes 2–3% moisture. The rice is then allowed to temper for 12–24 h to equilibrate the moisture within the kernel and then is passed through another cycle. The process is continued until the grain reaches the safe storage moisture content of 12.5% or less. Although the process is expensive, as it requires the grain to be handled multiple times, it is effective against cracking and checking, and it makes the rice more resistant to breakage in the subsequent milling of brown rice. On-farm drying of rice is usually accomplished by using bin-drying techniques with relatively low-temperature (<10°C) air. Use of such temperatures and relatively high airflow rates is effective in reducing the moisture content while not fissuring the grain.

Aeration

During storage of grain for extended periods, care must be taken that the temperature in the bin does not increase and that no hot spots form. This can be accomplished by turning the stored grain or simply moving it from one bin to another. However, in many parts of the world today, the grain is aerated. Indeed, a small movement of air through the mass also maintains the temperature satisfactorily. The amount of air used in aeration is, in general, too low to affect the average moisture content of the grain mass to any extent. However, aeration can decrease moisture accumulation at particular points in the grain mass. Such moisture accumulations can result from seasonal temperature changes, which lead to temperature gradients in the grain bulk. The temperature gradients then induce convection currents that lead to moisture migration, resulting in moisture accumulation at particular points in the mass (Figs. 7.7 and 7.8). Aeration corrects this condition, as the movement of air through the grain mass makes the temperature more uniform and decreases the moisture accumulation.

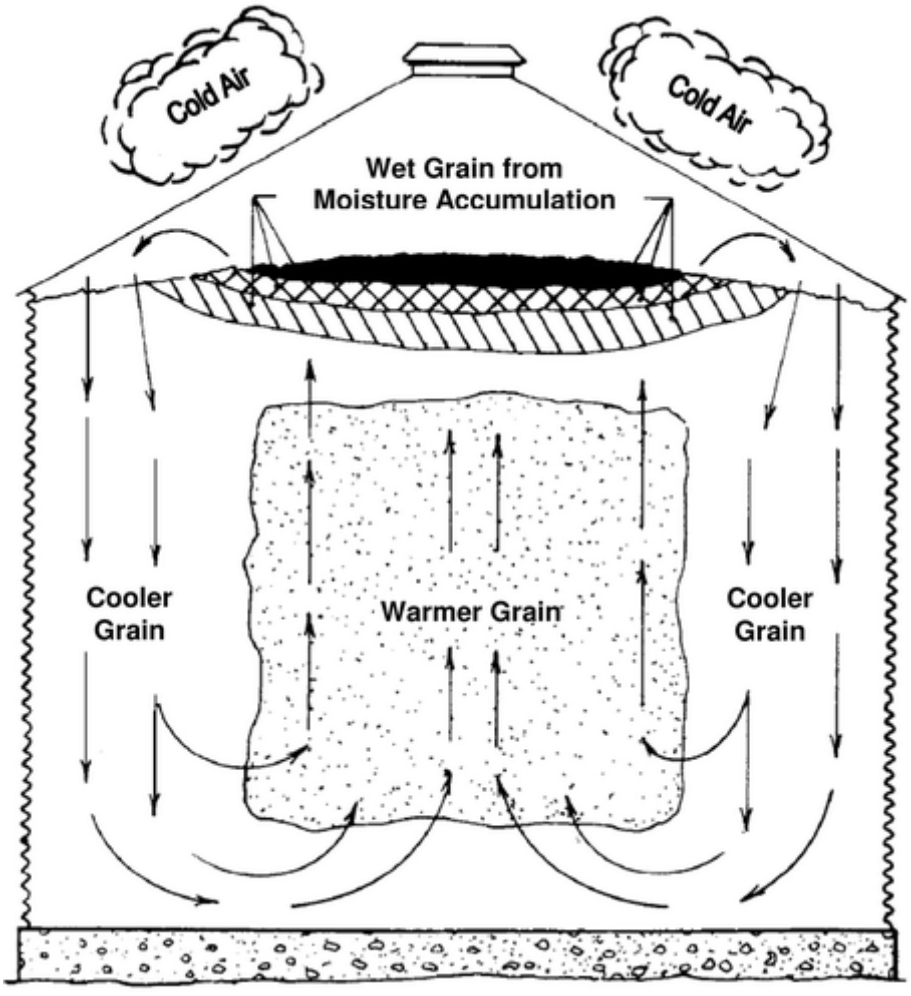


Fig. 7.7. Moisture migration in stored grain when outdoor temperatures are falling. The temperature gradients induce convection currents that lead to moisture migration, resulting in moisture accumulation at particular points in the mass. (Reprinted, with permission, from Foster and Tuite 1982)

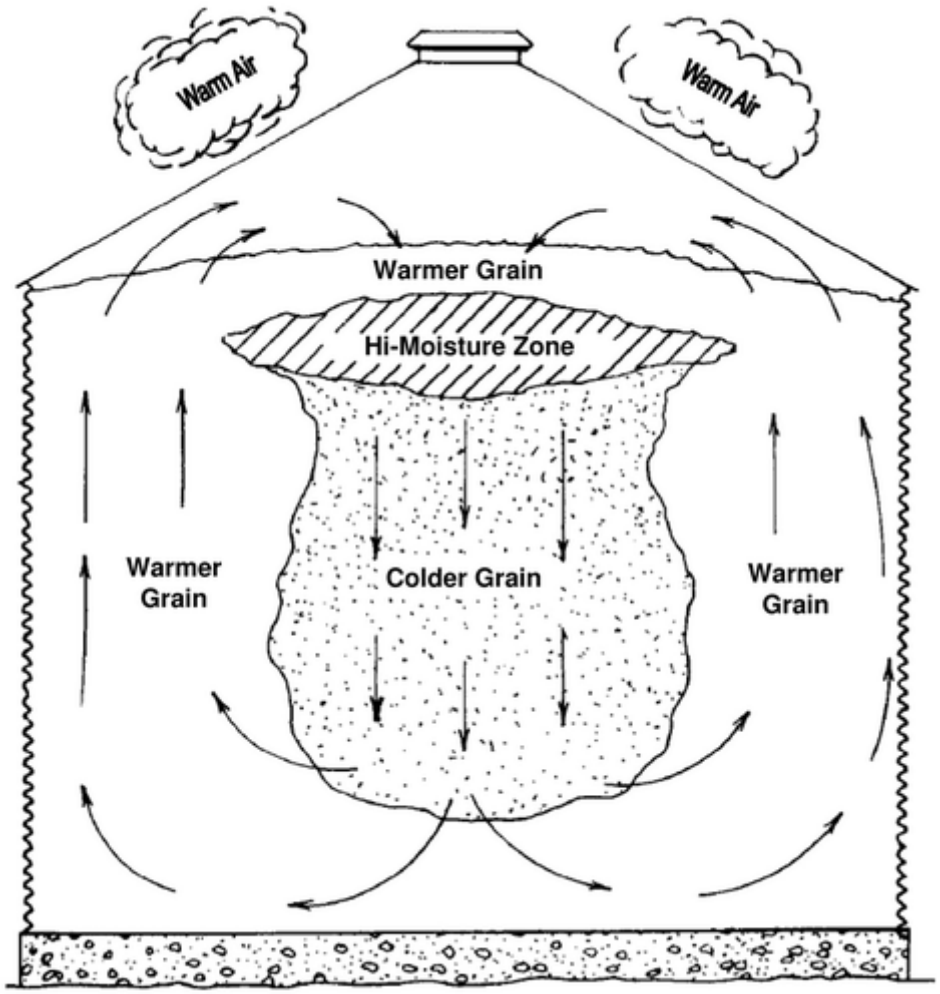


Fig. 7.8. Moisture migration in stored grain when outdoor temperatures are warmer than the grain temperature. The temperature gradients induce convection currents that lead to moisture migration, resulting in moisture accumulation at particular points in the mass. (Reprinted, with permission, from Foster and Tuite 1982)

Grain Respiration

As long as it retains its viability, grain respires and is thus "alive." Grain stored under reasonable conditions slowly loses weight because of its respiration. In general, the weight loss is very slow if the grain is stored properly. Probably the best way to measure respiration is to measure the carbon dioxide produced or the oxygen consumed or both. The ratio of moles of carbon dioxide produced to the moles of oxygen consumed is called the "respiratory quotient." The value of the respiratory quotient varies with the material used as the substrate. It equals 1.0 for carbohydrates and 0.7 for fats. Respiration can be measured either in a static mode or with gas being forced continuously through the grain mass. Both systems have advantages, but, in general, more information is obtained from continuous measurements.

However, one must be aware that the measurement of respiration does not distinguish between the respiration of the grain itself and that of the microorganisms that are always associated with the grain. Because of fungal development, the respiration rate rapidly increases when the interseed water activity approaches 0.75.

Respiration is also affected strongly by temperature. Indeed, higher temperatures accelerate respiration until the thermal inactivation of the enzymes involved reduces or stops respiration. Also, the amount of aeration affects respiration of both the grain and its associated microorganisms, as respiration consumes oxygen and produces carbon dioxide. With low aeration rates, respiration tends to be limited by the oxygen supply.

Respiratory activity tends to be higher in grain having a higher percentage of damaged kernels, even with other factors (moisture, temperature, and oxygen supply) held constant.

Functional Changes and Indices of Deterioration

Several tests have been used to measure the condition of grain and thereby predict its future storage behavior. These tests include the evaluation of physical changes in the grain, such as losing its natural luster and becoming dull in appearance. Also easily detected are changes in odor, such as acquiring a sour or musty smell.

One of the first signs of deterioration of grain is loss of viability. Thus, a germination test can be quite useful, particularly for grain that is to be used for seed or for malting. The value of such tests for predicting changes in grain for feeding, breadmaking, or breakfast cereals is less clear. A biochemical test for seed viability, generally referred to as the "tetrazolium test," is based on the reduction, by the germ's enzyme system, of 2,3,5-triphenyltetrazolium chloride. The grain is still viable when a red coloration appears in the germ.

Several attempts have been made to develop a reliable and convenient biochemical test to determine storability of grain. These include assays of fat acidity and glutamic acid decarboxylase activity. Neither of these tests gives useful information for sound grain. However, during storage, particularly under non-ideal conditions, the value for fat acidity increases and that for glutamic acid decarboxylase decreases. Both tests appear to be useful to judge the storage condition of grain.

In grain trade, wheat that has suffered storage deterioration often is called "sick wheat." The condition is manifested by kernels in which the germ is dead and has turned dark and become fluorescent. Although darkening of the germ can occur with no fungal attack, the two are always found together in commercial samples, and the major cause of the loss of germination capacity is thought to result from the fungal attack.

Microflora and Mycotoxins

Cereals are hosts to a large number of different types of microflora (Fig. 7.9). These include types that invade the seed as well as those that are surface contaminants. The most important of the microflora as far as grain storage is concerned are the fungi, which grow at a much lower interseed water activity (see above) than other microflora. If the system gets out of control and the moisture content in local regions of the grain increases, other types of organisms can become important, but, under good storage conditions, this does not occur.

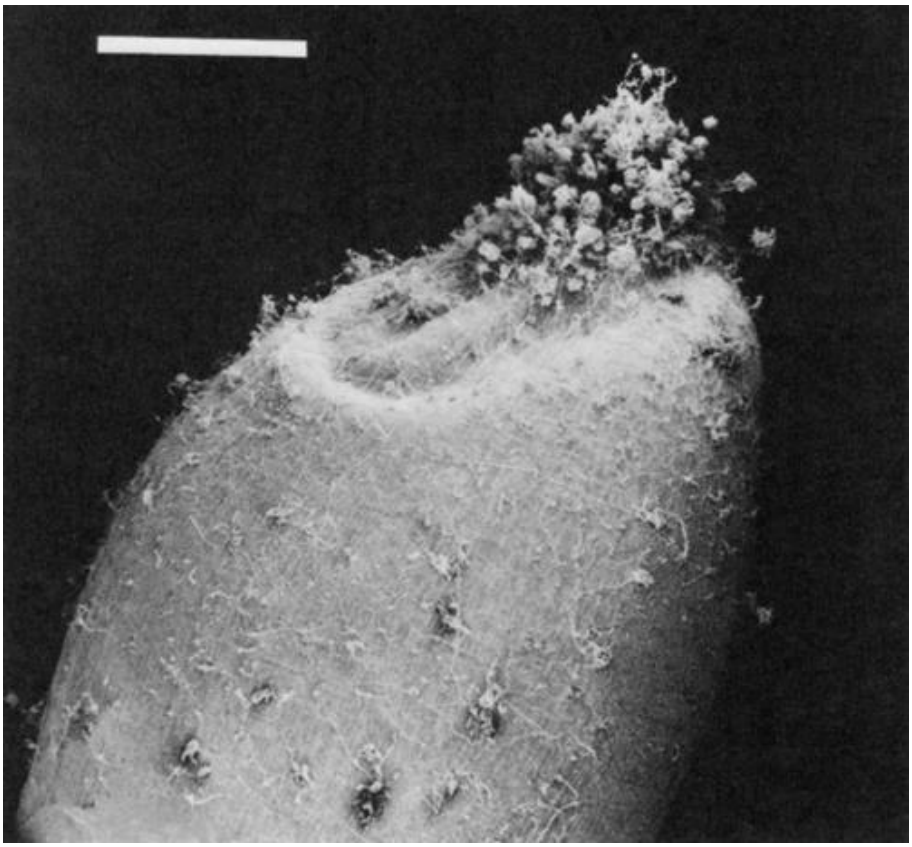


Fig. 7.9. Scanning electron micrograph of a wheat kernel, showing attachment by microflora. (Courtesy K. Zeleznak)

The storage fungi are always present. Because their characteristics are well known, the conditions necessary to stop their growth have been established. Prevention of damage is then simply a matter of keeping the conditions under proper control. Storage losses due to microorganisms can be controlled under almost any environment.

Only a few species of fungi attack stored grain. These are primarily species of*Aspergillus* adapted to living on low-moisture grain. Certain species of *Penicillium* also grow on grain at only slightly higher moisture contents. Other species grow only on grain containing relatively high moisture contents. Microbiological attack is also temperature-dependent. Thus, lowering the temperature of grain that is to be stored is always an advantage.

Certain fungi are capable of producing toxic compounds. Certain of these toxins are exceedingly toxic when consumed or, in certain cases, when they come in contact with the skin. This is the case both for *Fusarium* and for *Aspergillus flavus.*

Some *Fusarium* toxins have been shown to kill mice or rabbits within 24 h after being applied to the skin. Trichothecenes, zearalenone, and fumonisins are the major*Fusarium* mycotoxins occurring on a worldwide basis in cereal grains. Other important*Fusarium* mycotoxins include moniliformin and fusaric acid. Among the trichothecenes, deoxynivalenol (DON) and nivalenol occur together regularly throughout the world. Other co-occurring trichothecenes in grain include 3-acetyl DON (3-ADON), diacetoxyscirpenol, T-2 toxin, and HT-2 toxin.

In 1960, the death of a large number of turkeys in England led to the identification of a toxin produced by *A. flavus* on peanut meal. It was given the name aflatoxin. Subsequently, four aflatoxins have been identified.

The presence of mycotoxins in grain presents problems for grain usage. All over the world, maximum tolerance levels for different aflatoxins have been established. Both the organism and the right conditions are necessary for toxin production. Much of the mycotoxin produced is the result of field infestation of the grain, although mycotoxins can also possibly be produced by storage organisms.

Insects

Insects that can live on grain can be divided into those that develop inside the kernels and those that live outside the kernels. They present major problems for the storage of grains and seeds. Not only do they consume part of the grain, they also contaminate the grain and thereby constitute a major sanitation issue. Most of the losses caused by insects could be avoided if the available information on storage were utilized.

Insects that develop inside the kernels are responsible for the hidden infestation found in stored grain (Fig. 7.10). Five species (granary weevils, rice weevils, maize weevils, lesser grain borers, and *Angoumois* grain moths) are responsible for such hidden damage. Kernels provide little evidence of the presence of insects inside the kernels until they emerge as beetles or moths. Weevils deposit their eggs inside the kernels. Lesser grain borers and *Angoumois* grain moths lay their eggs outside the kernels, but the newly hatched larvae tunnel into the kernels to feed and develop.

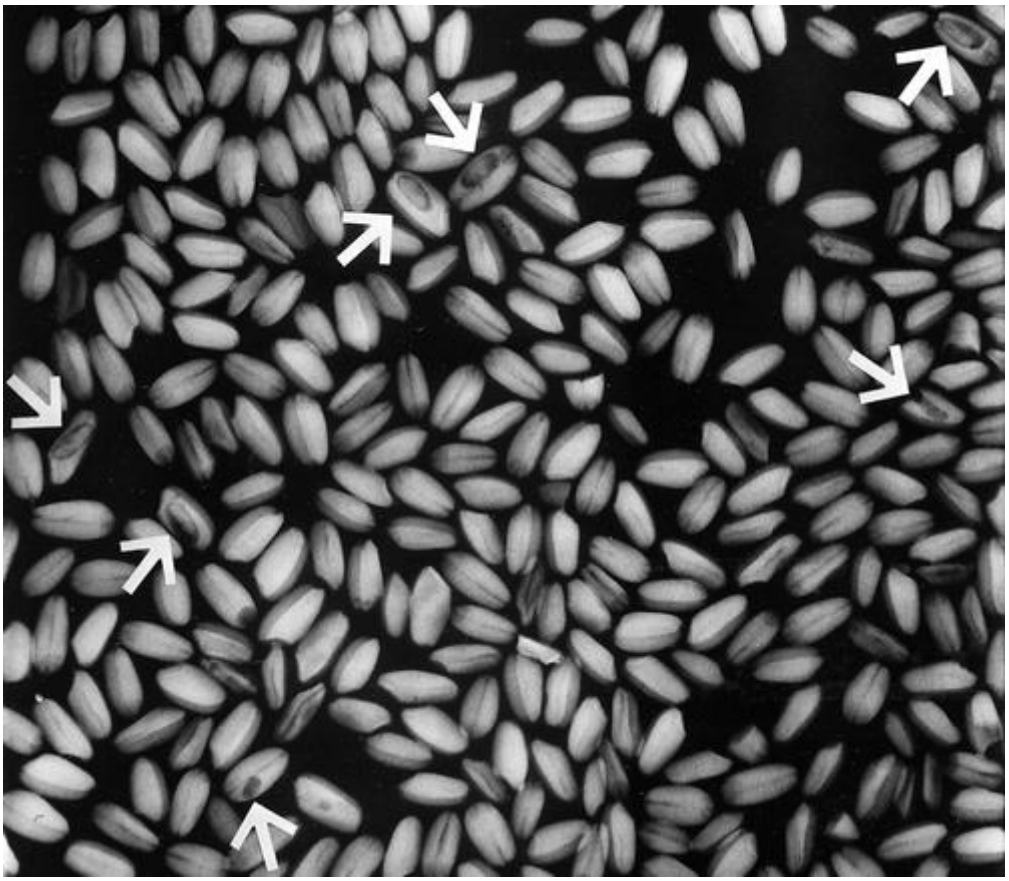


Fig. 7.10. X-ray of wheat, showing internal infestation (arrows). (Courtesy J. Pederson)

Insects that develop outside the stored kernels often feed on broken kernels, grain dust, etc. Important species of this group include confused and red flour beetles, saw-toothed grain beetles, cadelles, Khapra beetles, and Indian-meal moths.

Most grain-damaging insects are of subtropical origin and do not hibernate. Thus, the damage that they cause can be limited by low temperatures. Not only does low temperature make the insects inactive so that they no longer feed themselves, it is also lethal. Generally, temperatures below about 17°C limit the growth and development of most grain-damaging insects. Thus, in some parts of the world, cooling the grain to ambient temperatures is an effective deterrent to grain infestation.

Moisture is another important factor in controlling grain infestation. Insects that live on stored grain depend upon the moisture in the grain for their water supply. Generally, moisture contents of 9% or lower restrict infestation. Interestingly, higher moisture contents also limit infestation because fungi grow rapidly and destroy the insects. However, insects can sometimes result in grain heating, even though the grain is stored at storage moisture contents of 11–14%. The heating is then caused by the metabolic heat of the insects. If so, the increased temperature results in moisture migration and increased moisture contents in pockets of grain, which themselves lead to fungal development, and, ultimately, to large amounts of grain being damaged.

Rodents

Rats and mice destroy millions of tons of food each year when they either consume or contaminate it or both. Both have a tremendous ability to repopulate. A single pair of Norway rats and their progeny can produce more than 1,500 rats in a year. Thus, trying to kill a rat population, if other factors stay favorable for them, is clearly impossible. Given food, water, and a place to nest, rats and mice will maintain their population.

Killing of rodents, whether by baits, traps, or otherwise, is effective only over short time spans. These methods are helpful in reducing populations or eliminating small populations. The answer to rodent control is to keep them away by rodent-proofing of buildings and using good sanitation.

CHAPTER 8: Dry Milling

Milling transforms cereals into more-palatable, more-desirable food ingredients. Dry milling is the separation of the anatomical parts of the grain as cleanly as possible. Subsequently, some of the parts are reduced in particle size. Milling generally involves recovery of the main tissue (i.e., the starchy endosperm) and the concomitant removal of the material the miller calls "bran" (i.e., the pericarp, the seed coat, the nucellar epidermis, and the aleurone layer). In addition, the germ is usually removed from the endosperm. Because of the relatively high oil content of the germ, its presence increases the risk of the product becoming rancid and thereby less palatable. The bran and germ are relatively rich in protein, dietary fiber, B vitamins, minerals, and fat, and the separated endosperm is therefore lower in these components than the original grain. Thus, while milling increases the palatability of cereal products, it decreases the nutritional value of the main product obtained.

In dry milling, the particle size distribution of the endosperm products obtained is dictated by the end use of the product. In general, it is desirable for rice or barley endosperm to remain in one large piece, while a large grit is desirable from maize and coarse semolina from durum wheat. Wheat and rye, at opposite ends of the size spectrum, are generally milled into fine flour products. It follows that different types of equipment are used for dry milling. However, they consistently aim to produce palatable products with a good shelf life.

While the main part of the present chapter deals with the milling of common wheat, many of the unit operations described below are also used as part of dry roller milling for other cereals such as durum wheat, rye, and maize. The roller milling processes of the latter are therefore discussed only briefly. Finally, for some cereals such as barley, sorghum, and millet, decortication or attrition milling is used. Such processing is described briefly in the present chapter. Milling of rice and oats is discussed in Chapter 10.

Maize and rice are also wet milled by processes in which the goal is to isolate their starches from the endosperm tissue. The term *wet milling* refers to the fractionation of wet (soaked) endosperm tissue. These processes are covered in Chapter 9.

Unit Operations Before Milling

Several unit operations are necessary before a given cereal can be subjected to dry milling. First, the grain must be cleaned to remove impurities, and, in the specific case of roller milling, such as for common and durum wheat and for rye, the grain is generally tempered or conditioned.

GRAIN CLEANING

Grain that is dirty, infested, or out of condition because of poor storage conditions should not be used for milling. The cleaning described here is that applied to normal, relatively clean grain. Although large variations are found in the type and number of cleaning steps that different mills employ (Fig. 8.1), certain basic steps are necessary.

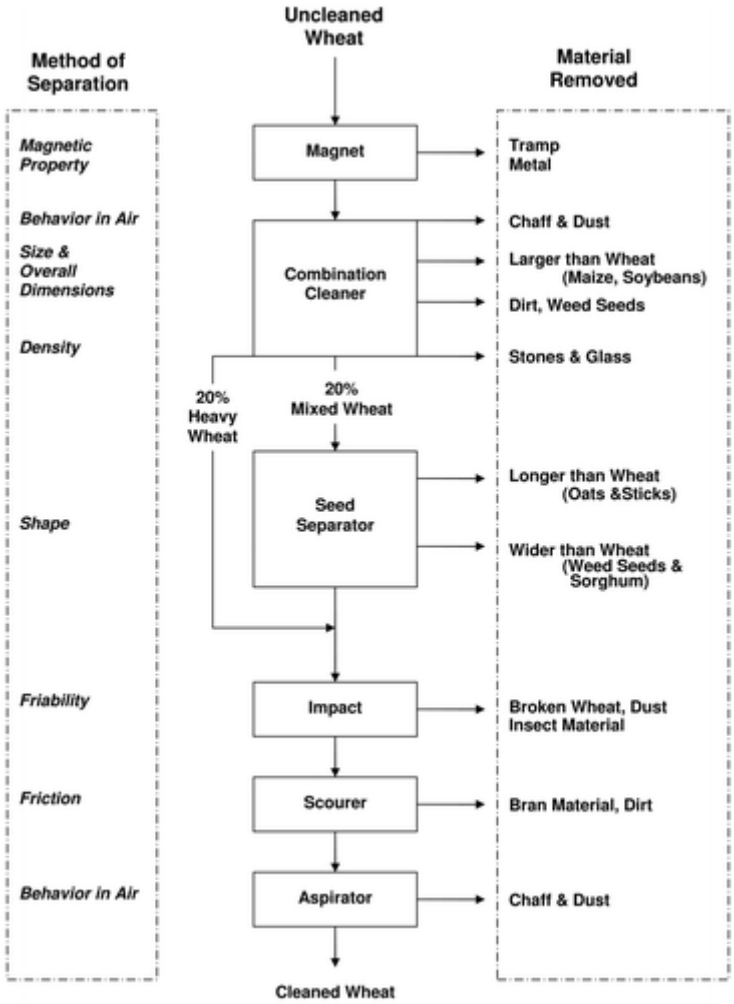


Fig. 8.1. Simplified flow of a wheat-cleaning operation yielding wheat ready for tempering. (Courtesy J. Gwirtz)

Early in the system, several magnetic separators remove any ferrous tramp metal. This is needed not only to remove metal that would be undesirable in the product but also to protect machines from damage and reduce sparks that might trigger an explosion.

Also early in the cleaning system, a receiving or milling separator removes sticks, stones, and other foreign material that is either larger or smaller than the grain being cleaned. The grain is separated with a set of reciprocating sieves, i.e., sieves that move back and forth. The first sieve onto which the grain is fed has openings larger than the dimensions of the desired grain. This removes large material, as well as grains larger than the desired grains. The next sieve retains the desired grains but allows smaller grains to pass through. An aspirator then removes chaff, small pieces of straw, etc., by aspiration; that is, air is pulled through the grain as it is fed into the machine.

In addition to the aspiration found in other machines, specific machines that use airflow to separate light or heavy material from the desired grain may be installed, such as for the removal of stones of dimensions comparable to those of the grain. Such stones can be removed, based on Archimedes' law, in an upward airflow, which, in a grain bed, results in layers of different density. In such destoners, the (heavy) stones move downward and hence can be easily separated. Two destoner types are used for this purpose. One is basically an aspirator with sufficient airflow to lift grain. The heavier stones drop out as the grain is lifted. The second type is referred to as a "gravity table" (Fig. 8.2). The machine separates grains on the basis of differences in their specific gravity, although resilience is also a factor. It consists of a deck supported on rocking legs and oscillated by an eccentric. Provided the inclination, amplitude, and oscillatory speed of the deck are adjusted properly, the denser and less-resilient material moves up the slope, while the lighter and more-resilient material moves down.

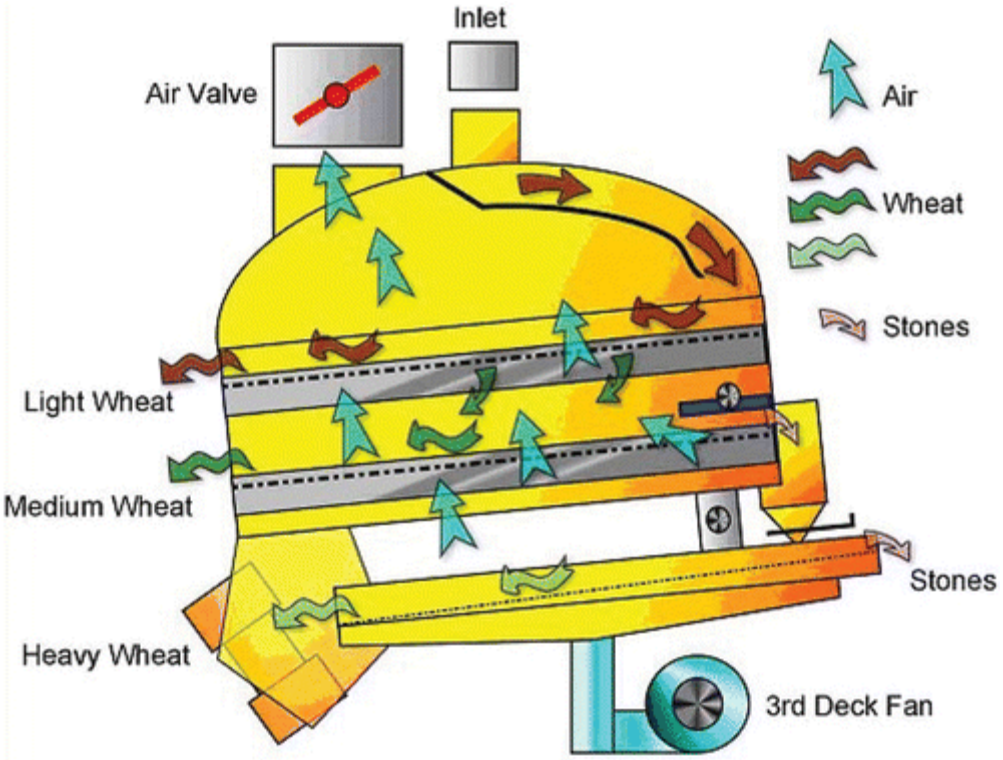


Fig. 8.2. Cut-away view of a gravity table. (Courtesy Satake, Tokyo, Japan)

To separate grains of about the same density from the desired grain, disk separators are used (Fig. 8.3). The separation is based on the shape and size of the kernels. The machine consists of a series of disks mounted a few centimeters apart on a horizontal central shaft. Both sides of each disk are pocketed. The pockets are designed to pick up grain of a certain shape and size, lift it out of the grain mass, and deposit it into another chamber. The grain enters at one end of the chamber and is conveyed to the other end by the inner spokes of the disk. Grain rejected by the disks then leaves at the end opposite the one from which it entered. Disk separators are generally used in tandem. The first rejects material larger than the desired grain and lifts out the desired grain plus smaller seeds. The second disk rejects the desired grain and lifts out the smaller seeds.

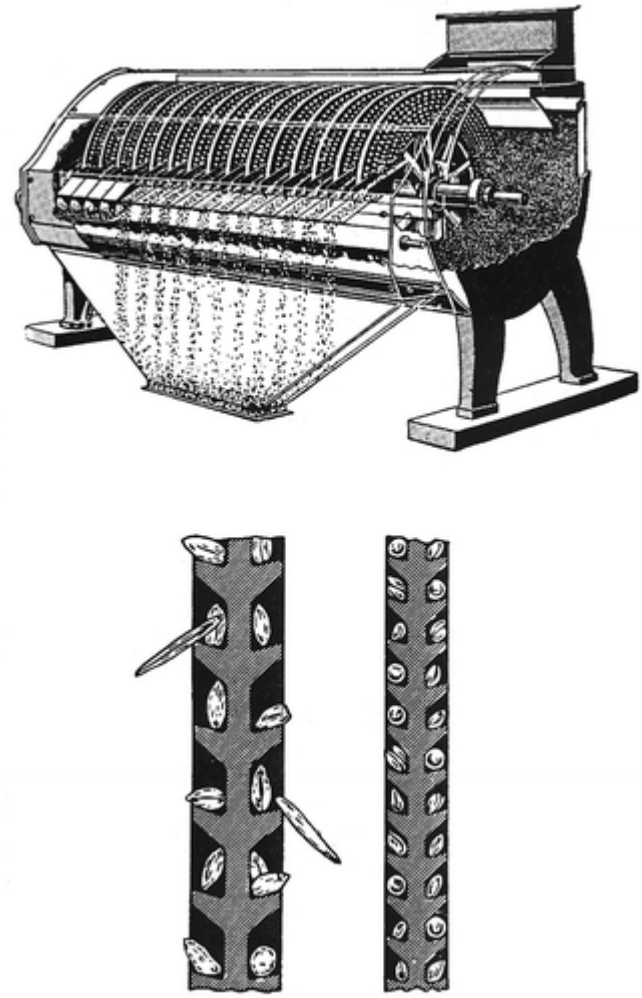


Fig. 8.3. Top, cut-away view of a disk separator. **Bottom,** grains of the correct size are held in the pockets, and large grains are removed (Courtesy Carter-Day Co., Minneapolis, MN)

Another important piece of cleaning equipment, the impact mill, removes grain infested with insects. It accelerates the grain and throws it against a hard surface. Infested grain is broken into small pieces that can be separated from the sound kernels. This mechanical treatment is equally effective in destroying the insects, irrespective of their life cycle status. In the process, sound grains are broken in half at the crease. The impact treatment is hence called a "prebreak."

Also important is the scourer, as it removes adhering dirt, smut, and rust from cereal kernels. Smut and rust are the result of common wheat diseases. The design of scourers varies, but the basic concept is that the grain kernels are scoured or rubbed against other grains, a perforated metal screen, or an emery surface. The adhering material loosened by this treatment is removed by aspiration.

A relatively recent pretreatment is debranning. For wheat debranning, grain is conditioned (see below) for a limited time. This ensures that water penetrates only into the outermost regions of the seed coat and allows the protective seed coat to be stripped away, layer by layer, separately from the aleurone. As outlined below, in conventional wheat milling, the seed coat layers and the aleurone are removed together. In debranning, friction passages (kernel to kernel) precede abrasion passages (kernel to rough surface). One advantage of debranning is a reduction of the microbial load and the enzyme activities in the resulting flour.

Rye selected for milling usually has less than 8% thin kernels (those passing a 1.6- × 9.5-mm screen), as such thin kernels yield low levels of white flour. During cleaning, care must be taken to remove ergot, a fungus (the fruiting body of *Claviceps purpurea*) that replaces the kernel in the head. Although occasionally found in wheat, ergot is more prevalent in rye. Rye containing a significant amount of ergot should not be used for milling. Ergot has roughly the same density as a grain kernel but is usually larger that rye kernels and thus can be removed by disc separators. Although it contains certain alkaloids that are quite toxic and can result in death if sufficient quantities are consumed, ergot is also a valuable co-product that can be sold to the pharmaceutical industry.

GRAIN TEMPERING OR CONDITIONING

Tempering

Tempering consists of adding water to dry grain (e.g., soft, hard, or durum wheat or rye) and allowing the grain to rest for a period of time before it is milled. Tempering aims not only to toughen the bran and thus make it resistant to fragmentation into small pieces during milling, but also to soften or "mellow" the endosperm to make it easier to grind. Indeed, bran with high moisture content is tough and stays in large pieces during milling. This greatly aids in its removal. Water makes the endosperm softer and thus easier to mill. The water presumably breaks, or weakens, the protein-starch bond that is responsible for grain hardness (see Chapter 1).

Conditioning

The term *conditioning* implies the use of heat in conjunction with water to weaken the endosperm. Because water penetrates the kernel primarily by diffusion, the rate of water uptake increases with temperature. In the particular case of conditioning wheat, temperatures exceeding 50°C should generally be avoided because wheat gluten can be damaged by heat, particularly when the grain is hydrated. However, for some applications, altered gluten properties, such as decreased gluten extensibility, may well be desired.

Water Uptake by Grain

Work using autoradiography to monitor the penetration of tritiated water into the kernel has greatly extended our understanding of the penetration of water into the wheat kernel. In general, such studies show that, immediately after wetting, the water is concentrated in the bran and germ. The water causes the cross and tube cells to open up, and the small capillaries hold the water very strongly (Fig. 8.4). Diffusion from the bran occurs in all areas of the grain. While the moisture uptake in the bran layers (see Chapter 1) generally occurs layer by layer, the outer layers of endosperm, particularly those cells just below the aleurone, appear to be the rate-controlling area for water uptake. With time, water penetrates into the dorsal region of the grain and finally into the crease area. The rate of water uptake varies for different cultivars, but the mode of uptake is essentially the same. Compact endosperm (i.e., with no air spaces; see Chapter 1) takes up water more slowly than does opaque endosperm (with air spaces; see Chapter 1). In this context, it is relevant that hard, vitreous wheat becomes soft and opaque as a result of wetting and subsequent drying. Also, low initial moisture content results in a slower uptake of water.

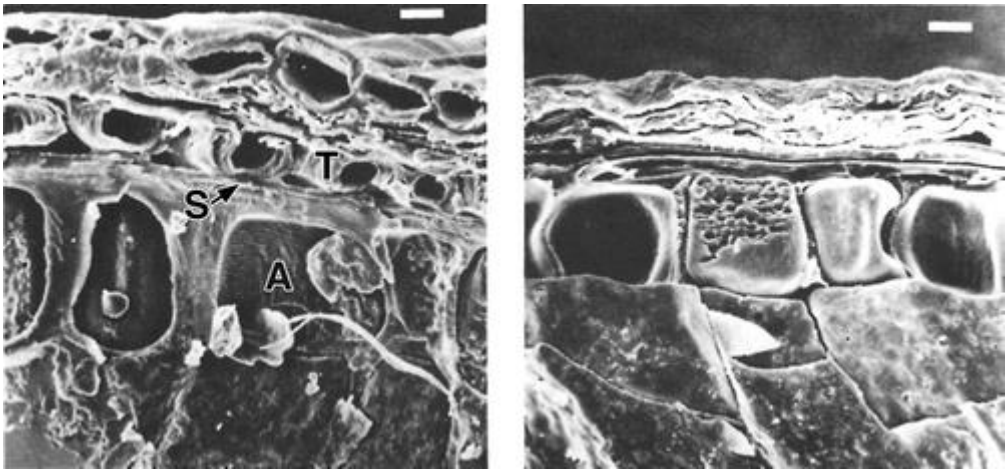


Fig. 8.4. Outer portion of a wheat kernel: **left,** wetted and lyophilized kernel; **right,** dry kernel. The wetting opens the cross and tube cells (T). S = seed coat, A = aleurone cells. Bar is 10 μm. (Courtesy K. Zeleznak)

The amount of water added to wheat differs depending upon its initial moisture content and the hardness of the grain. Soft wheat (North American terminology is used here and elsewhere in this chapter; see Chapter 1) is usually tempered to 15.0–15.5% moisture. Hard wheats are tempered to 16.5% and durum wheats to even higher moisture levels. The time given for the water to penetrate the grain also varies with the grain hardness. The time required to reach an even distribution of moisture in grain varies from 6 h for a soft, opaque kernel with low protein to more than 24 h for a hard, vitreous, high-protein kernel. In contrast, durum wheat, which is very hard, is usually tempered for short times, as the goal of durum milling is to produce semolina and not flour.

Rye is, in most cases, conditioned to a moisture level of 15%. The tempering time, in general, is 2–4 h, with an absolute maximum of 6 h. Water penetrates rye faster than wheat due to its softer structure. The tempering process can be eliminated to reduce bacterial counts. However, if rye is milled too dry, the risk of breaking the bran into smaller particle sizes and thus contaminating the rye flour increases.

Common Wheat Roller Milling

The grinding of most cereal grains, particularly those grains having a crease, is done with roller mills. However, one needs to realize that, even under the best conventional roller milling conditions, complete separation of starchy endosperm from other kernel constituents cannot be achieved. A major factor preventing complete separation is the crease. The present discussion focuses on milling of common wheat, which has a crease.

The grinding in a roller mill is accomplished by pairs of rolls (Fig. 8.5) rotating in opposite directions. At the nip (where the two rolls approach each other), the two surfaces move in the same direction. The rolls are generally run at different speeds, with the fast roll moving about 2.5 times as fast as the slow roll (the speed differential). Thus, in addition to the crushing action on a large particle as it passes the narrow gap between the two rolls, there is also a shearing action because of the speed differential.

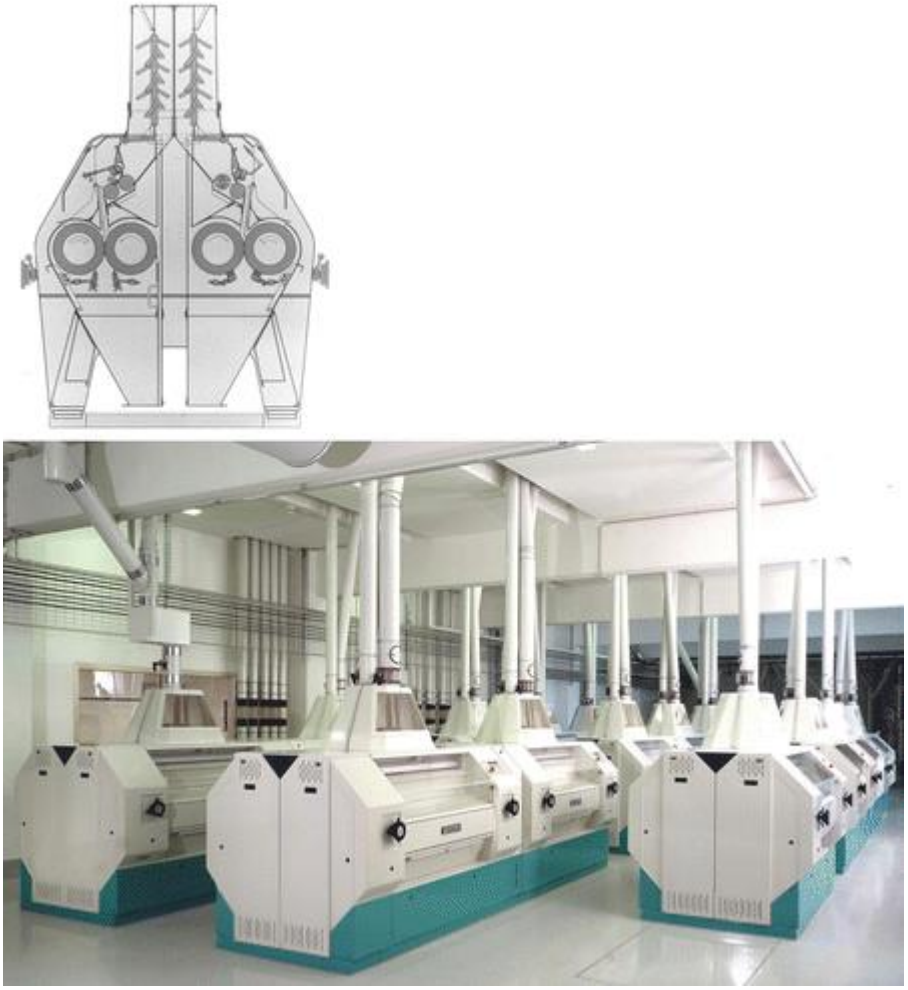


Fig. 8.5. Top, roll stand with two sets of rolls. (Courtesy Bühler, Inc, Minneapolis, MN) **Bottom,**typical set up of a series of roll stands. (Courtesy W. von Reding, Bühler, Uzwil, Switzerland)

The roller mill system (Fig. 8.6) first removes the bran from the endosperm. This is accomplished, for the most part, in the break system of the mill. The next objective is to reduce the endosperm to the desired particle size. This is accomplished in the reduction system.

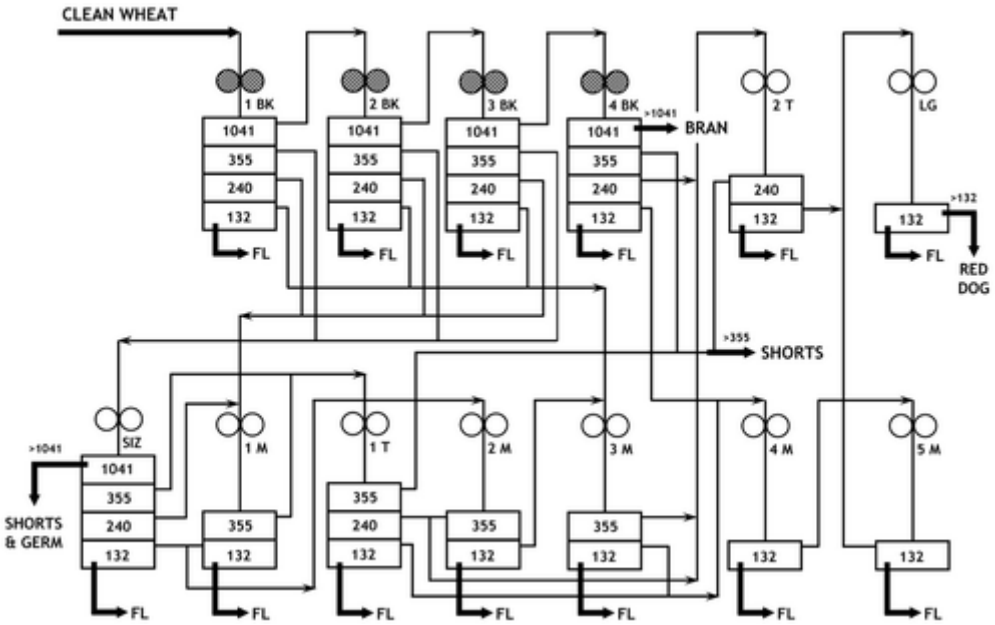


Fig. 8.6. Experimental milling flow sheet. Clean wheat is fed into the mill. The scheme shows four break (BK) systems. The sizes of the sieves openings (1041, 355, 240, and 132 μm) are indicated. Flour (FL) is a collection of the fractions passing through the 132-μm sieves. The five collected streams of middlings (M) are fed into the five sets of reduction rolls. Bran is collected as the material remaining on the 1041-μm sieve after the fourth passage through the break system. The sizing (SIZ) roll system helps remove flattened germ. The tailing roll system (T) is indicated as well. The rolls denoted LG (for low-grade) separate red dog product from higher-quality flour. (Adapted from Li and Posner 1989)

THE BREAK SYSTEM

The break system consists of several breaks (i.e., sets of rolls). The break rolls are always corrugated. The corrugations are variously shaped cuts that run spirally along the long axis of the rolls. The number of corrugations per centimeter varies from four to five for first break rolls up to 11–13 at the fourth or fifth break. The action of a set of break rolls can be described as the slow roll holding the material while it is being scraped by the fast roll. The rolls are gapped very precisely, so that, as the wheat kernels pass between them, the kernels are not crushed but sheared open to make the inner-endosperm portions of the wheat break away from their outer layers. If the wheat were merely crushed, the bran would break up into tiny fragments that would mix with the endosperm so thoroughly that they could never be separated properly. Their presence would then discolor the flour badly and also reduce its baking qualities.

In the early breaks, the kernel is broken into rather large pieces. Sieving separates the largest pieces (i.e., mostly bran) from the middlings (i.e., large pieces of endosperm) that are sent to the reduction system. Some flour is produced with each grinding step. In later breaks, the action is primarily a scraping of the bran to remove adhering endosperm. The pieces of endosperm that have bran attached after all the grinding are called "shorts" or "pollard," the latter term being commonly used in Australia. The last break rolls, which are termed "sizing" rolls (Fig. 8.6), flatten the germ. This allows some of the valuable germ to be separated from the shorts by sieving.

SIEVES AND PURIFIERS

After each grinding step, the ground stock is separated on sieves and is either classified as bran and sent on for further grinding, or, in the case of the smaller particle sizes, saved as flour. Indeed, a small amount of flour is produced on each break roll. Thus, a sifting system (Fig. 8.7) follows each set of rolls. The stock may be divided on as many as 12 sieves. The large pieces of bran, containing considerable amounts of endosperm, are sent to the next break. The medium-sized endosperm particles (middlings, see above) that contain bran particles are sent through a purifier. A purifier is essentially an inclined sieve that becomes coarser from head to tail. The sieve oscillates, and an air current passes upward through the sieve, causing the stock to stratify. Light bran particles are removed by the air; endosperm chunks are graded (i.e., separated by size) and sent to the various reduction rolls.

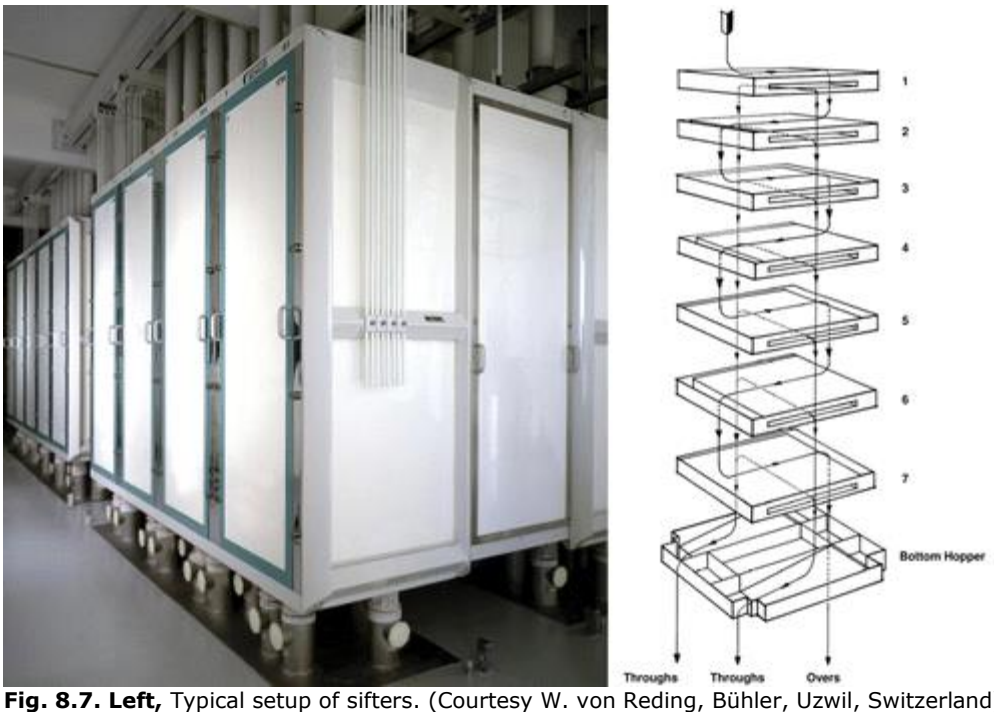


Fig. 8.7. Left, Typical setup of sifters. (Courtesy W. von Reding, Bühler, Uzwil, Switzerland) **Right,**illustration of the seven sieves in a sieve box, showing the flow of product. (Courtesy Allis-Chalmers Corp., Milwaukee, WI)

Sifting of soft wheat flour is much more difficult than sifting of hard wheat flour. Soft wheat produces flour with a much smaller average particle size than that from hard wheat. In addition, the particles of soft wheat flour have a rougher surface than do those of hard wheat. The small, soft-wheat flour particles tend to interact with each other, forming aggregates that bridge the sieve openings, and thus will not pass a flour cloth (i.e., a sieve of silk or other fiber). The interactions between flour particles are enhanced by water and lipids on the surface of the flour particles and by frictional forces created by the rough surfaces of flour particles of soft wheat (contrast Figs. 1.9 and 1.10).

THE REDUCTION SYSTEM

The reduction rolls are generally smooth rather than corrugated. The purpose of the reduction system is to reduce the middlings to a particular level of flour fineness (i.e., to pass a 10XX flour cloth, 132-µm openings) and to remove the last remaining particles of bran and germ. For this purpose, at the end of the reduction system, "tailings" and "low-grade rolls" (Fig. 8.6) are used to recover the last quantity of flour. The higher-grade flour is produced on the various middlings rolls (Fig. 8.6). As with break grinding, after each grinding, the stock is sifted, the flour removed, and the coarser particles sent to the appropriate reduction roll. Purifiers are also used after the reduction rolls, mainly to separate particles that are mixtures of bran and endosperm from denser particles consisting of pure endosperm.

PRODUCT YIELDS AND COMPOSITIONS

Yields

Endosperm-derived flour has a higher value than the co-products; thus, the yield of the former is an important parameter in milling. The common expression of yield used by millers, "extraction," is based on the flour yield as a percent of total product, not as a percent of the starting material. The percentage of total product in any desired fraction is called the "extraction yield." In other words, flour that is 72% of the total products obtained is 72% extraction flour.

In determining yields, one must realize that many different flour streams are produced by a roller milling operation, i.e., one from each grinding step. A composite of all the flours produced by the mill is referred to as "straight-grade flour" (Fig. 8.8). Depending upon the details of the process, it represents about 72% of the total products. The other main product from the mill is millfeed, i.e., bran (large pieces consisting of pericarp, seed coat, nucellar epidermis, and aleurone layer) and shorts (pieces of endosperm with bran attached). Millfeed also contains germ that was not separated and small pieces of bran. Bran represents about 11% of total products and shorts about 15%. As its name implies, millfeed is mainly sold as an animal feed ingredient. Germ can be an additional product and is typically recovered at about 0.5–1.0%. It is high in both fat and

enzymes. As long as the germ is intact, it is relatively stable. However, during milling, the germ is flattened, and the fat and enzyme are brought into contact. As a result, the germ rapidly becomes rancid. To stabilize the germ, it is roasted or dry-heated to denature the enzymes.

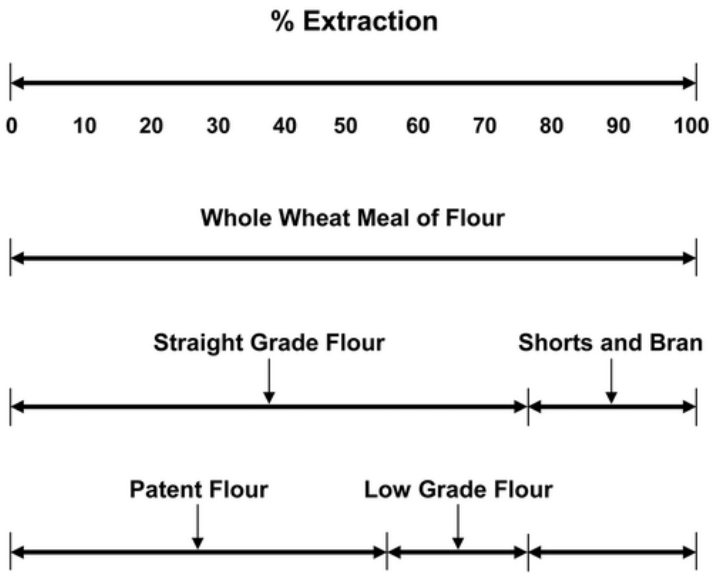


Fig. 8.8. Grades of flour obtained from wheat. Whole wheat flour corresponds to 100% extraction (line 2) but can be divided into straight-grade flour plus shorts and bran (line 3). The straight-grade flour can be further divided into patent and low-grade flours (line 4).

Straight-grade flour consists of (long) patent flour (about 65%) and low-grade flour (about 7%). (Long) patent flour is the flour produced at the head of the reduction system (i.e., in the first grinding steps). It consists of short patent flour, i.e., the flour with the lowest ash (mineral content) and therefore the least contamination with non-endosperm material, which represents about 45% of the total products and originates mainly from the center of the endosperm (see below), and cut-off flour, i.e., the 20% between the short and long patents. The low-grade (clear or red dog) flour comes from the last grinding steps of the break and reduction systems and has high ash content and dark color.

Product Compositions

The chemical compositions of bran and germ are quite different from that of the endosperm, and hence of flour (Table 8.1). Thus, milling results in changes in composition (Table 8.2). All the components reported in Table 8.2 except starch and chlorine decrease in concentration going from wheat to flour. The changes in the concentration of certain vitamins and minerals provide the rationale for enriching flour and other cereal products.

TABLE 8.1
Typical Analysis[a] of Mill Fractions[b]

	Wheat	Patent Flour	Germ	Shorts	Bran
Protein	12.0	11.0	30.0	16.0	14.5
Ash	1.8	0.40	4.0	4.1	6.0
Fiber	2.5	…	2.0	5.5	10.0
Fat	2.9	0.88	10.0	4.5	3.3

[a] Percent of dry matter.
[b] Adapted from Ziegler and Greer (1971).

TABLE 8.2
Change in Composition from Wheat to Flour[a]

	Wheat	70% Extraction Flour
Ash, %	1.55	0.4
Fiber, %	2.17	Trace
Protein, %	13.9	12.9
Oil, %	2.52	1.17
Starch, %	63.7	70.9
Thiamin, µg/g	3.73	0.70
Riboflavin, µg/g	1.70	0.70
Niacin, µg/g	55.6	8.50
Iron, mg/g	3.08	1.42
Sodium, mg/g	3.2	2.2
Potassium, mg/g	316	83
Calcium, mg/g	27.9	12.9
Magnesium, mg/g	143	27.2
Copper, mg/g	0.61	0.18
Zinc, mg/g	3.77	1.17
Total phosphorus, mg/g	350	98
Phytate phosphorus, mg/g	345	30.4
Chlorine, mg/g	39	48.4

[a] Adapted from Ziegler and Greer (1971).

Consistent with what is shown in Table 8.2, wheat typically has an ash content of about 1.5%. However, the ash is not distributed uniformly in the grain. The inner endosperm is relatively low in ash (about 0.3%), whereas the bran may contain as much as about 6%. It follows that increasing the extraction yields results in flour of increasing ash contents. Thus, ash is a convenient assay for the presence in flour of outer tissues in general and bran in particular, as its determination is relatively simple and reproducible. Most purchasing specifications for flour stipulate a maximum ash content that the flour should have.

Curves of ash or protein extraction (Fig. 8.9) are useful in determining the maximum flour yield one can obtain and still meet the ash and protein specifications. In general, the higher the ash content, the higher the tolerated bran contamination, and hence the lower the flour price. This is clearly justified, as it is well established that bran has a negative impact on the breadmaking potential of flour. However, wheats vary in the amount of ash natively found in the endosperm; thus, small variations in ash content do not necessarily imply the presence of different levels of bran in flours.

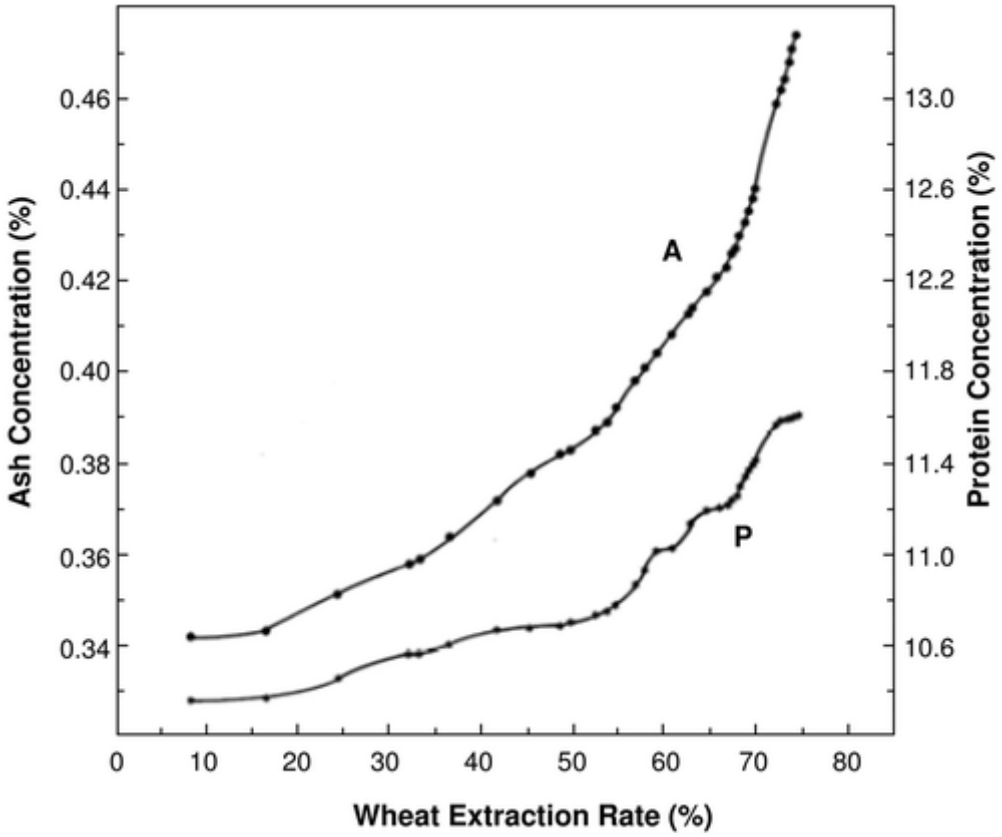


Fig. 8.9. Curves showing ash (A) and protein (P) concentrations in commercial milling products of wheat as a function of the total extraction rate. The inner endosperm is relatively low in ash, whereas the bran may contain as much as about 6% ash. Curve A shows that increasing the extraction yield results in flour of increasing ash contents. Curve P shows that the protein concentration also increases with the extraction yield.

Starch Damage

Roller milling damages a small but significant number of the starch granules in the flour. In general, the level of damage depends not only on the hardness of the wheat used but also on the settings of the milling rolls. Indeed, given a constant wheat supply, flour with increasing water-absorption characteristics can be produced by adjusting the roll settings such that increasing levels of starch damage are produced. However, if the level of damaged starch becomes too high, the dough rheology and baking performance are negatively affected. Soft wheat can be milled to flour with essentially no starch damage, an essential quality characteristic when it is to be used for cookie production. Even so, because of the analytical methods used to measure starch damage, the value for starch damage may be 2–3% (see below).

There are two types of starch damage. The first is that which results in the starch granule being broken in two, as illustrated in Figure 1.9. Although the granule is clearly damaged, this type of damage results in starch that is still birefringent, not soluble in water, and not susceptible to attack by fungal α-amylase. The second and more classic starch damage produced during milling results in granules that have partially or completely lost their crystallinity, are no longer birefringent (see Chapter 2), swell in cold water, appear as "ghosts" under the microscope, stain with Congo red, and are susceptible to fungal α-amylase. Only the latter type of damaged starch is measured in the procedure of AACC International for measuring starch damage, as it is based upon the fact that damaged starch is susceptible to fungal α-amylase while undamaged starch is not.

A limited level of damaged starch seems necessary in breadmaking formulas containing little or no added sugar. It seems logical that its (partial) hydrolysis by α-amylase releases maltose, which can then be fermented by the yeast to form carbon dioxide, resulting in dough rise (see Chapter 12). In bread, excessive damaged starch produces weak crumb side walls and a sticky crumb.

PROCESSING OF FLOUR

Before being shipped, flour is passed through an impact mill to kill any insect eggs. In addition, the flour may be further treated to better meet end-use specifications. The treatments can be classified as purely physical (e.g., air classification, fine grinding, and agglomeration), chemical (e.g., addition of vitamins and minerals, bleaching and oxidizing chemicals, and leavening agents), or biochemical (e.g., addition of α-amylase or endoxylanase [see Chapter 4]). Also, in Europe, breadmaking flour is sometimes supplemented with wheat gluten (see Chapters 3 and 12).

Physical Treatments

Air Classification and Fine Grinding. Most flour is sieved through a 10XX flour cloth, which has openings of about 132 µm. Thus, flour is composed of particles (Fig. 8.10) ranging from very small (<1 µm) up to about 200 µm. Indeed, some particles larger than the opening can pass through a sieve. Viewed microscopically (see Chapter 1), flour can be seen to be made up primarily of two components, starch and protein, as well as particles made up of both. The smaller particles are composed of pieces of endosperm protein or small starch granules with adhering protein. Thus, the small particles tend to be high in protein. As particle size increases, a larger proportion of the particles consists of free starch granules, and the protein content is lower. The even-larger particles primarily consist of the starch embedded in a protein matrix, just as was the case in the intact endosperm. That fraction has a protein content equal to that of the original flour. Thus, by separating the flour into particle size classes below those attainable by normal sieves, one can obtain subsamples of the flour that, in comparison with the protein level in the original flour, have much higher protein content (i.e., in particles smaller than 17 µm), lower protein content (i.e., in particles of sizes ranging from 17 to 35 µm), and equal protein content (i.e., in particles larger than 35 µm). Air-classifiers are used for these separations.

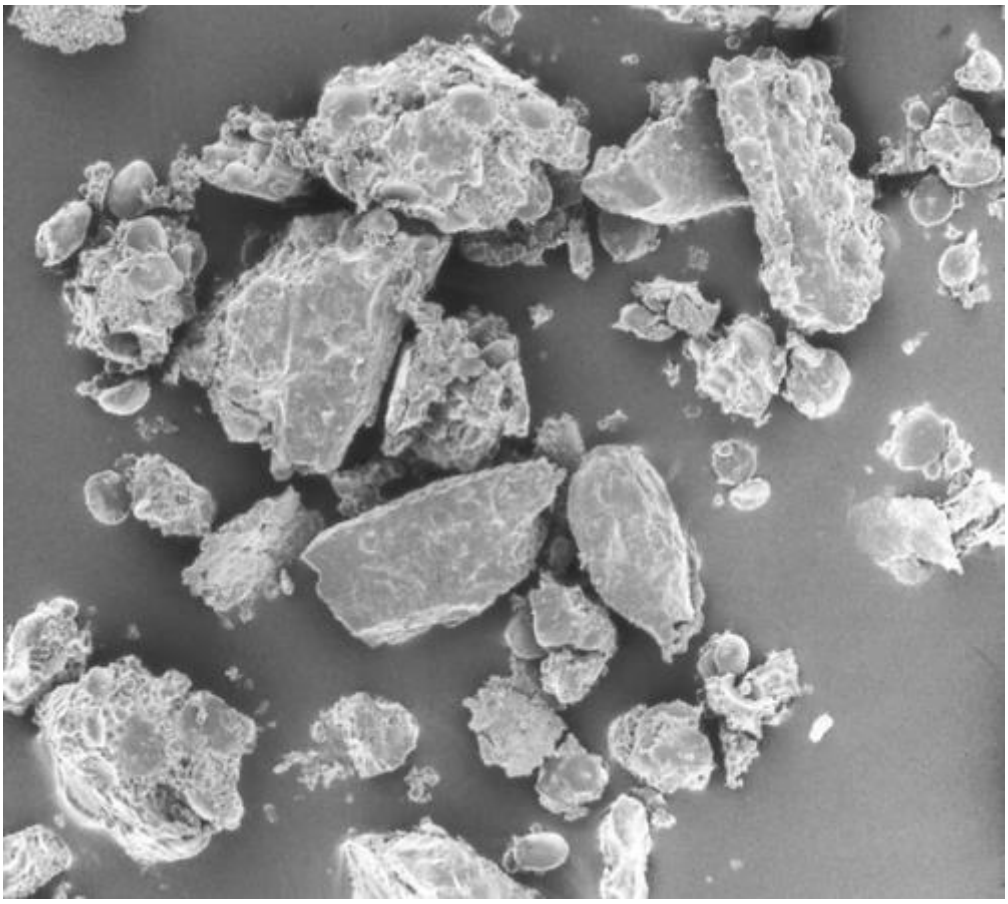


Fig. 8.10. Scanning electron micrograph of hard wheat flour particles.

Soft wheat flour air-classifies better than hard wheat flour does. Because of its soft texture, milled soft wheat produces flour with a much smaller particle size than milled hard wheat. In hard wheat, the protein and starch tend to remain together in the flour and cannot be efficiently separated by air classification without additional grinding to reduce the particle size. Pin mills are effective in reducing the particle size. However, at high speeds, they produce considerable levels of fractured starch, which generally is undesirable.

Flour Agglomeration. Flour can be agglomerated by wetting the outside of the flour particles, bringing them in contact with other particles, and drying them. This is accomplished by agitating flour in an atmosphere of water droplets followed by drying in an airstream. The agglomerated flour is dust free, has a controlled bulk density, has good flowability, and disperses in water without lumping.

Chemical Treatments

Addition of Vitamins and Minerals. Since 1940, in the United States, all "family" flour and baker's bread flour have been required to be enriched with the vitamins thiamin, riboflavin, and niacin and with the mineral iron. The purpose is to replace part of the vitamins and minerals lost as a result of milling. Since 1998, flour in the United States is also supplemented with folic acid.

Addition of Bleaching and Oxidizing Chemicals. We here list a number of treatments used in different parts of the world. However, their use and dosage is subject to local legislations, and the fact that they are discussed here does not necessarily imply that they can be or are used universally.

If flour is stored long enough after milling, it slowly bleaches, presumably as a result of air-induced oxidation. However, chemical bleaching is more common. For bread and all-purpose flours, the most common bleaching agent is benzoyl peroxide. It is added as a dry powder and whitens flour over a two-day period. It only bleaches flour pigments and has no effect on the breadmaking or baking properties.

Flour also undergoes aging or maturing with storage times of several weeks. As a result, its breadmaking potential generally improves. To create effects similar to those of aging, several oxidizing agents are added at the mill as maturing agents. Agents used include azodicarbonamide, acetone peroxide, chlorine dioxide, and ascorbic acid. They are discussed in more detail in Chapter 12.

Cake Flour Chlorination. Cake flour is sometimes treated with chlorine gas, which immediately destroys and thus bleaches the pigments and produces very white flour. Chlorine is detrimental to breadmaking flours but beneficial to cake flours, in which it is used both as a bleaching and an improving agent. High-ratio cakes (i.e., cakes that contain more sugar than flour; see Chapter 13) cannot be made without treatment of flour with chlorine gas. The pH drop in flour when it is chlorinated is not beneficial itself but gives a way of monitoring the amount of reaction between the gas and the flour.

Addition of Leavening Agents. Self-rising flour is prepared by addition of chemical leavening agents. The resulting flour contains added sodium bicarbonate, acid salts (either monocalcium phosphate or sodium acid pyrophosphate, or both), and salt (see Chapter 13). The acid added is sufficient to neutralize the sodium bicarbonate. Self-rising flour must contain enough leavening to evolve an amount of carbon dioxide not less than 0.5% of the flour weight.

Biochemical Treatments

α-Amylase Addition. Sound wheats are low in α-amylase activity. However, in flour used for breadmaking, some α-amylase activity is desired. α-Amylase addition improves loaf volume, decreases the firming rate of the bread, and reduces the rough texture of the crumb. It also decreases keyholing, i.e., the shrinking of the bread sidewalls to give pan bread a keyhole shape. Its main impact in breadmaking may well be related to degradation of damaged starch during fermentation and reduction of dough viscosity during the gelatinization process in the oven. The often-stated advantage of having α-amylase produce sugar is of importance only if no, or little, sugar is added in the formula.

To increase the α-amylase activity in flour, the options are to use malted barley flour, malted wheat flour, or fungal α-amylase. Malt flour is typically added at a level to produce about 0.25% in the end product. The proper treatment level can be determined by amylograph or falling number tests. The thermal stabilities of the two types of α-amylase are quite different. In general, the thermal stability of malt α-amylase is higher than that of fungal α-amylase. Most of the fungal amylase activity is lost before starch is gelatinized. In contrast, some bacterial α-amylases are very thermostable and may survive the baking process. They are hence difficult to control during baking and storage and can result in reduced crumb structure properties if added in excess.

Endoxylanase Addition. It has increasingly become clear that endoxylanases, which degrade water-unextractable arabinoxylan in breadmaking, improve bread volume. Because of the presence of endoxylanase inhibitors (see Chapter 4) in wheat flour, the most efficient endoxylanases are those that are insensitive to inhibition. The addition of endoxylanase enzymes to flour is more common in Europe than in the United States.

DURUM WHEAT MILLING

Durum wheat, the ideal raw material for pasta production, is so hard that it is difficult to reduce to flour fineness. When it is reduced to flour, the percentage of damaged starch is several times higher than that found with common wheat. Durum wheat is generally milled into semolina, i.e., the purified middlings from durum wheat. A product comparable in size to semolina, i.e., the purified middlings from hard common wheats, is named farina (see Chapter 15).

The objective of the durum milling process is to produce as much semolina as possible. To accomplish this goal, durum wheat is generally conditioned to higher moisture levels (about 17%) and for a shorter time than common wheat (see above), and the mill has fewer reduction rolls. In addition, the process uses a large number of purifiers to remove those particles containing bran. The bran-containing particles would otherwise cause specks in the final pasta products produced from the semolina. The number of specks is an important quality factor and is kept to a minimum.

RYE MILLING

In a rye mill, all the rolls are corrugated, as a smooth roll tends to flake the product rather than grind it. Because of the soft texture of the endosperm, rye flour sieves with difficulty; thus, a larger amount of sifter surface per unit of production is needed than is the case for wheat flour production. Purifiers are not used in rye mills. In general, two types of rye flour are produced in North America: a white rye which makes up about 80% of the total flour produced and a dark rye that constitutes the other 20%. Other flours are produced by a combination of these two basic flours. Some of the white rye flour is treated with a small amount of chlorine gas as a bleaching agent.

In Western Europe, rye is tempered at about 15% for about 5–6 h. This is similar to conditions used in North America. The rye is processed with five to seven breaks, two or more bran finishers, and four to six reduction rolls. All the rolls are corrugated. In Eastern Europe, the rolls are run at greater speed. Sifter cloths are more open than those used in the United States or Western Europe. The result is a coarser flour granulation, darker flour color, and a much greater plant throughput.

Rye flour dough does not have the gas-holding ability of wheat flour dough. Therefore, rye bread made entirely from rye flour is very dense. Most rye bread produced in North America contains relatively small amounts of rye flour (about 20%) for flavor and high levels of wheat flour to produce the light texture. Rye flour contains higher levels of arabinoxylan than does wheat flour (see Chapter 4). The arabinoxylan-to-starch ratio is generally believed to be the primary factor responsible for the breadmaking quality of rye flours.

DRY MAIZE MILLING

The maize kernel (see Chapter 1) presents several problems for the miller. It is large, hard, and flat and, in addition, contains a larger germ than other cereals (about 12% of the kernel). The germ is high in lipid (typically 34%) and must be removed if the product is to be stored without becoming rancid. In the traditional stone-grinding of maize meal, the germ is not removed, which results in products that become rancid in a short time.

In maize milling, the desired products are low-fat grits rather than flour. Thus, the miller wants to remove the bran (i.e., the pericarp, seed coat, and aleurone layers) and germ without reducing the endosperm to a small particle size. The most effective way to accomplish this is to degerminate the maize (after it has been temperered to high moisture content, i.e., about 21%) with a degerminator, a special type of attrition mill, i.e., a mill in which the material is reduced in size by friction. The mill basically consists of two cone-shaped surfaces, one rotating inside the other, which rub the kernel to remove the bran and release the germ. The high moisture content allows an easier separation of the germ from the endosperm without reducing the endosperm to smaller pieces. Of course, the grits must be dried before they can be stored.

Impact milling has also been used for degermination. The maize enters the machine by falling on a rapidly rotating disk containing pins. It is forcefully thrown against the wall and degermed by the impact.

After removal of the germ and bran, the endosperm is reduced to grits of the desired size by break roller milling much as in the case of wheat milling. The product is usually dried to a specified moisture content. The bran is sold as animal feed, and the germ is processed to recover the valuable oil.

Decortication is the removal of the bark (Latin *corcus*), or outer layers, of the grain. It is also referred to as "pearling" (in the case of barley) or "milling" (in the case of rice). It is most commonly used in those instances where the desired product is the endosperm or whole grain without the bran, such as in barley pearling or rice milling, as roller milling would break the kernel. In addition, for those grains that do not have a crease, this type of dry milling is an alternative to roller milling. Barley, sorghum, and millet pearling are discussed here. Rice and oat processing are discussed more fully in Chapter 10.

BARLEY PEARLING

The amount of barley used for human foods is very small compared with that used for feed or for malting. Barley is harvested with the hull on. However, for food purposes, because of its lack of palatability, the hull needs to be removed. It is difficult to dehull barley by the techniques employed for rice and oats (see Chapter 10), because the hull is strongly attached to the pericap. It is therefore generally pearled. Pearling abrades the outer surfaces of the grain to remove the hull and the pericap. During pearling, the hull, pericarp, seed coat, and aleurone are removed, leaving the remainder of the endosperm relatively intact. The pearling device has an abrasive surface, and the outer layers are essentially sanded off the grain. This is an attrition process. The amount removed from the grain can be controlled by the length of time the grain remains in the machine.

Pearled barley is a common ingredient in many soups. The pearled grain can also be reduced to flour by a hammer mill. The resulting flour can then be used in baby foods, breakfast cereals, or breadmaking recipes.

SORGHUM AND MILLET DECORTICATION

In areas where they are consumed as food, mainly India and Africa, sorghum and millets are often milled by decortication processes. While such processes are quite effective with these cereals, as the grains are nearly round and do not have a crease, the germ is often left with the endosperm. The presence of the high-fat germ often leads to the flour rapidly becoming rancid. After decortication, the endosperm is reduced by further pounding or by milling with either a hammer mill or a burr mill.

CHAPTER 9: Wet Processing for Production of Maize, Wheat, and Rice Starches and Their Co-Products

Maize is by far the most important source of industrial cereal starch in North America, while wheat is the most important source in Europe and Australia. In comparison, only minor volumes of rice starch are produced industrially. The present chapter discusses the isolation processes for the two main starches as well as their co-products and also briefly deals with rice starch isolation.

The fact that, in North America, maize is the main source of starch is mainly because of the availability of this cereal in this part of the world and the higher yield of high-quality starch from maize than from wheat (see below). In contrast, in Europe and in Australia, relatively little maize is grown, and the obvious raw material for starch isolation is wheat.

Maize is processed into starch, protein, fiber, and oil-rich germ in a process generally referred to as "wet milling." Indeed, in contrast to what at first sight would seem logical, in industrial practice, the kernel disintegration occurs only following the softening of the kernel by steeping it in water. In contrast, in the production of wheat starch, the raw material is high-extraction flour (typically 78%, see Chapter 8) obtained by dry milling. The flour is subjected to wet processing, which yields starch and gluten as the main products. In industrial rice starch isolation, broken milled rice (see Chapter 10) is subjected to wet processing as well.

Sorghum has been wet milled by essentially the same system as that used for maize. However, sorghum starch isolation is not a very attractive process for the following reasons. First, the presence of pigments (mainly polyphenolics) in the pericarp can give the starch an off-color, particularly if it is placed in an alkaline solution. Second, sorghum bran breaks into small pieces that interfere with the separation of the protein and starch in the process. Finally, its germ is quite small, and the recovery of sorghum oil is hence not worthwhile.

The main constituents of maize are starch, protein, the fiber-containing bran, and its oil-rich germ. The actual wet milling is preceded by grain cleaning and steeping steps and then makes use of sieving and density-based separations in an aqueous environment to subsequently isolate germ, bran, protein, and starch. We here outline the basics of the process, as shown in Figure 9.1.

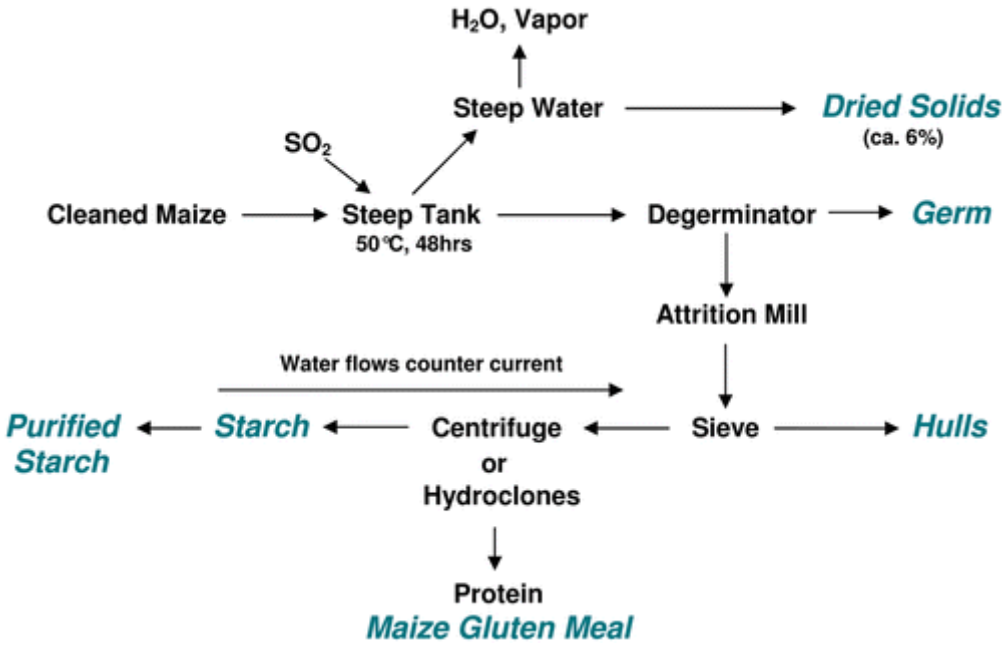


Fig. 9.1. Simplified flow of a maize wet mill.

RAW MATERIAL

For reasons outlined below, maize used for starch production should not have been dried at excessively high temperatures, as heat-damaged kernels lead to greatly reduced yields of starch. Before being used in the actual starch-isolation process, the maize is subjected to cleaning steps similar to those used in dry milling (see Chapter 8).

STEEPING

In the first step, the maize is submerged or steeped industrially in tanks that can hold about 75 metric tons. The steeping system normally uses a countercurrent battery of about 10 tanks, with the maize moving from tank 1 to tank 10 and the steeping water from tank 10 to tank 1. The temperature is controlled at 48–52°C, and the steep time varies from 30 to 50 h. As a result of steeping, the kernel contains about 45% moisture and is softened sufficiently so that the softness can be detected by squeezing.

Role of Sulfur Dioxide

The steeping water contains 0.1–0.2% sulfur dioxide, often generated by burning sulfur, which is used for two reasons. First, it aids in stopping the growth of putrefactive organisms. Second, the bisulfite ion reacts with disulfide bonds in the matrix proteins of the maize (Fig. 9.2) and reduces the average molecular weight of the proteins, making them more soluble. As a result, the release of starch from the protein matrix is much easier and more complete. During steeping, the level of sulfur dioxide in the steep water decreases as more of the bisulfite ion reacts with the protein.

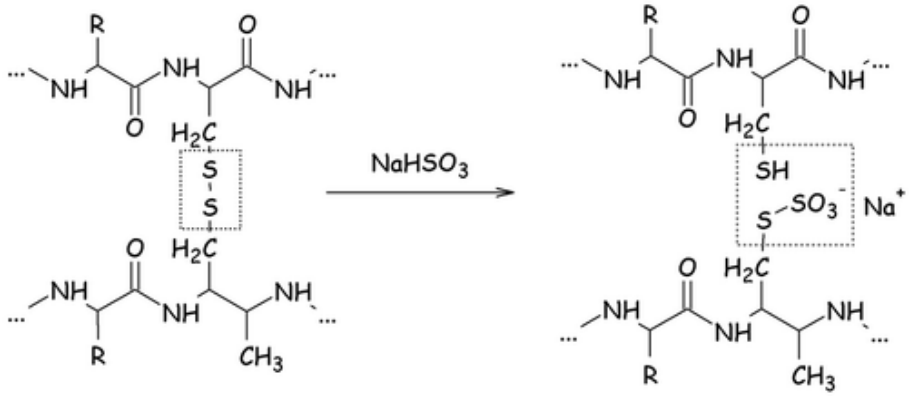


Fig. 9.2. Reaction of sodium bisulfite with a disulfide bond of a protein. (Courtesy M. Verswyvel)

The bisulfite releases lower levels of soluble protein from maize that has been dried at excessively high temperatures than from unheated maize. As a result, heat-damaged maize also gives greatly reduced yields of starch and therefore is not a desired raw material for wet milling. In general, processors will not use any maize that has been artificially dried.

Development of Lactobacilli

Although sulfur dioxide slows the growth of putrefactive organisms, it does not stop certain lactobacilli. The maize itself appears to be the source of the organisms, and steeping at 45–55°C favors their development. Lower temperatures lead to production of butyric acid. The role of the lactic acid produced during the steep is not clear. It appears to have only a minor effect on the softening of the maize kernel. Perhaps its major effect is to lower the pH and stop the growth of other organisms. In addition, its effect on the pH facilitates the later separation of protein from starch. The lactic acid bacteria are believed to produce proteolytic enzymes, which may assist in protein solubilization.

After steeping, the steep water contains a total of about 60 g of soluble matter per liter. This corresponds to about 6% of the kernel weight. The soluble matter contains about 35% protein, 26% lactic acid, 18% ash, and 7% phytic acid. In addition, it contains B vitamins. Generally, the steep water is concentrated by reverse-osmosis membrane filtration to about 55% solids and mixed with the bran and/or the spent germ to be used as animal feed. Alternatively, the solids from the steep can be used as a growth medium for the production of desired microorganisms.

COARSE MILLING AND GERM RECOVERY

After steeping, the softened grain is coarsely ground in water by an attrition mill. The mill breaks the grain and frees the germ, which, as a result of steeping, is swollen and rubbery and can be recovered as an intact entity. Two passes through the mill may be needed to free the germ, after which it is separated from the remainder of the kernel with a liquid cyclone separator, or hydroclone (Fig. 9.3). The hydroclone works in water on the same principle as a cyclone separator does in air; thus, the separation is based on density. The germ has a lower density because of its oil content. The recovered germ is washed free of adhering starch and dried. It is then used to produce oil (see below).

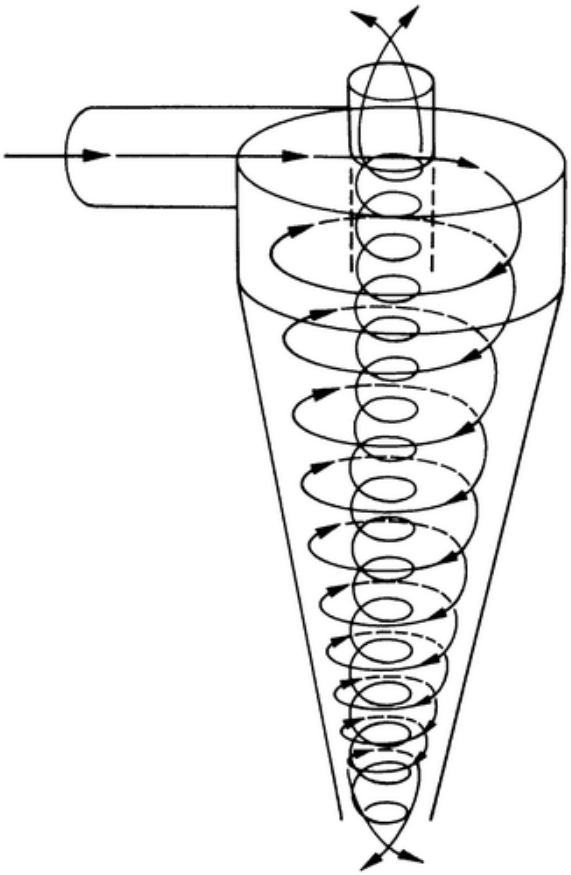


Fig. 9.3. Operation of a hydroclone to separate material of different densities. (Courtesy Dorr-Oliver, Inc., Stamford, CT)

SIEVING, FINE MILLING, AND FIBER RECOVERY

After removal of the germ, the remaining material is sieved to remove the larger particles. These larger and coarser particles, mainly from the hard, horny endosperm, are ground again, using stone or steel burr mills or an impact mill. The objective is to free the starch, protein, and fiber from each other. The bran tends to stay in larger pieces and is removed by sieving. Generally, the fiber is given a series of screenings on various-sized screens and is washed to remove adhering starch. The finest screen may be 75 μm. The washed fiber is dewatered under pressure and dried for use in animal feeds.

PROTEIN AND STARCH RECOVERY

The major stream contains the protein and starch in water. Because the starch is denser than the protein, they can be separated from each other with large continuous centrifuges or with additional hydroclones. The less-dense maize gluten, containing 60–70% protein on a dry basis, is dewatered by centrifuges and then dried. It is a valuable co-product used as an animal feed. The starch still contains too much protein (about 1%) at this point and must be purified by renewed centrifugation or with hydroclones. The hydroclones used here operate by the same principle as those used to separate germ. However, they are much smaller, and large numbers of them are used in sequences. Starch coming from them contains less than 0.3% protein and is ready for chemical modification, conversion to syrup, or drying to be sold as starch. Most drying is accomplished with flash dryers. The dewatered starch is injected into a rapidly moving stream of heated air. The granules are dried rapidly and collected with dust cyclones.

As shown in the schematic diagram of the maize wet-milling process (Fig. 9.1) all of the water (about 1.5 L/kg of maize) enters at the final washing step and eventually works its way back to the steep tanks. The concept of counter-current flow of the water and maize does not imply that water flows one direction in a pipe and that the maize or its components flow in the opposite direction. It means that, as the starch is washed, the wash water removed from the starch is used in a preceding step of the flow. This process is then repeated until the water is in the steep tanks. There are no effluent streams. The system is bottled up, and water leaves the plant only as water vapor.

The main products of wheat flour fractionation are gluten and both high- and low-quality starch. Indeed, apart from the better availability of wheat than of maize in Europe and Australia, the major driver in developing the wheat-processing industry in these parts of the world has been the accompanying production of the valuable wheat gluten fraction. We here describe the processes used as well as the commercial applications of gluten.

Over the years, numerous attempts have been made to produce gluten and starch from whole wheat rather than from dry-milled flour. Starting with the whole grain, in principle, has several advantages. For one, the cost of dry milling and the starch damage produced in the process are avoided. However, it has proven to be extremely difficult to design economically viable processes based on whole grain as the starting material.

STARTING MATERIAL

At present, high-extraction flour (typically 78%, see above) rather than wheat, is the starting material for the production of wheat starch and gluten. The use of high-extraction flour rather than low-extraction flour ensures that less of the starch remains in the co-products of dry milling, which are not used for starch isolation. An important flour characteristic is the level of damaged starch. Damaged granules reduce the yield of intact starch granules. In addition, they can absorb many times more water than native starch and can therefore interfere with gluten protein agglomeration, an essential step in the processes outlined below. Finally, damaged starch contamination of prime starch may restrict the use of wheat starch in certain applications.

PROCESSES

We here describe three types of processes that typically are used, i.e., the Martin dough process, the dough-batter process, and the batter process. All these processes yield not only starch and gluten, but also a considerable fraction of wheat water-extractables. Indeed, during the processing of flour, as much as 10% of it becomes soluble. Because of the presence of water-extractable arabinoxylans (see Chapter 4), the fraction cannot be concentrated in a manner similar to that used for the solubles from maize steep, as the viscosity would become very high unless endoxylanases are used (see below).

Irrespective of the process, sulfur dioxide is not used in wheat starch isolation for two reasons. First, it is not needed, as water alone softens the wheat flour particles sufficiently and allows separation of the protein from the starch. Second, the sulfur dioxide would weaken the gluten matrix and make the recovery of the gluten more difficult. More importantly, sulfur dioxide would destroy the character of the vital wheat gluten and make it much less valuable. The term *vital* is used in industry to identify gluten that has not been damaged and thus has the ability to form gas-retaining dough.

In contrast, in wheat flour fractionation, endoxylanases can be (and in many instances are) used, as they facilitate flour processing. Endoxylanases that 1) hydrolyze the water-extractable arabinoxylans while leaving their water-unextractable counterparts intact and 2) are not inhibited by the wheat endogenous endoxylanase inhibitors (see Chapter 4) have the most beneficial impact. This is presumably because they are the most efficient in reducing the viscosity of the aqueous phase. In dough-batter systems (see below), for instance, their use increases the average size of the gluten agglomerates formed.

Dough Process

The well-known Martin, or dough, process is the traditional method for obtaining gluten from wheat flour; it has been widely used since 1835. In this process, a stiff dough with approximately 40–60% water is made. It is allowed to rest and fully hydrate, thereby producing a strong, cohesive gluten matrix. The dough is then washed in a continuous kneader with additional water to remove starch and the water-extractable fraction from the gluten, which adheres to itself in large pieces. The gluten can be enriched to more than 75% protein (dry basis) by additional washings with water. The remaining 25% is composed of more-or-less equal quantities of small-granule starch, lipid, and water-unextractable arabinoxylan.

Dough-Batter Process

The first step in this process is the formation of stiff dough. The gluten matrix is (partially) dispersed by addition of extra water and mixing, resulting in a batter, which is then separated to obtain starch and gluten.

Batter Process

A variation of the Martin process was developed during World War II. This procedure, also known as the "batter," "slurry," or "screening" process, has been adapted for continuous processing. It includes the formation of a slack dough or batter by mixing approximately equal amounts of flour and water. The batter is mechanically broken up in the presence of additional water, yielding suspended curds of gluten particles containing low levels of residual starch. In this process, millimeter-sized gluten particles are produced. Typically, temperatures of 40–55°C are used. The gluten curds are recovered on gyrating sieves, while the starch milk and the water-extractable fraction pass through. The starch is recovered and subsequently dried.

Starch Separation

Starch can be separated from the protein fraction by centrifugation, in hydroclones, by tabling, or in decanters, all of which take advantage of the greater density of starch granules than of gluten particles. Sieving obviously takes advantage of the size difference between starch granules and agglomerated gluten particles.

Centrifugation yields a dense bottom stream, called "prime starch" or "A-starch." Prime starch consists of the large, lenticular starch granules and part of the small, spherical starch granules. The top streams are the part of the gluten that made it through the sieves. The gelatinous layer obtained is generally referred to as "squeegee starch," "starch tailings," "sludge," "low grade starch," or "B-starch." It consists of small starch granules, water-unextractable arabinoxylan and/or cell wall material, damaged starch granules, and small levels of protein and ash. It makes up as much as 20% of the total starch. This fraction is of much lower value than the A-starch. In practice, it is increasingly converted to glucose by appropriate enzyme technology and, for instance, fermented to alcohol, which is then recovered by distillation.

In hydrocyclones, the starch-gluten suspension is fed tangentially into the upper part of the cone. The resulting spinning effect generates the centrifugal force that separates the starch granules from the gluten particles and from the water-extractable fraction. The dense starch granules exit the bottom of the cone, while the gluten and the water-extractable fraction exit in the overflow of the cone.

In starch tabling, a suspension of starch and gluten flows over an inclined table, which allows the starch to settle and the gluten particles, water, and water-extractable fraction to run off. The surface of the starch deposited on the table is then washed with water to remove the B-starch.

Sieving retains the agglomerated gluten proteins, while the starch milk (also containing the water-extractable fraction) passes through the sieve. Starch is recovered by centrifuging or tabling the starch milk.

Starch and Gluten Drying

The drying of both starch and gluten is a major problem in starch gluten plants but for different reasons. The challenge in drying wheat starch is to avoid explosions. Starch, particularly the small-granule starch, much like grain dust, can form a very explosive mixture in air. Unless precautions are taken and adhered to, explosions are likely. The challenge in drying gluten is to preserve its vital character. Heating hydrated gluten to dry it can alter the protein and, if not done properly, makes it lose its vitality and, hence, its economic and functional value. Most gluten plants use a type of ring dryer that purports not to damage the gluten. The basic process is to extrude wet gluten into a stream of heated air containing previously dried gluten. The concept is that evaporating water will keep the product cool until it is dry.

Gluten Uses

The largest usage of wheat gluten is by the breadmaking industry. In Europe, it is a common practice to add wheat gluten at the mill to increase the protein content of the flours and to improve their strength. This is not common practice in North America. However, a major use of gluten both in Europe and North America is at the bakery. A particular benefit of adding gluten at the bakery is to allow the bakery to inventory only one type of flour, which can be adjusted to meet product requirements by addition of gluten. For instance, many of the bread formulas that are enriched in fiber also contain relatively large dosages of gluten. The gluten is added to strengthen the dough and to produce a product with good texture and volume. Another major usage at the bakery is in the production of hamburger and hot dog buns. Gluten is used to produce buns with a strong hinge. When buns are sliced, a small part (i.e., the hinge) is not cut so that the two halves of the bun remain attached.

Other uses of gluten are as a binder and texturizing agent in sausage-type products and in some breakfast cereals, where it increases the protein content and adheres to other ingredients. It is also used in calf milk replacers, aquaculture, and pet foods.

Rice Starch Production

As shown previously (Chapter 1), rice starch occurs as compound granules tightly held in a protein matrix. The individual granules are very small (4–8 μm in diameter) and polygonal in shape. Rice starch is apparently not produced commercially in North America. Although it is a starch of commerce in Europe, only relatively small amounts are imported into North America.

The protein-starch association in the rice kernel is very strong and is not weakened when the grain is soaked in water or dilute sodium bisulfite. However, it is weakened by soaking in dilute sodium hydroxide, as, under such conditions, most of the rice protein becomes soluble. Hence, commercial processes use alkaline solutions for isolation of rice starch, with good recovery and low residual protein content because large portions of the rice protein consist of alkali-soluble, high molecular weight glutelins. In practice, the basic process for production of rice starch consists of soaking broken rice (often pulverized first by dry milling) in 0.3% sodium hydroxide for about 12 h. The starch is then recovered by centrifugation. After a series of washings with water, the starch is dried in a manner similar to drying of wheat starch. The protein, recovered from the combined steep solution and wash water by neutralization with acid, is used as a supplement for cattle feed.

Production of Oil from Cereals

Cereals vary widely in the amount of oil they contain (Table 9.1). However, in all cases, the amount of oil is too low to justify its recovery. Hence, it is solely produced as a co-product of other manufacturing processes, and the amount of oil produced from cereals is small compared to those produced from oilseeds and animal sources.

TABLE 9.1
Oil Content of Cereal Grains[a]

Cereal	Oil Content, % dry basis
Barley	2.1
Maize	4.4
Millet	4.4
Oats	5.1
Paddy rice	2.1
Rye	1.8
Sorghum	3.4
Wheat	1.9

[a] Source: National Academy of Science (1969).

Some oil is produced from wheat, rice, and maize. Wheat germ oil is more unsaturated than the other cereal oils. In general, the higher the degree of unsaturation, the more problems encountered in storing the oil. It is extracted from wheat germ and sold mainly in health food stores as a nutritional supplement. Rice bran oil, as one might expect, is found in Asia.

The major cereal oil produced is from maize germ. Maize germ oil (corn oil) generally sells at a higher price than the other oils. The reasons for the premium are that it has a good nutritional image and that it can be refined to a light-colored and light-tasting product that most people prefer. Thus, most maize oil is consumed as a salad or cooking oil, with smaller amounts used in margarine. Practically none is converted to shortening.

Figure 9.4 outlines the principles of maize oil production. Maize germ from either wet-milling or dry-milling plants is used for oil pressing and extraction. Generally, the germ is flaked to give a coarse meal, heated with steam, and run through an expeller unit. In the expeller, the germ meal is subjected to high pressure in a slotted barrel. Most of the oil is pressed out through the slots, and the residue of the germ is discharged at the

end of the barrel. In several passes, perhaps up to 95% of the original oil can be expelled. The residue from the expeller, called "foots," is often solvent-extracted with hexane. The resultant residue contains about 0.5% oil. The product obtained by pressing or by being extracted and then stripped to remove the hexane is referred to as "crude oil."

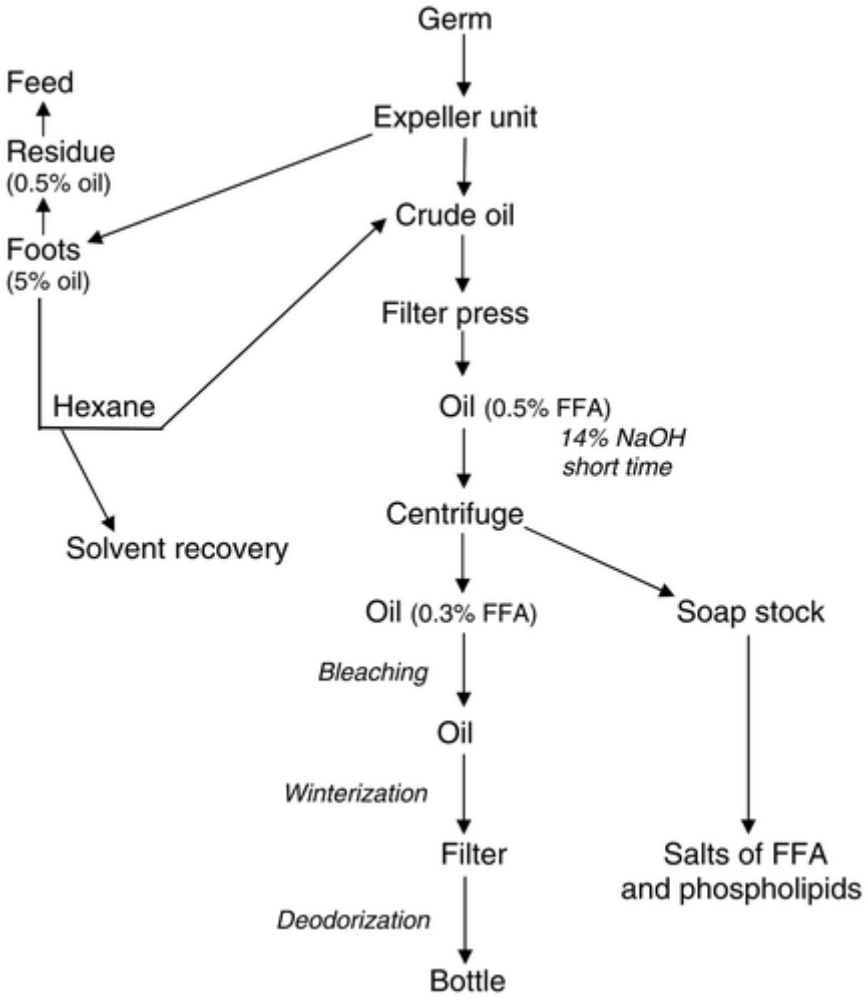


Fig. 9.4. Simplified flow for the refining of maize oil. FFA = free fatty acid.

The crude oil is filtered to remove solid impurities. The filtered oil is then treated with a strong alkaline solution, usually at high temperature (93°C) for several minutes. Longer treatment must be avoided to reduce saponification, i.e., deesterification of the triacylglycerol population. The object of the treatment is to convert the free fatty acids and phospholipids to water-soluble salts. These two lipid classes, which are subsequently removed by an aqueous wash, are called "soap-stock" and are used in soap manufacture. The free fatty acids must be removed because they reduce the storage stability of the oil, the phospholipids because they lower its smoke point. While the crude oil generally contains about 0.5% free fatty acids and about 1.5% phospholipids, after the alkali treatment, it typically contains about 0.01% free fatty acids and less than 0.05% phospholipids.

After the alkali treatment, the oil is bleached by adsorbing the pigments on an adsorbent. Acid-activated clay (about 2% of the amount of the oil) is vigorously mixed with oil at about 105°C. After a short equilibration period, the oil is filtered to remove the clay. The clay is then discarded.

The next step in the oil-refining process is winterization. Its objective is to remove material that would become insoluble at lower temperatures and produce cloudiness in the oil. The cloudy appearance is undesirable, particularly in salad oils. In maize oil, the cloudy appearance is caused by waxes that naturally occur on the outside of the maize kernel. These can be easily removed by winterization, i.e., cooling the oil to a low temperature and filtering off the insoluble material.

The final step in oil refining is deodorization. The oil is held at a high temperature (218–235°C) under reduced pressure. The relatively volatile constituents, such as aldehydes, that are responsible for the odors and flavors are removed, as are the free fatty acids, colored materials, and peroxides. The vacuums used are very high, and oxygen must be rigidly excluded at those temperatures. The oil is then ready to bottle. Typical analytical

data for maize oil would show a free fatty acid content (expressed as oleic acid) of 0.20%, a saponification value of 190, an iodine value of 125, and a smoke point of 232°C.

CHAPTER 10: Rice and Oat Processing

The two grains discussed in this chapter are similar in that, like barley, they are harvested with the hulls attached. The other cereals lose their hulls during the threshing step and are handled as naked grains. As might be expected, the first step in processing these cereals is to remove the hulls. Whereas barley's hull tightly adheres (in fact, is cemented) to the outer layers of the pericarp, the hull of rice or oats is, instead, a separate, intact structure that essentially surrounds the grain with no bonding between the grain and the hull. The present chapter discusses the processing of rice and oats, starting with these cereals and covering the industrial chain through the various intermediates to consumer products.

Rice Processing

In a series of unit operations, paddy rice, or brown rice, can be converted to *milled rice*, a synonym for *white rice*. The white rice can undergo further manipulations to produce quick-cooking rice or enriched rice. Alternatively, paddy rice can be processed to parboiled rice. The main aspects of both processing routes are discussed below.

RICE MILLING AND FURTHER PROCESSING OF WHITE RICE

As outlined in Chapter 1, rice with the hull on is called "paddy" or "rough" rice. About 20% of paddy rice is hull. The kernel remaining after the hull is removed is brown rice. Following removal of the bran, white rice is obtained. Figure 10.1 shows the subsequent steps in the preparation of white rice.

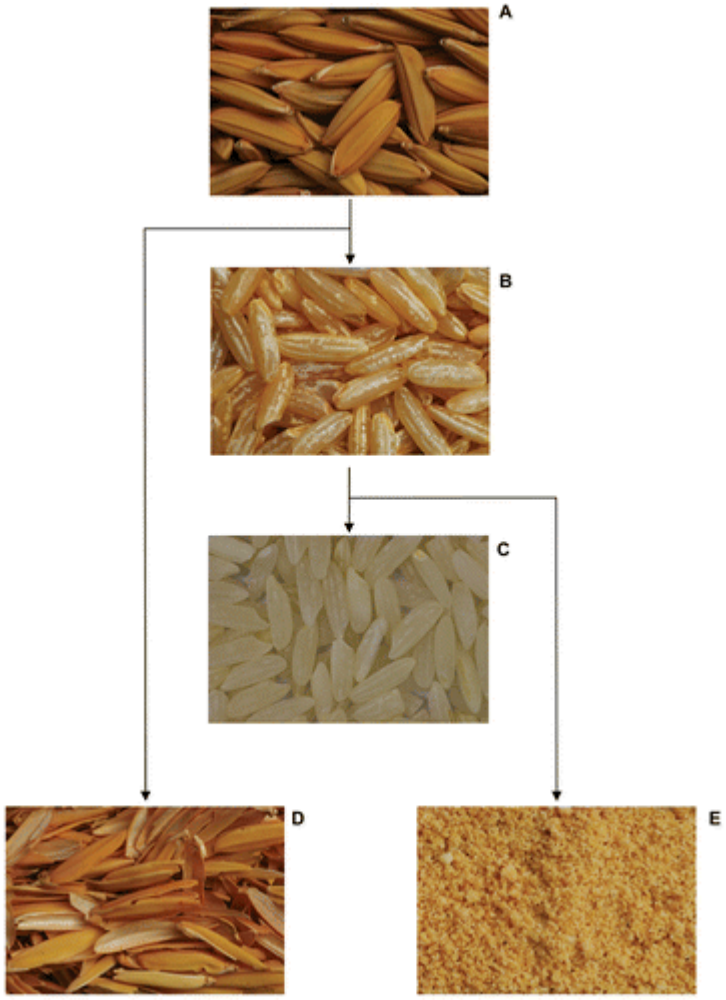


Fig. 10.1. Photographs of the different products obtained in the conversion of paddy rice (**A**) into white rice (**C**). First, paddy rice is separated into brown rice (**B**) and husk (**D**). The brown rice is then milled to give white rice and rice bran (**E**).

Rice Dehulling

The Process. The most common dehuller used today is the rubber-roll sheller (Fig. 10.2). Rough rice is passed between two rubber-coated rolls that turn in opposite directions and are run at a speed differential. The pressure and shear remove the hulls, much as rubbing peanuts between hands removes their shells. The pressure exerted by the rolls can be varied, as different cultivars may require different pressures for adequate shelling. Excessive pressure may discolor the grain and also cut down the life of the rolls, which is already limited. The rolls must be replaced every 100–150 h.

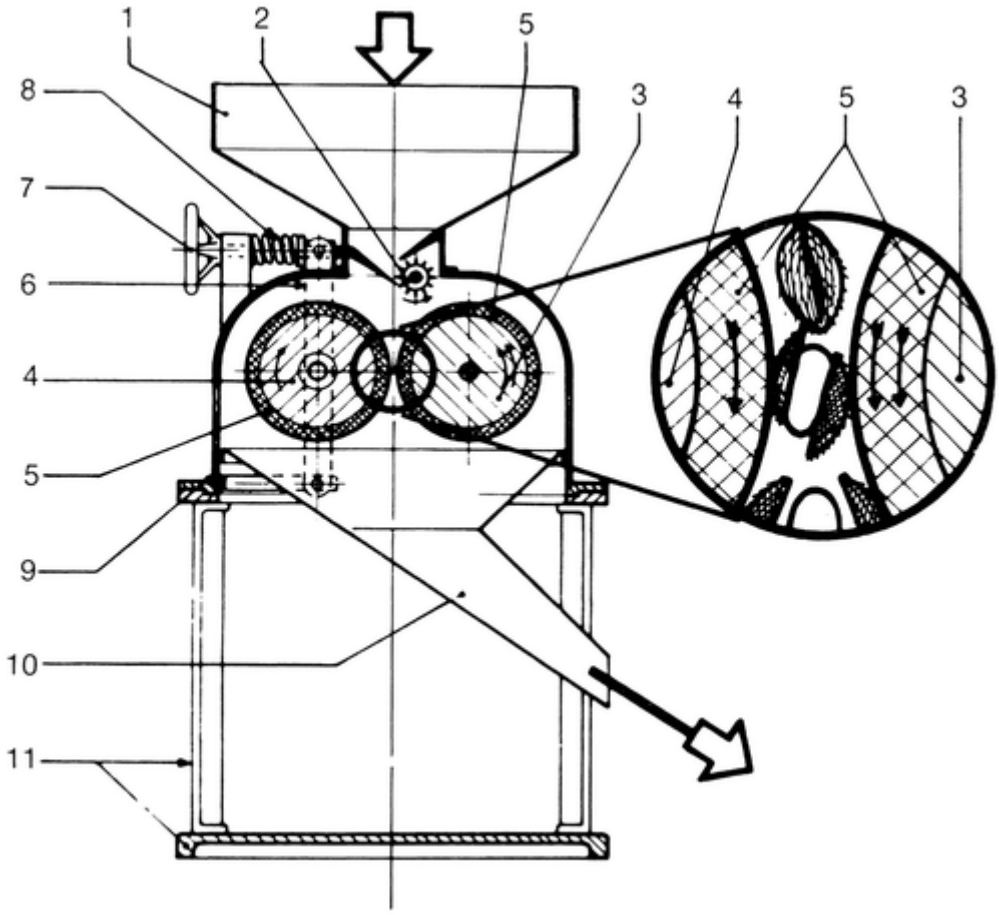


Fig. 10.2. Illustration of a rubber-roller rice dehulling machine, showing the hopper (1), feeding roll (2), drive rolls (3 and 4), rubber coating (5), pressure adjustment system (6–8), housing (9), delivery spout (10), and stand (11). (Reprinted, with permission, from Borasio and Gariboldi 1957)

Rubber-rolled shellers are preferred because of their efficiency in removing hull (>90%) and because they cause less breakage than the older types of shellers. An older type is the disk sheller, which has a horizontal abrasive-surfaced wheel that rotates on a vertical axis just below a stationary abrasive-surfaced wheel (Fig. 10.3). Rough rice enters through an opening in the center of the stationary top wheel and, because of the spinning bottom wheel, brown rice flows out between the two wheels. The abrasive action of the wheels on the rice hull essentially sands off part of the hull and frees the brown rice. This type of sheller is less efficient and results in more breakage.

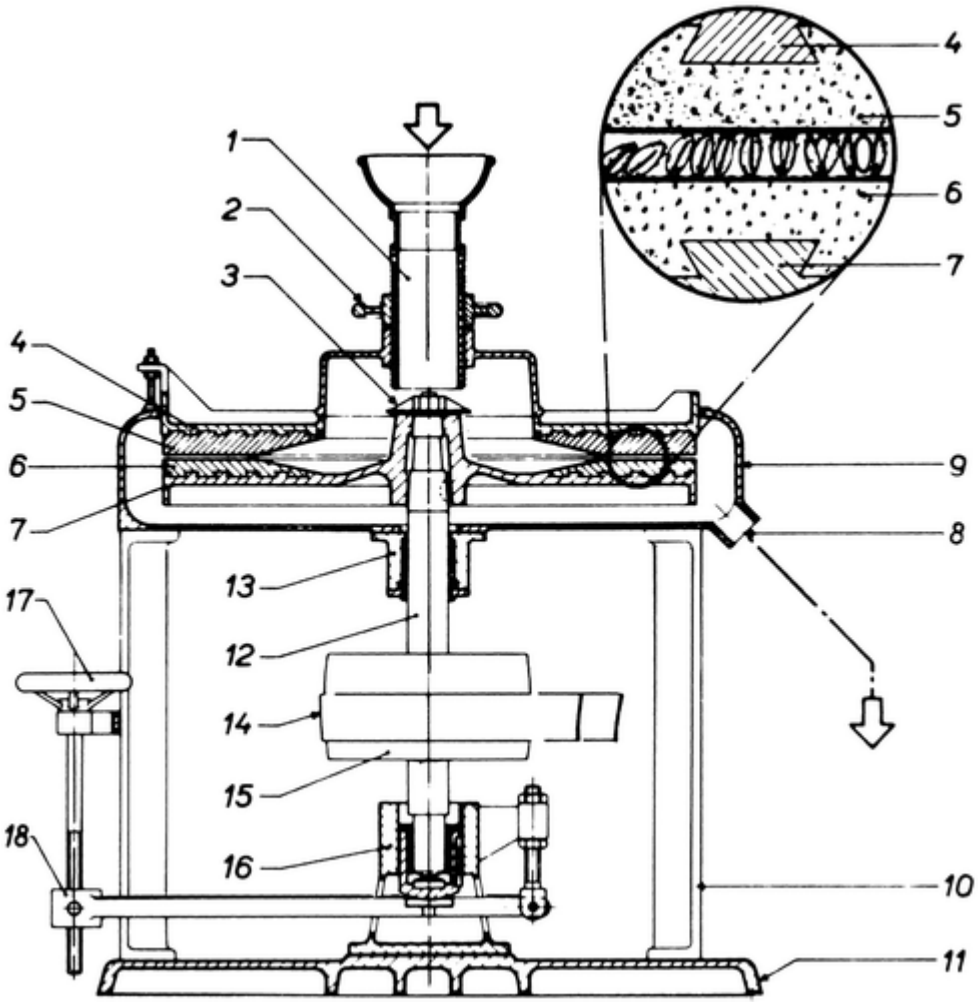


Fig. 10.3. Illustration of an abrasive rice dehuller, showing the feed spout (1), slide gate (2), rotating abrasive wheels (3 and 7), fixed wheel (4), abrasive stones (5 and 6), outflow spout (8), housing (9), stand (10 and 11), drive mechanism and bearings (12–16), and adjustment system for distance between stones (17 and 18). (Reprinted, with permission, from Borasio and Gariboldi 1957)

After separation, the hull is removed by aspiration, and the remaining rough rice is separated from the brown rice. The separation, which is based on bulk density, can be made on a gravity separator (sometimes called a "paddy machine"; see Fig. 8.2). The paddy is returned for another pass through the sheller. Products at this point are hulls, brown rice, and broken brown rice.

Rice Hulls. Rice hulls are mostly a nuisance to the miller. They are tough, fibrous, abrasive, and have low nutritive value. As already described in Chapter 1, they consist of two interlocking halves. The larger is the lemma, the smaller the palea. The interlocking of the two makes removal of the hull from the kernel difficult.

Rice hulls are high in ash (about 20%), cellulose (about 30%), arabinoxylan (about 20%), and lignin (about 20%) and contain small levels of protein (about 3%) and fat (about 2%). In addition, they contain small levels of vitamins.

The predominant component (94–96%) of the ash from rice hulls is silica. The uptake of silica, in all cereals except rice, is passive. This means that the soil water contains a certain level of soluble silica, and that silica is taken into the plant along with the water. Because plants do not have an elimination system for nonvolatiles, whatever is taken in must be deposited in the plant. This fact has been used to determine the water requirements of plants. Rice, however, is different. It actively takes up silica, which implies that it takes up more silica than would be calculated from the water uptake. Why the rice plant takes up these amounts of silica is unknown. However, silica has been related to disease resistance in rice. Whatever the reason, the silica must be deposited somewhere in the plant, and the hull is the depository for much of it.

Numerous uses for rice hulls have been suggested in the literature. However, their disposal or utilization still remains a major problem. Estimates indicate that, of the hulls produced, as much as one third is not utilized. Early workers felt that hulls were dangerous in feed, but this has been disproved. The most common use of

hulls is to mix them with rice bran and sell them as rice millfeed. Such products generally contain about 61% hull, 35% bran, and 4% polish. Hulls can also be used as bedding or litter, as a fertilizer or mulch, and in a number of industrial uses, including burning for fuel. Hulls are essentially sulfur free. The heat produced may be two-thirds that from wood. Small amounts of hulls are used to produce carbon or furfural, an important organic intermediate. The rice hull yield of furfural is low compared to the yield from such sources as oat hulls, cottonseed hulls, or maize cobs and is generally related to the arabinoxylan level of the starting material. Small amounts of hulls are also used as filter aids or abrasives.

Brown Rice Milling

The Process. Although it is common knowledge that brown rice is more nutritious than white (milled) rice, hardly anyone eats brown rice. For one thing, the cooking time for brown rice is much longer than for white rice. Therefore, brown rice is milled. The milling of brown rice is essentially the removal of the bran by pearling to produce white rice. In the pearler or milling machine (Fig. 10.4), some rice breakage inevitably occurs. In some cultivars of rice, the bran is more difficult to remove than in others. In such cases, a small amount of water can be added to soften the bran layers before milling. Dry calcium carbonate (about 3.3 g/kg) is added to the brown rice. It is an abrasive that helps in removing the bran. In a typical pearler, the brown rice enters through a flow-regulating valve and is then conveyed by a screw to the pearling chamber, where the mixing roller causes the grains to rub against each other, abrading off the bran. Most of the bran is removed by the grain rubbing on other grains, although a small amount is also removed by the grain rubbing on the steel screen surrounding the chamber. At the discharge end of the pearling chamber is a plate that is held in place by a weight. The position of the weight varies the pressure on the plate and thus the back pressure on the rice in the pearling chamber. The degree of milling can be controlled by varying the pressure and thereby changing the average residence time in the chamber. Generally, the miller visually determines the proper setting and the degree of milling and tries to achieve a reasonable throughput, with a uniform degree of milling, while keeping breakage to an absolute minimum. The head rice (unbroken milled kernels) brings a much higher price than the brokens, which are generally sold to be used as adjunct in brewing (see Chapter 11) or as raw material for industrial rice starch isolation (see Chapter 9). The miller therefore takes every possible action to increase head rice yields and minimize the quantities of brokens.

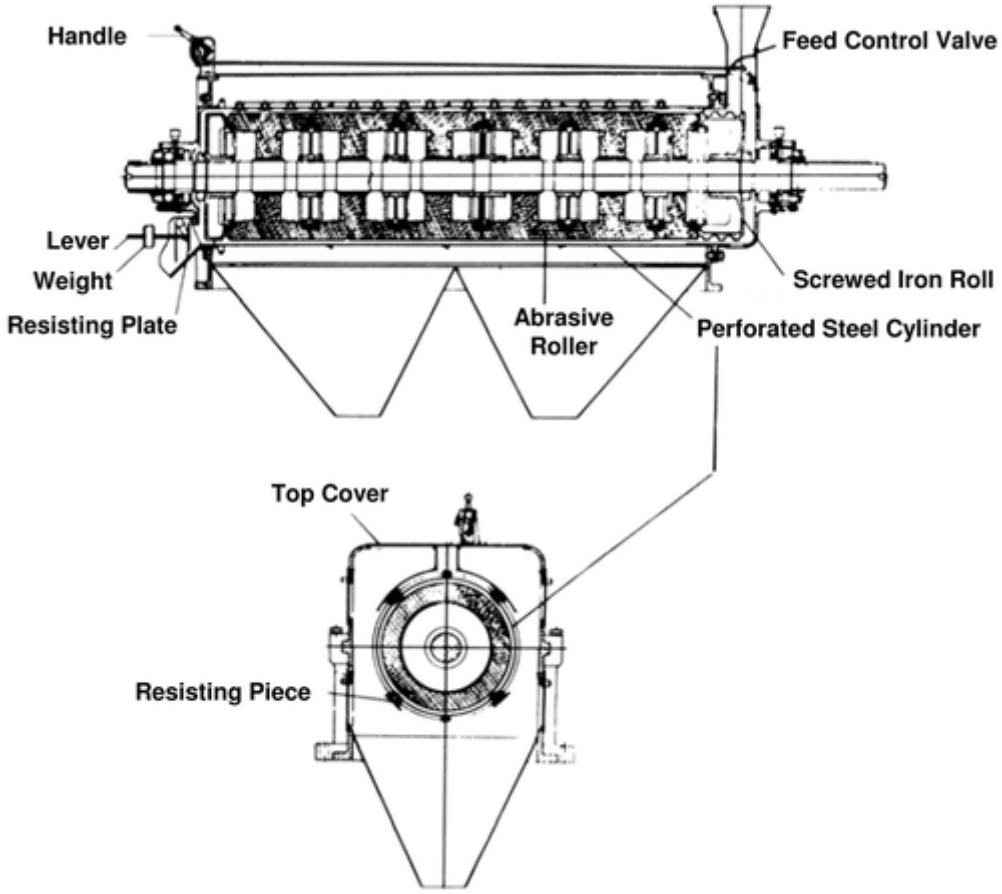


Fig. 10.4. Illustration of a pearler that can be used to mill rice or to pearl barley. (Courtesy Satake Engineering Company, Tokyo, Japan)

After milling, the loose bran is removed by an aspirator, and the milled rice can then be polished. The polisher consists of a rotating vertical cylinder to which straps of leather are attached. The milled rice passes downward

between the rotating cylinder and the surrounding wire screen. An additional amount of bran is removed by the polisher. Some mills have discontinued the use of polishers because of the increased breakage produced. After being polished, the head rice is separated from brokens by screening or by disk separators.

The products from the mill are head rice, brokens, rice bran, rice polish, and hulls. In general, paddy rice yields about 20% hulls, about 8% bran, and about 2% polish. The remaining about 70% are brokens and head rice. The level of brokens varies widely and depends on the rice cultivar, the milling scheme, and the skill of the miller.

Rice Bran and Polish. Rice bran and polish are co-products from rice milling. Bran consists of the outer layers of the brown rice pericarp. Polish consists of the inner layers, containing aleurone cells and small levels of starchy endosperm. As might be expected, the levels of bran and polish vary widely, depending on the milling procedure employed. As stated earlier, bran normally represents about 8% of brown rice and polish about 2%.

Table 10.1 shows the general composition of the two fractions. In addition to the values shown, rice bran ash is high in magnesium, potassium, and phosphorus. It is also an excellent source of B vitamins (typical values [in µg/g] are thiamin, 10.6; riboflavin, 5.7; niacin, 309; and pyridoxine, 19.2) and vitamin E (149 µg/g), but it contains little, if any, vitamin A, C, or D. Rice bran has also been shown to reduce cholesterol.

TABLE 10.1
Composition of Rice Bran and Polish[a]

Constituent	Bran	Polish
Protein, %	12.0	12.0
Fat, %	13.0	16.0
Ash, %	10.0	8.0
Nitrogen-free extract, %	40.0	56.0
Crude fiber, %	12.0	7.3
Pentosans, %	10.0	…

[a] Adapted from Houston (1972).

The utilization of rice bran and polish is not as great as one might expect from their composition. Both bran and polish are excellent sources of nutrients in animal feeds. However, when rice bran is stored without inactivation of lipase, the fat in the bran rapidly becomes rancid and unpalatable. Furthermore, damp bran is an excellent growth media for microflora, which can produce mycotoxins if they are fungal and bacterial toxins if they are bacterial. Rancid or infected bran cannot be used as a feed and therefore is used as fuel or fertilizer.

Rice bran is a source of food-grade oil. Generally, the bran is solvent-extracted. It contains appreciable amounts of wax that must be separated from the oil. After refining, rice oil is comparable to other edible oils.

Milled Rice Quality

As with most food products, the quality of rice is determined by its ability to produce the desired end product. Consumer acceptance varies from country to country and even between regions and ethnic backgrounds within a specific country. Most North American and European consumers prefer rice that cooks to produce dry and fluffy kernels. For them, each kernel should retain its shape and separate identity after cooking. Other consumers, particularly in Asia, prefer rice that cooks to be moist and chewy, with the kernels sticking together. It follows that rices of different composition and physicochemical properties are needed to meet consumer demands. In practice, the amylose content of rice is an important characteristic, as is sufficient after-ripening (see below) of the cereal.

Rice Amylose Content. Unlike that in other cereals, the amylose content of rice starch varies widely, depending upon the cultivar and growing region. In southern Europe, both long-grain and medium-grain rices

are cultivated. Waxy rice is not cultivated in Europe. Most of the European rices are translucent, while some of the medium-grain varieties have opaque endosperm. The majority of aromatic (i.e., having an aroma) rices in Europe are imported from India, Pakistan (basmati), and Thailand (jasmine). North American long-grain cultivars (Fig. 10.5) have higher amylose contents (23–27%) than short- and medium-grain types (15–21% amylose). Typical long-grain types cook to be dry and fluffy and are preferred for quick-cooking rice, canned rice, canned soups, and convenience foods containing rice. In contrast, typical short- and medium-grain types are moist and sticky after cooking and are suitable for breakfast cereals, baby foods, and brewing.

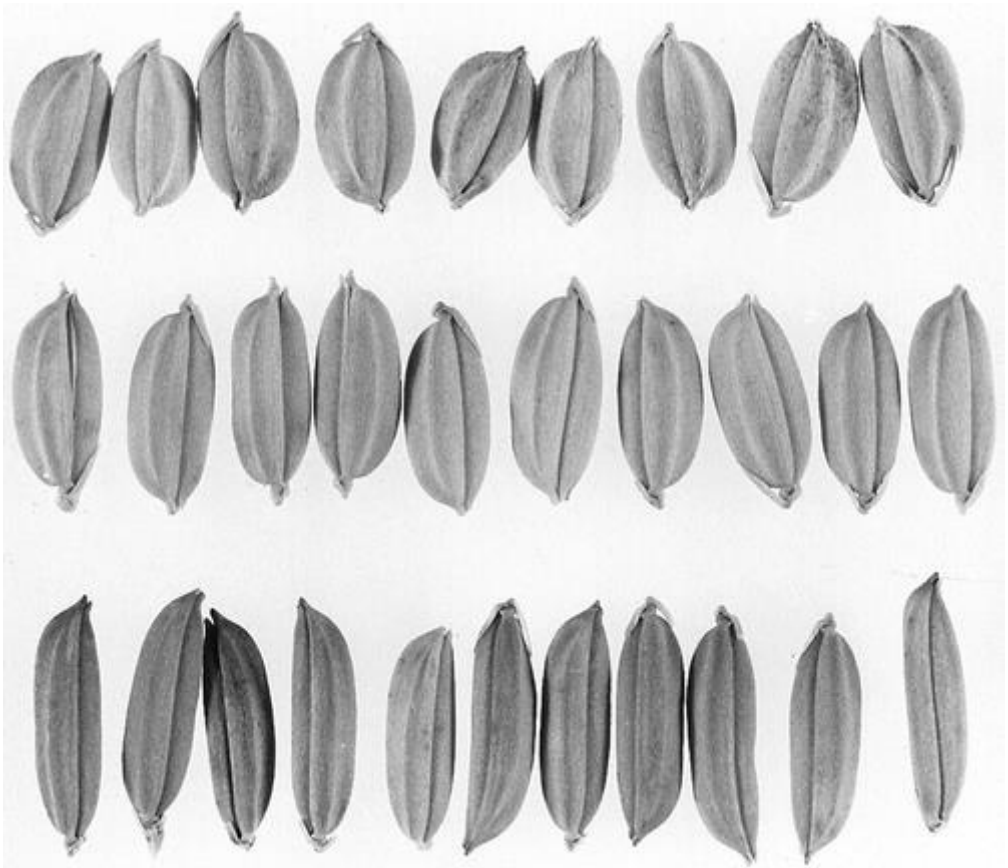


Fig. 10.5. Rice, showing short- (top), medium- (middle), and long-grain (bottom) types.

In North America, most rice is bland in taste and translucent in appearance. However, an aromatic basmati is gaining in popularity and is available in most areas. A small amount of waxy rice (rice with all-amylopectin starch) is grown. In other parts of the world, many rice cultivars are aromatic. These usually yield poorly, but in many countries small areas are grown by farmers for their personal use.

After-Ripening. Like all cereals, rice undergoes after-ripening. The term *after-ripening* (see also Chapter 11) is used to collectively describe the biochemical changes that occur in dry, sound grain as a function of storage time after harvest. The phenomenon is not well understood, but the changes it causes are shown easily. White rice milled from freshly harvested paddy gives very pasty and sticky kernels after cooking. If the paddy is stored under appropriate conditions, within weeks, the milled grains cook with much less tendency to stick together. Storing of milled rice also produces decreased cohesiveness, drier surfaces, larger volumes, and firmer texture in cooked kernels. In addition, cooking time tends to become longer with increased storage time.

Although many changes can be demonstrated in physicochemical properties and enzyme activities (generally a decrease in activity) with aging, we do not yet know which of these changes result in the changes in cooking quality described above.

Further Processing of Milled Rice

Several further processing steps can be used to increase the value of milled rice. Their goal is, in many instances, to reduce the cooking time of rice or to increase its nutritional value. The conditions used for parboiling (see below) brown rice determine whether the resultant parboiled white rice has a reduced or increased cooking time.

Quick-Cooking Rice. Milled rice requires 20–35 min to cook. This relatively long time is caused by the slow rate at which water diffuses into the kernel. Most rice endosperm is translucent and thus tightly packed, with no air spaces or other channels for water to penetrate the kernel. For cooking to occur, water must penetrate to the center of the kernel with sufficient heat capacity to gelatinize the starch.

Several techniques are used to produce quick-cooking rice. Their principle is mostly that they facilitate water uptake, for instance, by providing channels for water to move through. One method is rapid heating of dry rice at about 10% moisture, which causes internal fissuring. Other methods are based on cooking with about 60% moisture rather than the approximately 80% moisture necessary to give fully cooked rice. Following cooking at the reduced moisture level, the rice can be slowly dried, be rolled or bumped by being passed between rolls that are set to slightly and temporarily deform the grain, and then either be dried or, alternatively, frozen, thawed, and dried or puffed. Rolling or bumping followed by drying produces a relatively flatter grain, which means that water has less distance to travel during cooking. Freezing, thawing, and drying or puffing by rapid changes in pressure have also been used to produce quick-cooking rice. As a result of most of the methods used to produce quick-cooking rice, the uncooked kernels become opaque and larger in volume.

Rice Enrichment. The consumption of white milled rice as a large part of one's diet can lead to a deficiency in the B vitamin thiamin, leading to the disease beriberi. To avoid the problem, rice can be enriched with nutrients.

The most popular method of enriching rice in North America is to add powdered nutrients. However, such nutrients are often washed off by the consumer, and, in many parts of the world, rice is cooked in excess water and the cooking water is discarded, along with a significant part of the nutrients.

Another method of enriching rice is to produce a rinse-resistant premix and coat the rice with it. Milled rice is tumbled in a slowly rotating polishing cylinder and sprinkled with an acidified aqueous solution of thiamin and niacin. The moisture is removed by aspiration, and a coating of stearic acid, zein, and abietic acid in alcohol is sprayed on the rice. This mixture gives a rinse-resistant coating. The rice is then dusted with ferric pyrophosphate to supply iron.

In Japan, other approaches to enrichment have been used. One example is the addition of water-insoluble derivatives of thiamin (benzoyl thiamin disulfide). Another approach is to add to consumer rice products imitation rice kernels produced from cereal flour dough that contains the enrichment. A disadvantage of the latter technique is that the added imitation rice kernels look different from the regular rice kernels, which may lead to their being removed by the consumer during rice preparation. Another drawback is that, if they are too inert, they may pass the intestine unutilized.

RICE PARBOILING

The term *parboiling* originates from the wording *partial boiling*. In southern Asia, for several centuries, paddy rice has been soaked and heated before it is dehulled and the bran removed. Early in the twentieth century, it was discovered that eating parboiled rice prevented the occurrence of beriberi, a disease caused by thiamin deficiency. Indeed, during parboiling, thiamin migrates from the pericarp into the endosperm. After subsequent removal of the bran, the thiamin content is preserved in the rice kernel. Parboiling makes cooked rice firmer and less sticky, features that are preferred by most Western consumers. The reduction in the percentage of broken kernels during milling, the improved resistance to adverse storage conditions, and the altered cooking properties led to the introduction of this type of rice in Western cultures. Europe consumes a total of about 1.7 million tonnes of rice, of which about 0.6 million tonnes is parboiled. Parboiled rice is also used for the production of canned, expanded, and flaked rice products.

In traditional parboiling, paddy rice is the raw material. In modern industrial practice, brown rice is also used because transportation of the hulls from the field to the factory increases costs, and soaking of paddy rice takes much more time and energy. Mostly, long-grain rice cultivars of intermediate and high amylose contents are used for parboiling.

Not much is known in the public domain about the parboiling processes used in industrial environments. However, parboiling invariably comprises rice soaking, heating, and drying unit operations (Fig. 10.6).

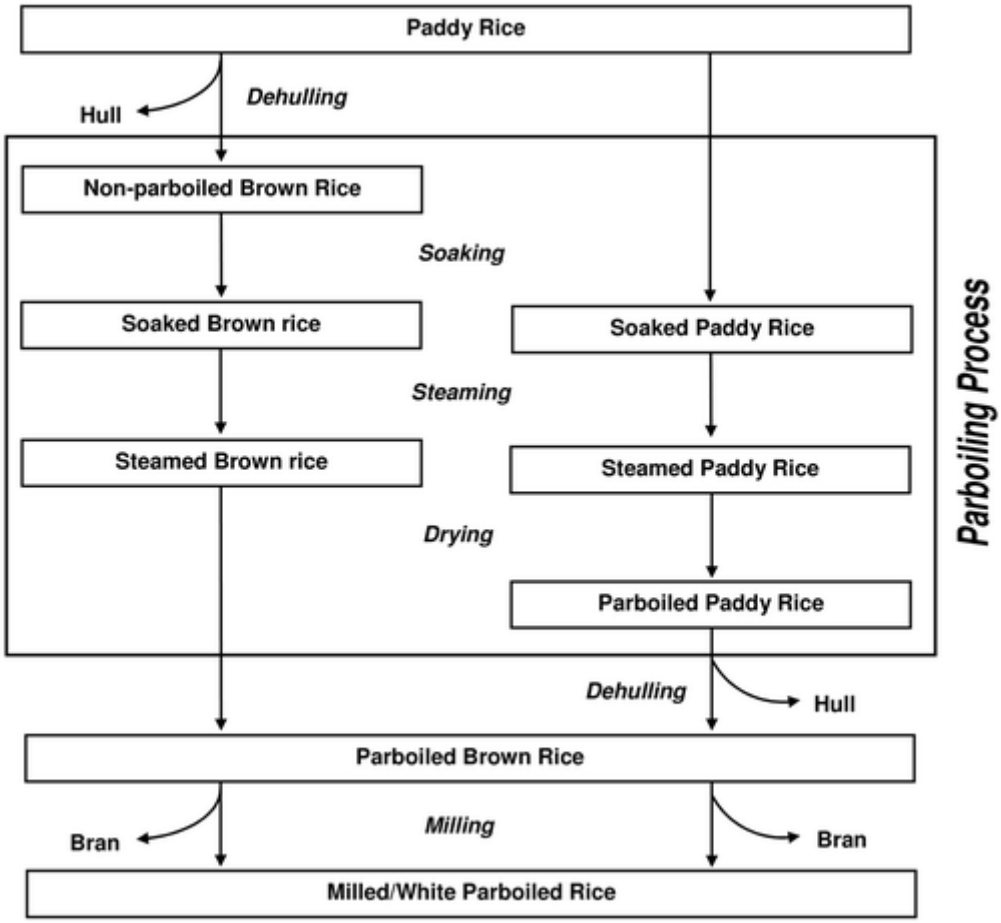


Fig. 10.6. Steps in the conversion of paddy rice to white parboiled rice. (Courtesy V. Derycke and L. Lamberts)

In conventional parboiling, paddy rice is mostly soaked in water at 50–70°C water for 2–4 h to yield rough rice having an average moisture content of 30–35%. This enables complete and uniform gelatinization of the starch during the following heating step. When brown rice is soaked, the soaking time is shorter. In an alternative parboiling method, called "pressure parboiling," the rice is not fully soaked but only wetted. In the subsequent heating step, high-pressure steaming is needed to obtain gelatinization of the starch. In the most drastic version of pressure parboiling, the soaking step is omitted and the dry rice is steamed at very high pressure.

The objective of the heating step is to completely gelatinize the starch. Most frequently, steam under pressure is used for 8–20 min. Microwave energy can also be applied. The time and temperature regimes for the treatments are variable and, to a large extent, determine the quality of the parboiled rice. After the parboiling process, the rice has a moisture content of about 35%. For safe storage, it must be reduced to below 14% moisture under conditions avoiding steep moisture and temperature gradients to prevent breakage of the kernels.

In the specific case of parboiling paddy rice, the hull is removed after the drying step. Because the process splits the hull, its removal is easy. The conversion from brown to white parboiled rice is made by abrasive milling.

The exact process conditions for the steps leading to the final product determine the final quality of the product and its cooking time. For instance, conditions that lead to surface cracks and fissures are likely to lead to shorter cooking times than those designed to minimize such physical damage to the kernel structure.

The major advantages of the rice parboiling process over the classical milling process are a higher yield of head rice from milling because the kernel is more resistant to breakage, more resistance to insects, better nutritional value (particularly more vitamin B_1), and less tendency for the rice to become sticky or mushy during cooking. This, of course, explains why the process is not popular in Asia, where consumers want sticky rice. The major disadvantages are a darker color, a slightly different flavor, and increased susceptibility to rancidity.

Most oats are used for feed for horses, poultry, or other animals. Only limited levels of the crop are processed for human consumption. Oats are classified by color. They prefer a cool, moist climate, so, in the United States, most oats and all milling oats are grown in the north central part of the country. In Europe also, most oats are grown in the more northern countries.

In this section, the processing of harvested oats to groats is described, as is their further conversion to either rolled or quick-cooking oats. For better understanding, the reader is encouraged to review the description of oats and groats in Chapter 1.

CLEANING

When milling oats are received at the mill, the first step is a thorough cleaning. Besides removing the usual foreign material (i.e., seeds, sticks, and dirt, etc.), one also must remove oats that are unsuitable for milling. These include double oats (Fig. 10.7), those in which the hull also covers a secondary grain. In double oats, the groats of both the primary and secondary grains are usually poorly developed, resulting in a high percentage of hull. Also removed are pin oats and light oats. Pin oats are usually very thin with little or no groat. Light oats have a normal size but little or no groat. All these types are removed and sold as feed material.

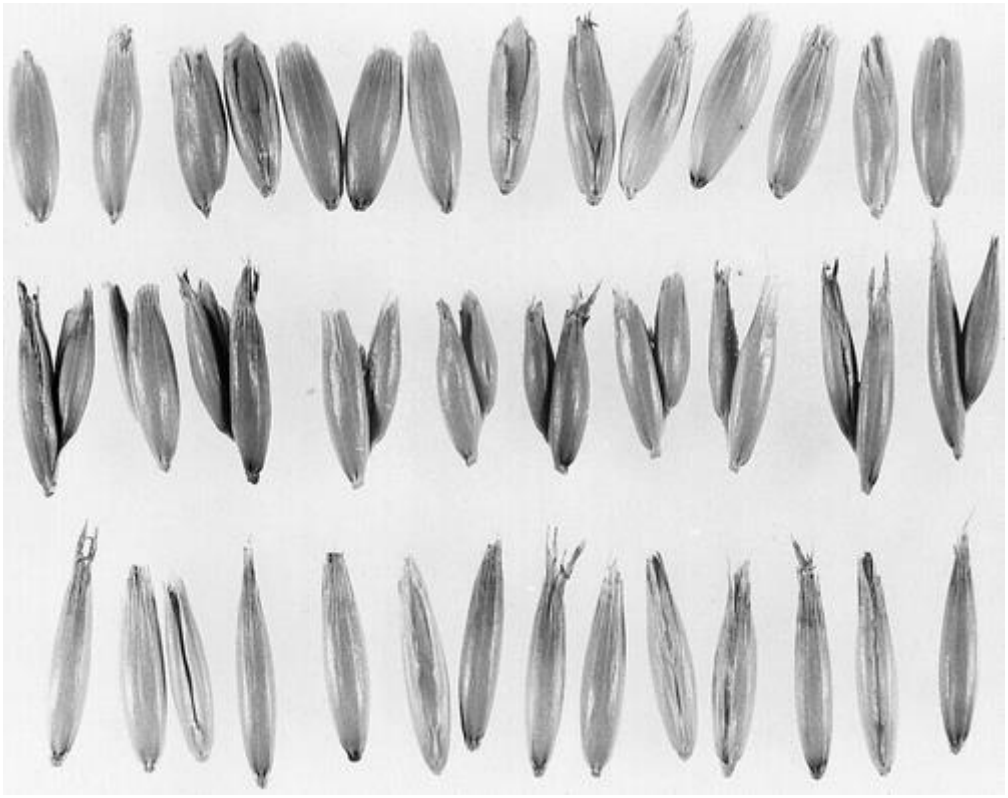


Fig. 10.7. Oats: regular (top), double (middle), and pin (bottom).

HEAT TREATMENT

After cleaning, the oats are heat-treated or dried. The heat treatment generally consists of heating the oats for about 1 h in large, open pans heated with steam. The oats reach a temperature of about 93°C and lose 3–4% moisture. The treatment has several beneficial effects. The oats take on a slightly roasted flavor that is considered desirable; drying makes the hulls more friable and thus easier to remove; and the heat inactivates lipolytic enzymes in the kernel. The denaturation of these enzymes is critical for producing products with good shelf life.

GRADING AND DEHULLING

Once heat-treated, oats are graded for size and dehulled. This is done by disk separators that divide them into large and stub, or short, oats. Both grades are dehulled, but not together. The most common dehuller in use now is the impact dehuller (Fig. 10.8). Oats enter the center of a high-speed rotor, which throws the oats against a rubber liner fixed to the outside casing of the machine. The rubber liner reduces breakage and assists in separation of the hull from the groat. The hulls that are freed by the huller are light enough to be removed by aspiration. Care must be taken not to remove small chips of groats with the hulls, as this lowers the yield. The groats are then removed from the unhulled oats by sieves or disk separators. Paddy separators (see above, in rice processing) can also be used to separate oats destined for another pass through the dehulling machine. Paddy machines are quite effective in making the separation but have very limited capacity.

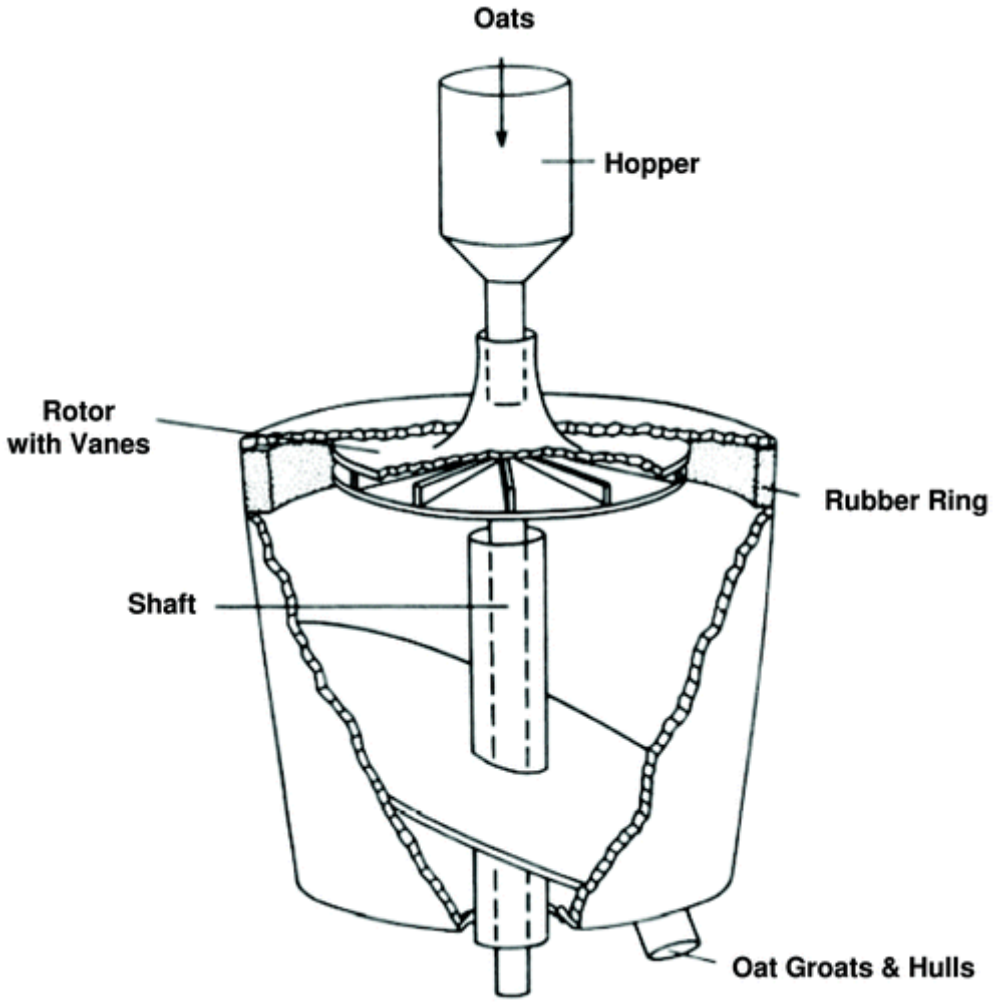


Fig. 10.8. Cut-away view of an oat dehuller. (Reprinted, with permission, from Youngs et al 1982)

FURTHER PROCESSING OF OAT GROATS

To convert the groats to consumer products, they are steamed and flaked. This section discusses the production of rolled oats as well as their quick- and instant-cooking counterparts.

Production of Rolled Oats

For the production of rolled oats, groats free of hulls must be used. The groats are steamed and rolled immediately afterward. Steaming (the use of live steam at atmospheric pressure) just before flaking by rolling makes the groats more flexible so that fewer of them are broken during the flaking operation. Steaming also helps to denature enzymes that cause rancidity.

Production of Quick- and Instant-Cooking Oats

To produce quick-cooking oats (typically needing 1 min of cooking time), the groats are cut into three to four uniform pieces and then steamed and flaked by rolling. For cutting, the groats position themselves endwise in the perforations of a rotating perforated drum and are cut by stationary knives at the outside surface of the drum. The cut groats are steamed and flaked in a process similar to that used with the whole groats. However, the rolled flakes produced from the cut groats are much thinner. It follows that, during cooking, water must diffuse a much shorter distance and, hence, that the thin flakes are quick-cooking.

Instant-cooking flakes are even thinner. The thinner the flake, the faster it cooks, but it also tends to lose its identity much faster. This makes the quick or instant product become mushy much more quickly.

After flaking, the flakes are cooled with air. The airstream helps to remove any hull slivers that have escaped the previous efforts of removal and have become loose during the cutting and flaking operations. The flakes are then packaged in material that allows exchange of the volatiles in the package with outside air. As a result, rancid odors produced during storage are removed. As a matter of fact, even though enzymes causing lipid oxidation are denatured during oat processing, a small amount of rancid odor is produced. However, a reasonable shelf life can be obtained if the product is allowed to breathe.

The products of oat milling are the rolled flakes (of various thicknesses); hulls (about 25% of the oats), which are used as a high-fiber feed ingredient or for furfural production; and oat flour, produced as a co-product of the cutting and flaking operations. This last is used in baby foods and breakfast cereals.

CHAPTER 11: Malting and Brewing

Simply stated, malting is controlled germination followed by controlled drying of a cereal seed. The goal is to produce high enzyme activity, endosperm modification, and a characteristic flavor with a minimum loss of dry weight.

Worldwide, huge quantities of malted cereals are used as raw materials for the production of beer. This, along with the fact that significant tonnages of malt are also used in the production of distilled products, in the breadmaking industry (i.e., as an enzyme or flavor source), and in the breakfast food industry (mainly as a flavoring agent), justifies covering the principles of malting and brewing in this book.

The cereal most often malted is barley, although sizable quantities of wheat and rye are also converted to their respective malts. In parts of Africa, sorghum and millet, particularly finger millet, are malted. In theory at least, any cereal could be used. However, the type and amount of enzymes produced vary from one cereal to another.

The predominant use of barley today is based on a number of factors. To start with, it has traditionally been the cereal of choice. In addition, barley malt contains a good balance of the desired enzymes and has tightly adhering hulls that protect the modified grain after malting and provide a natural filter bed later in the brewing process. Because, during malting, the seedling grows under the husk, it is not removed during deculming (i.e., removal of the rootlets) of barley malt. In contrast, in the case of wheat malt, the seedling is completely removed during deculming.

Many definitions exist for the term *brewing*. Generically, the entire beer making process is referred to as *brewing*. Technically speaking, the term covers only the part of the process during which the beer raw materials are first converted to sweet wort, i.e., the liquid that has been extracted from mashing malt and/or adjuncts, and then to hopped wort, i.e., the sweet wort that has been boiled with hops. It contains fermentable carbohydrates. After brewing, the resulting product, i.e., the pitching wort, is fermented into "green" beer. The final beer is the result of maturation and filtration of the green beer.

The following section covers the main aspects of malting. It is limited to the malting of barley, although some aspects relevant to malting of wheat are also mentioned.

GRAIN QUALITY

Grain quality is important for producing good malt. Grain selected for malting must be sound and plump, have a high capacity for germination, and be free of trash and broken kernels and relatively free of molds or diseases that attack grain. Problems, especially with barleys harvested at moisture levels exceeding 14%, can be avoided by drying them soon after harvesting to 12–13% moisture, which corresponds to a water activity of less than 0.65.

Dormancy and after-ripening are two major problems associated with malting barley.

True dormancy, i.e., the physiological condition of sound seeds that prohibits them from germinating even under suitable conditions, precludes malting. Dormancy is found in all seeds to some degree. If seeds were not dormant at the time of ripening, they would sprout while still in the head. Cereal grains, in general, have relatively low levels of dormancy. In most cases, within a few weeks after harvest, their dormancy has disappeared, and one refers to this as dormancy being "broken." In fact, many times, the major problem with cereals is a lack of dormancy, which allows the grain to sprout in the field. This gives high enzyme activities and lower-grade products. The problem is particularly severe in northern Europe, where the weather is often wet and humid during harvest. In North America, only in rare years is sprouting not a problem in some areas.

After-ripening (see also Ch. 10) is a collective term used to describe the biochemical changes that occur in a seed after it is mature, has naturally dried, and has been harvested. Indeed, a healthy seed, even though it contains only 12% moisture, is alive and continues to undergo biochemical changes after harvest.

Not all the biochemical changes that occur after harvest are understood, but their consequences are well known. Barley that is malted soon after harvest produces poor-quality wort (characterized by a lower soluble extract) and a hazy appearance. The malt from barley that has been aged for three months after harvest does not give these problems. Consequently, in practice, new-crop barley is not malted until it has been stored about three months.

After-ripening is not restricted to barley but appears to be a general phenomenon of all cereals, albeit expressed in a variety of ways. For example, as rice ages, it swells more during cooking, produces less soluble material, and is not as sticky as freshly harvested rice. Thus, in India, a significant price differential is often found between old and new rice. The phenomenon is also seen in wheat, both hard and soft types, with "new" wheat giving flour that does not perform satisfactorily. It is well known that every year, as processing of new-crop grain is started, large problems occur in terms of quality of the obtained products. After two to three months of problems, the crop can be processed satisfactorily.

GRAIN CLEANING AND MALTING

The malting process starts with a rather rigorous cleaning of the barley to remove all foreign seeds, broken kernels, and other contaminants. In addition to cleaning, the barley is graded into three classes: thin, plump, and very plump. The thin barley is sold as feed, and both the plump and very plump kernels are malted, in some parts of the world separately.

STEEPING

The primary purpose of steeping, i.e., soaking the grain in water, is to introduce water into the grain. Steeping is generally complete when the moisture content of the grain is raised to 42–44%. This moisture level is an equilibrium value. It is the point at which the hydrostatic pressure in the cell equals the osmotic pressure generated by the cell sap.

It is important for the moisture to penetrate to the center of the kernel. Because diffusion is the mechanism by which this occurs, steeping is a slow process. The time required depends on the distance the water must diffuse, and, therefore, more time is required for a very plump kernel than for a less plump kernel. This, of course, is why the grain is graded for plumpness before steeping. The other major factor affecting steeping time is the steeping temperature. Higher temperatures lead to shorter steeping times because water diffusion is faster. However, the higher temperature also promotes the growth of microorganisms. Steeping is generally done at relatively cool temperatures, i.e., about 15°C.

If the steeping time is too short, the barley is understeeped. This means that insufficient water has been absorbed, resulting in the center of the kernel being underhydrated. Generally, the resulting malt is of low quality unless further moisture adjustment is done directly after transfer to the germination box.

In spite of what the term seems to suggest, oversteeping is not the uptake of too much water. As outlined above, after reaching equilibrium, no additional water can be absorbed. However, extended steeping times delay the onset of germination and lead to increased growth of molds and bacteria, with the consequent production of undesirable odors.

Several steps are taken to protect against the effects of oversteeping. In general, they are designed to keep microorganisms under control and stop the production of undesirable odors, and, in many instances, they rely on providing an adequate supply of air. If air were not provided, barley respiration would use the available oxygen and create an anaerobic condition, which would favor anaerobic respiration of molds. Aeration also removes carbon dioxide from the water, which otherwise would lower the pH and hence encourage the growth of bacteria.

The steeping grain can be aerated either continuously or intermittently. The grain may be agitated or turned. Turning discourages the buildup of bacteria between kernels that are touching. Finally, the steep water may be frequently or continuously changed.

During steeping, soluble components from the hull are leached out and are lost to the steep water.

GERMINATION

After steeping is completed, the water is drained off, and the grain is placed in beds typically 2 m high to germinate. Physiologically, germination is the process by which a new plant starts to form, with the formation of rootlets and an acrospire (Fig. 11.1). In addition, during germination, as the new plant starts to develop, a large number of enzymes are synthesized (e.g., α-amylase) or activated (e.g., β-amylase). Germination usually takes four to six days. During that time, moist air is forced continuously through the germinating bed of grain to maintain the relative humidity close to 100%. The temperature is held at about 15°C, and the grain bed is usually sprinkled two to three times with about 0.2 kg of water per kilogram of barley during the germination period.

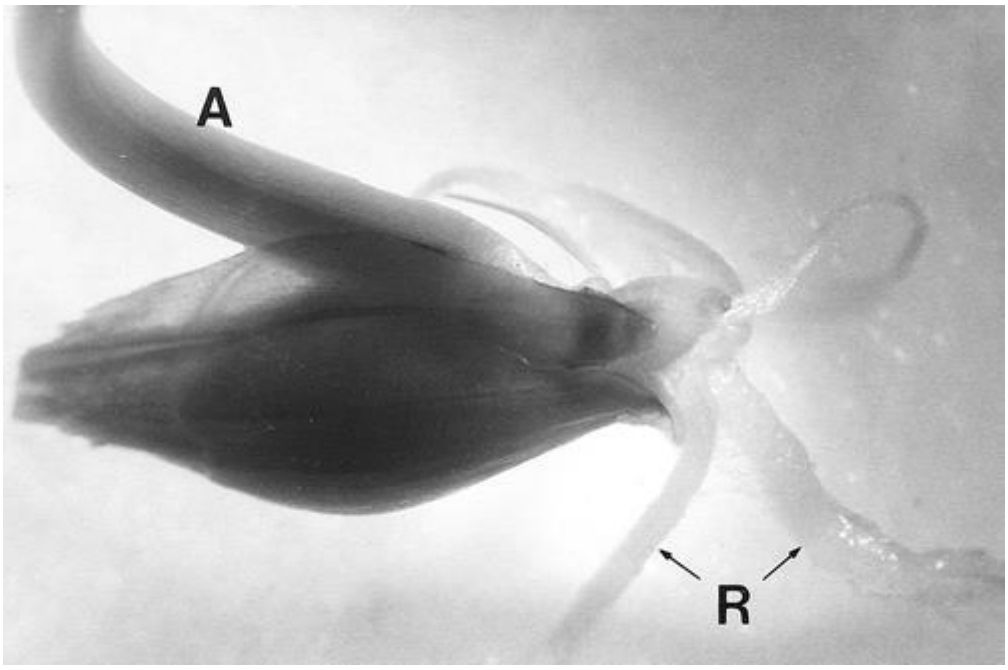


Fig. 11.1. A germinated barley kernel, showing the rootlets (R) and acrospire (A). (Courtesy K. Zeleznak)

The growth of the new plant is controlled by the moisture of the grain, its temperature, and the amount of air forced through the grain bed. The goal is the minimum amount of growth that will obtain a maximum endosperm modification, i.e., the change in its friability, and hence a maximum yield of malt of high enzyme activity. This requires control of the temperature. Germinating at temperatures exceeding 15°C would give a higher rate of growth of the new plant, but the yield of malt would be lower. As a rule of thumb, the germinating process for malting is considered to be complete when the acrospire, which grows below the husk,

is about one-third to three-fourths the length of the kernel. The resulting product is referred to as "green malt." The adjective *green* does not imply that the product has a green color. The adjective is used in the way it is used in "green wood" and thus rather indicates that the malt is undried.

KILNING

After the grain has germinated, the green malt has about 45% moisture. It is then dried to halt growth, give a storage-stable product, and develop the characteristic malt flavor and color. The drying and flavor/color development process is called "kilning." A main challenge in kilning is to dry the green malt in such a way as to remove the moisture and produce a desirable flavor without losing too much of the enzyme activity needed in the brewing process.

At high moisture contents, many enzymes are sensitive to heat. Figure 11.2 shows stylized curves of protein solubility as a function of temperature for various moisture contents. Because enzyme activity in general is affected in the same way as protein solubility, to protect enzymes, the first phases of kilning warm the green malt carefully and at low temperatures. Once the malt has a relatively low moisture, the temperature can be increased to bring about the Maillard browning reactions that give the malt its characteristic flavor and color. These are heat-induced reactions between reducing sugars and the free amino groups of amino acids, peptides, or proteins. By varying the level and severity of drying and browning, a range of malt colors and flavors can be produced. More than 80% of the world's malt production is lager malt. Its color is much lighter than that of specialty malts with dark color. While the former are used for Pilsner-style beers, the latter are used to produce dark beers. Other malts are dried at low temperatures to produce malts that are stable and have high enzymatic activities. In general, there is a trade-off between enzyme activity and flavor and color. Malts of high enzyme activity are produced at the expense of flavor. Conversely, malts with high flavor and dark color are kilned so severely that a great deal of enzyme activity is lost.

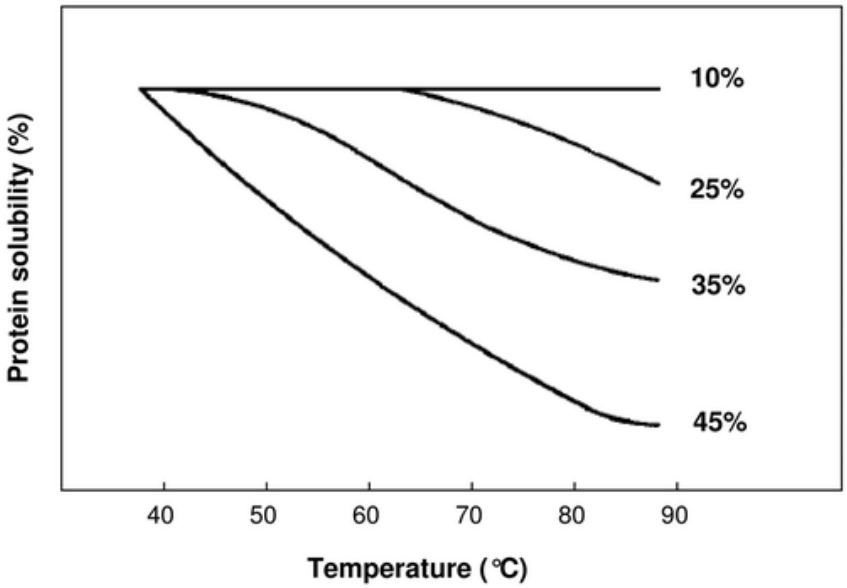


Fig. 11.2. Conceptual curves showing protein solubility as a function of heating during a given time at different temperatures and for the indicated moisture contents. The curves clearly show that, under otherwise standardized conditions, higher moisture contents and temperatures induce more loss of protein solubility.

During malting, typically a 10% loss of dry weight occurs. The loss is caused by the growth of rootlets, which are removed during the malt cleaning. In addition, a part of the endosperm is consumed to provide the energy to drive the germination process.

Some malt is bleached by being treated with sulfur dioxide at the initial drying stage. In addition to its effect on color, the sulfur dioxide increases the soluble protein content and the activity of proteolytic enzymes. It also blocks nitrosamine formation and reduces the microbial load in the malt.

The fermentation of cereal grains to produce beer is as old as recorded history. The ingredients required in the production of beer are malt, water, yeast, and hops. Malt serves as both a source of enzymes and a source of fermentable carbohydrate and contributes to flavor and color. Traditionally, malt was the only source of carbohydrates, and, until 1987, this continued to be so in Germany, in line with that country's *Reinheitsgebot,* which stipulated that beer could be made only from barley malt, hops, yeast, and water. However, in most of the world today, other sources of carbohydrates are used in addition to the malt. These are known as "adjuncts."

In the following section, the various ingredients commonly used to make beer as well as the basics of beer production are described.

RAW MATERIALS

Malt

As mentioned above, malt is a source of both enzymes and fermentable carbohydrates. In addition, it makes a major contribution to the flavor and color of the final beer. For yeast to produce carbon dioxide and ethanol from cereals, the starch must first be converted to simple sugars (glucose, maltose, and maltotriose) by the malt amylases, which are collectively referred to as the "malt diastatic system." Actually, the mixture of α- and β-amylases converts starch to mainly maltose. Other hydrolysis products include maltotriose, oligosaccharides of a higher degree of polymerization, and/or limit dextrins (see Chapter 2). While glucose and maltose are readily utilized by yeast, maltotriose is utilized very slowly. The larger oligosaccharides are not utilized and thus end up in the beer, where they contribute to mouthfeel.

Most of the beer in the world is produced with barley malt. The most predominant exceptions appear to be the sorghum beer produced in Africa and the white beers such as those produced in Germany, where wheat malt is the primary source of enzymes.

Adjuncts

Adjuncts are nonmalt sources of fermentable carbohydrates. The trend toward paler and more mildly flavored beers in North America and other parts of the world has led to their increased use. In addition, a strong economic force also favors the use of adjuncts, as the costs associated with the malting process and the nearly 10% loss of dry material are steep.

Virtually any starch source can be included as adjunct as long as it does not adversely affect the flavor of the final beer. Currently used adjuncts include rice or maize grits, unmalted barley, wheat starch, syrups produced from maize or wheat starch, and sorghum grits. Unmalted cereals usually result in paler and more mildly flavored beer.

Rice adjunct consists of kernels broken during milling (see Chapter 10) and then reduced to uniformly sized grits before being used in the brewing process. Maize and sorghum are also milled to grits before use as adjuncts. Any off-flavor from the grits causes serious quality deffects in the final beer. Grits for brewing must therefore be made from sound grain that is free of mold and foreign seeds. In addition, a very important quality specification for grits, other than particle size, is a low level of fat, generally specified at less than 1%. The grits must not be rancid, as such flavor notes would carry over to the beer and adversely affect its quality.

Except when the adjunct is syrup produced from maize or wheat starch, the enzymes for conversion of the adjunct are delivered by the malt. These enzymes convert the malt and adjunct starch to fermentable materials.

Hops

Brewer's hops are the dried fruit (i.e., the cones) of the perennial plant *Humulus lupulus*. Hops have separate male and female plants, and only the female plant produces the cones. The main European hop-producing countries are Germany (about one-third of the world's hop-growing area), the Czech Republic, Poland, Slovenia, and Slovakia. In the United States, hops are grown in the Pacific Northwest. Following harvest, the cones are dried at relatively low temperatures (less than 50°C) to about 12% moisture. If they are not dried properly, most of the essential oil (including myrcene; see below) is oxidized and polymerized. The cones can be used as such, as hop powder or pellets, or as extracts. All must be prepared properly to have a positive effect on beer properties.

Three hop components have an impact on the properties of beer. These are the essential oils, the bitter resins, and the polyphenols.

The hop oil is responsible for both aroma and flavor. Its composition is complex, with 70–80% consisting of terpene-like hydrocarbons. Myrcene, the largest component, generally accounts for 40–70% of the total oil content. However, most of the flavor is thought to come from the oxygenated compounds, a mixture of aldehydes, ketones, alcohols, and carboxylic acids.

The characteristic bitterness of the hops comes from the resinous materials. Three α-acids, i.e., humulone, adhumulone, and cohumulone (Fig. 11.3), are peculiar to the hop plant. Following isomerization to iso-α-acids during the brewing process, they contribute to the bitter taste. Hops also contain lupulones referred to as β-acids. They are known for their bacteriostatic activity and have limited solubility in wort. During storage, the resins can become oxidized and polymerized, and the hops lose their bitterness potential.

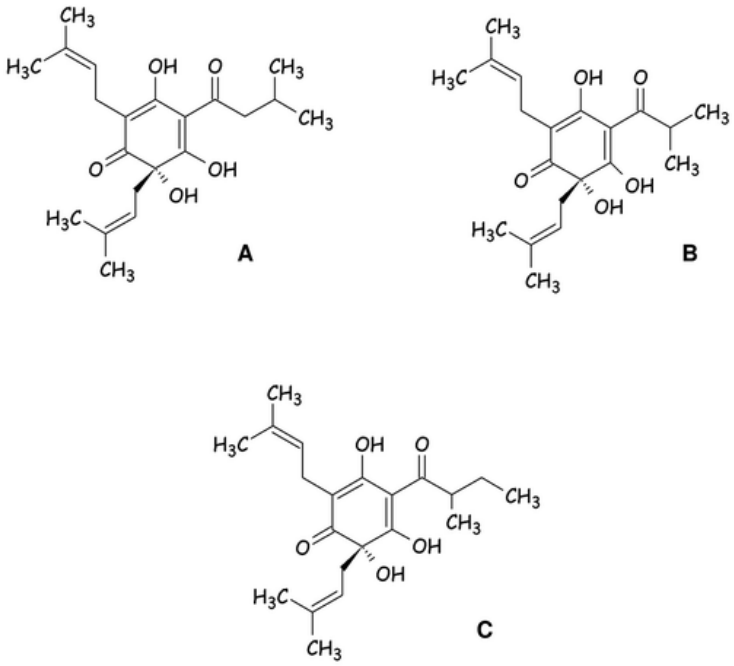


Fig. 11.3. Structures of humulone (A), adhumulone (B), and cohumulone (C). (Courtesy M. Verswyvel)

Hops also contain polyphenols of the flavanol type, including proanthocyanidins. These are polymers of condensed flavan building blocks. Those with a molecular weight in a range of 500–3,500 bind to protein and make it insoluble. These and similar polymers, when applied to raw hides, tan it to leather and give the compounds their name, i.e., condensed tannins. The hop and barley malt proanthocyanidins, when present in beer at sufficient levels, can interact with beer proteins and make the beer hazy.

Water

The properties and quality of the water used are of the utmost importance in brewing. Any odor or flavor in the water is usually carried over into the beer. In addition, the mineral levels and their identities are important, as is the pH.

The salts in the water have a pronounced effect on the flavor and character of the beer. In general, a light-flavored beer requires soft water, i.e., low in salts, whereas a dark, heavy beer requires hard water, i.e., high in salts. Water that is too soft produces a very flat-tasting beer. In industrial practice, brewing water can be treated to remove or add salts if it is too hard or too soft, respectively. The addition of gypsum, i.e., calcium sulfate, increases the hardness of brewing water and also lowers the pH. Sulfuric acid can also be used to adjust the brewing water pH. Another important factor is the water's content of iron ions. Iron ions can cause off-flavors and discolorations, even if their level is lower than 1 ppm.

Yeast

Yeast (*Saccharomyces*) strains for brewing are developed, maintained, and utilized based on their ability to affect beer characteristics. A first important yeast characteristic is the vigor with which the strain attacks the fermentable carbohydrate and produces ethanol, carbon dioxide, and the minor constituents that affect flavor.

A second important property of yeast is its tendency of its cells to aggregate or stick together, i.e., its flocculence. Individual yeast cells are small enough to stay suspended for long periods of time, particularly in high-gravity solutions such as wort. The rate at which they form aggregates determines how fast they settle from solution. If the cells aggregate and settle to the bottom, the yeast is called "bottom yeast." Bottom yeasts are used for lager beers. They generally are strains of *S. pastorianus* (formerly referred to as *S. carlsbergensis*). "Top yeasts" are yeasts that clump together and trap gas, becoming buoyant enough that they are carried to the top. Top yeasts are used for ales and are generally strains of *S. cerevisiae*.

Yeast that has a high or rapid flocculating tendency separates from the fermentable carbohydrates early and produces beer with a low attenuation, i.e., a low degree of conversion of sugar to alcohol. Such yeast results in rather sweet beers that are full-bodied. In contrast, powder-yeasts, i.e., yeasts that do not flocculate well, produce dry (i.e., nonsweet) beers with high attenuation and a watery mouthfeel. Powder yeast is difficult to remove from beer and, if retained in the beer, gives a yeasty taste.

MILLING AND MASHING

Milling

Before the actual brewing process, the malt's particle size is reduced. When it is received at the brewery, the dried malt still consists of intact kernels, but with the rootlets removed (see above). Either wet or dry milling can be used. In general, the goal is to reduce the endosperm to a fine particle size and still maintain the husk and bran in relatively large pieces when lauter tuns (see below) are used for mash separation. The most common reduction system is a short-flow roller mill. In malt milling, the whole grind obtained is used in brewing. If thin-bed filters (see below) are used for mash separation, the malt is finely ground, generally by hammer mills.

Mashing

Various mashing systems exist for the production of sweet wort, i.e., the liquid that is extracted from mashing malt and/or adjuncts and that contains fermentable carbohydrates. We here briefly mention infusion and decoction mashing.

Infusion Mashing. The double-mash infusion system is the most widely used system in North America. It allows the efficient use of adjuncts and results in the light, less-satiating beers that are popular in North America. The system relies on the preparation of two separate mashes, an adjunct-based mash and a malt-based mash. The adjunct-based mash is prepared in a cereal cooker, the malt-based mash in what is referred to as a "mash tun" or "mash kettle." Most adjuncts, i.e., those with a gelatinization temperature exceeding the optimal activity temperature of the malt β-amylase (i.e., 62°C), must first be boiled to gelatinize the starch before mashing, as the enzyme requires the starch to be gelatinized in order to be effective. Those that do not need gelatinization, such as pregelatinized cereal flakes and syrups derived from wheat or maize starch, are added directly to the mash kettle.

The adjunct-based mash is prepared in the adjunct cooker, where the starch is gelatinized; the resulting mixture is thinned; the adjunct protein is made insoluble; and the mixture is sterilized. In practice, the adjunct is placed in a cooker with water along with a small part of the malt. The pH of the mixture is adjusted to about 5.5, the optimum pH for the enzyme activity, and the temperature is held at 35°C for about 30 min for the acid rest (Fig. 11.4). The temperature is then raised to about 70°C and maintained for 20–30 min. At 70°C, the starch in the adjunct is gelatinized and therefore becomes much more susceptible to the amylolytic enzymes of the malt. The enzymes in the small amount of malt in the adjunct cooker thin the gelatinized starch paste, which, as a result, allows the mixture to be pumped at a high ratio of solids to water. After the thinning step, the temperature is raised to boiling for about 30 min. This not only denatures the adjunct protein and reduces its solubility but also sterilizes the system.

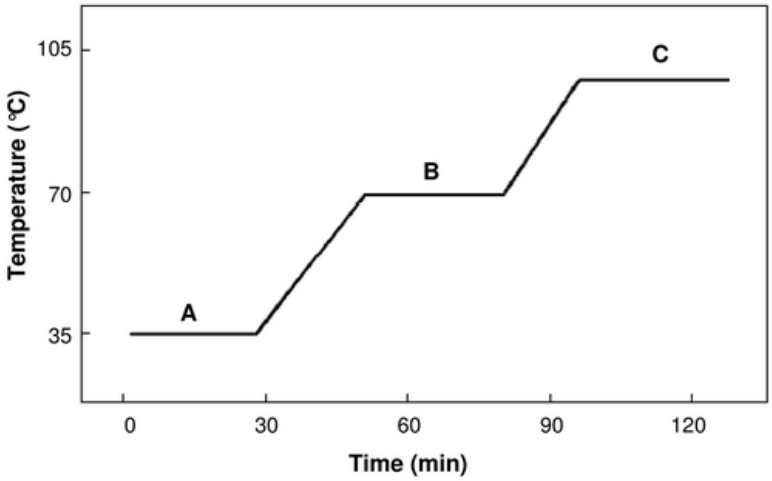


Fig. 11.4. Outline of a typical adjunct cooking process, showing acid rest allowing adjunct hydration (A), α-amylase thinning of the gelatinized starch (B), and sterilization and protein denaturation (C).

After cooling, the contents of the adjunct cooker are transferred to the mash tun that contains the remainder of the malt slurried in water. The objective of the mashing step is to convert the starch into low molecular weight fermentable carbohydrates. The pH of the mash is maintained at about 5.5 during mashing. Such pH allows an optimum conversion of starch to fermentable carbohydrates by the amylases and also helps to avoid turbidity caused by incomplete hydrolysis of protein. Generally, mashing involves a series of programmed temperature rises and holds. As with the adjunct cooking step, mashing starts with a 30-min rest at about 35°C (Fig. 11.5). This allows the malt to become hydrated. The temperature is then raised to about 45–50°C and held for 30 min. This stage is referred to as the "proteolytic rest" because it allows the proteolytic enzymes to act. In practice, about two-thirds of the malt protein remains insoluble, but the other one-third is made permanently soluble and plays an important role at subsequent stages of brewing. The temperature is then raised, typically to 62°C. This temperature increase causes the barley malt starch to gelatinize. In addition, a temperature rest at this temperature for 20–30 min allows β-amylase to be optimally active. Mashing is completed after another temperature rise and 20-min hold at 72°C, i.e., the optimum temperature for α-amylase to be active. With a well-modified malt, the mashing-in process can already be started at about 63°C. This shortens the total mashing process without impairing final product quality.

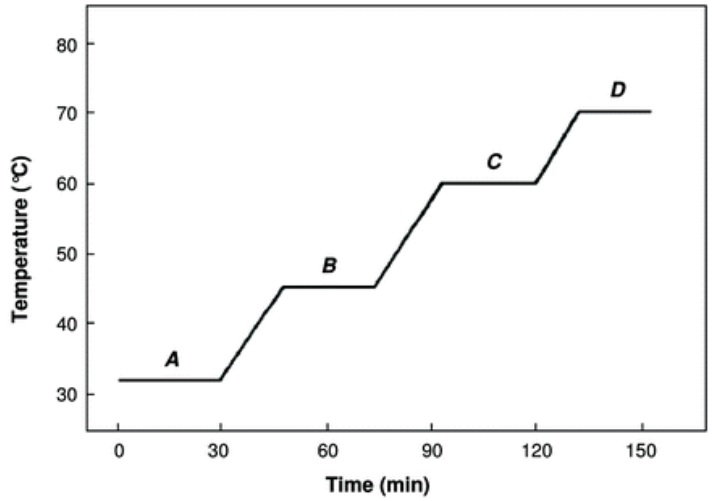


Fig. 11.5. Outline of the mashing process, showing acid rest allowing malt hydration (A) and stepwise increases of the temperature to those of the proteolytic rest (B), optimal β-amylase activity (C), and, finally, optimal α-amylase activity (D).

Decoction Mashing. Decoction mashing has been the traditional method used in the production of sweet wort for European Pilsner-type beers such as in the production of the German beers according to the *Reinheitsgebot*. In decoction mashing, a portion of the mash is withdrawn, boiled, and returned to the main mash to increase the temperature of the mass. Decoction mashing includes up to three decoction steps. In one-step decoction mashing, the temperature raise is designed to result in optimal conversion of starch to fermentable

carbohydrates. When three decoction steps are included, they are aimed to provide for acid, protein, and starch conversion rests. The acid rest allows the particles of malt to hydrate.

The Process. Irrespective of the mashing system used, after mashing is complete, the sweet wort is separated from the spent grain. This is usually accomplished in a lauter tun, which is essentially a large tank with a screen bottom. The mash is pumped into the tun and allowed to settle for about 30 min. The husk and bran particles settle onto the screen and form a filter mat. This is why the husk is left on the barley during malting and also one of the reasons barley is the preferred grain for malting. After settling, the sweet wort is pumped back into the tank, recycled through the filter mat until it is clear, and then pumped off.

The spent grain in the mat is then mixed with hot water and allowed to settle before the residual soluble material is pumped off and added to the sweet wort. This process is called "sparging." The remaining spent grain is recovered and used mainly as an animal feed. Because the starch has been removed, the brewer's spent grains are enriched in protein and crude fiber content.

The clear sweet wort can also be obtained using a thin-bed filter, which is essentially a plate and frame filter. In this case, the malt must be finely milled. Filtration of the first wort takes significantly less time than filtration with lauter tuns. Depending on the way the various chambers are filled with sparging water, sparging takes the same or significantly less time than when lauter tuns are used.

WORT BOILING AND COOLING

The sweet wort is boiled for typically 1.5–2.0 h in the presence of hops. Because wort has a pH of about 5.5, boiling at atmospheric pressure sterilizes it. Boiling also allows the hop bitter substances, i.e., the iso-α-acids, to be formed from their precursors (see above). In addition to killing the microorganisms, boiling coagulates part of the proteins and protein-tannin complexes, producing insoluble material for subsequent removal. This insoluble material is called the "hot break."

Generally, one-half of the hops is added near the start of wort boiling. Many of the flavor components from both the malt and the hops are volatile and thus are lost during the boiling stage. To retain the appropriate amount of hop flavor and aroma, the remaining half of the hops is added near the end of the boiling stage. During wort boiling, the wort becomes darker in color because of Maillard reactions (see above), but presumably also because of oxidation.

After boiling is complete, the hopped wort obtained is allowed to settle in a tank, which allows the hot break to be removed. After this unit operation (which in earlier days was done in open, shallow vessels and nowadays is done in semiclosed vessels), the wort is cooled to less than 12°C. Often, cooled and filtered sterile air is pumped through the wort, not only to aid in cooling but also to raise the oxygen content of the wort. As a result of cooling, more protein and protein-tannin complexes are precipitated. This is the "cold break," which must be removed. After being cooled, the wort is pumped to pitching tanks.

PITCHING AND FERMENTATION

Pitching is the process of adding yeast to the hopped wort, typically at a rate of about 200 g/hL (i.e., about 7.5 g per U.S. gal) of wort. Ideally, fermentation starts with a cell density of 10–20 million yeast cells per milliliter. The oxygen added during cooling helps to shorten the lag phase of yeast growth. Following pitching, the hopped wort is pumped to fermentation tanks, which are generally semiclosed tanks. Part of the carbon dioxide produced by the fermentation can be collected to be added back later in the process, or it can be sold as a by-product. When one disregards side reactions occurring during the fermentation process, starting from 1 mol or 180 g of glucose, one theoretically obtains 2 mol or 88 g of carbon dioxide and also 2 mol or 92 g of ethanol. At the same time, considerable heat is produced, as is shown by the general equation for the process:

$$C_6H_{12}O_6 \rightarrow 2\ CO_2 + 2\ CH_3CH_2OH + 66.5\ kJ/mol$$

Because of the heat produced, the fermentation tanks are equipped with cooling coils so that a constant temperature can be maintained. The yeast not only consumes fermentable carbohydrate but also amino acids that result from the hydrolysis of malt protein. It uses them not only for its own anabolism, but also for the production of flavor compounds. In addition, yeast is always contaminated with small levels of bacteria, which produce both lactic and acetic acid. The acids are responsible for most of the pH drop during fermentation, typically from a wort pH of about 5.5 to an end pH value of about 4.3–4.0.

The temperature used in bottom fermentations (see above) is typically 10°C, although temperatures up to 15°C can also be used. In top fermentations, the temperature is typically 15–20°C. The fermentation rate clearly depends on the pitching rate. It typically increases during the first phase of the fermentation (e.g., for 18 h),

holds steady (e.g., for 72 h), and then slowly declines. Fermentation is generally complete in seven to nine days. Its progress can be followed with a saccharometer, a simple device that measures the density of sugar-water mixtures. Fermentation is complete when the desired sugar content has been reached.

In the case of bottom-fermented beers, a head of foam forms during fermentation. This foam contains some of the remaining hop resins and nitrogenous materials and is carefully removed. When fermentation is complete, the beer is typically cooled to 4°C and carefully pumped off the yeasty sediment in the bottom of the fermentation tank. The yeast crop is four to five times the amount of yeast originally used. Thus, in brewery fermentations, both yeast growth and fermentation take place. The yeast is washed and either used for the next pitching or sold as a feed or food ingredient.

The changes that take place during fermentation can be summarized as follows. Glucose, maltose, and maltotriose are converted to alcohol and carbon dioxide. The pH drops from 5.5 to about 4.0–4.3. The nitrogen content falls by about one third, chiefly because of its utilization by yeast. The oxygen content decreases to about 0.3%. Part of the hop resins are lost as they adsorb onto the yeast cell walls. The beer becomes lighter in color, partly because of the pH change, and its final specific gravity is reduced because of the consumption of fermentable carbohydrate and the concomitant production of alcohol.

LIGHT AND NONALCOHOLIC BEERS

A number of approaches can be used to produce light or low-calorie beer. The simplest is to dilute beer by adding water. Most of the techniques used today, however, rely on removing the limit dextrins (see Chapter 2) left in the mash after the malt α- and β-amylases have degraded the starch (Fig. 11.6) or on the use of adjuncts that have much lower concentrations of limit dextrins. The limit dextrins are not fermented by yeast and thus remain in the beer to contribute calories, body, and mouthfeel to the final product. They consist of glucose moieties linked α-1,6 and four to eight other glucose residues linked α-1,4 near the 1,6 bond. Conversion of these dextrins to maltose or glucose allows the yeast to use them and, at the same time, reduces the beer calorie content. This can be accomplished by using glucoamylase (see Chapter 2) in the mashing step. As indicated above, an alternative approach is to use an adjunct that contains little if any α-1,6 bonds, such as a maize syrup with a high dextrose equivalent.

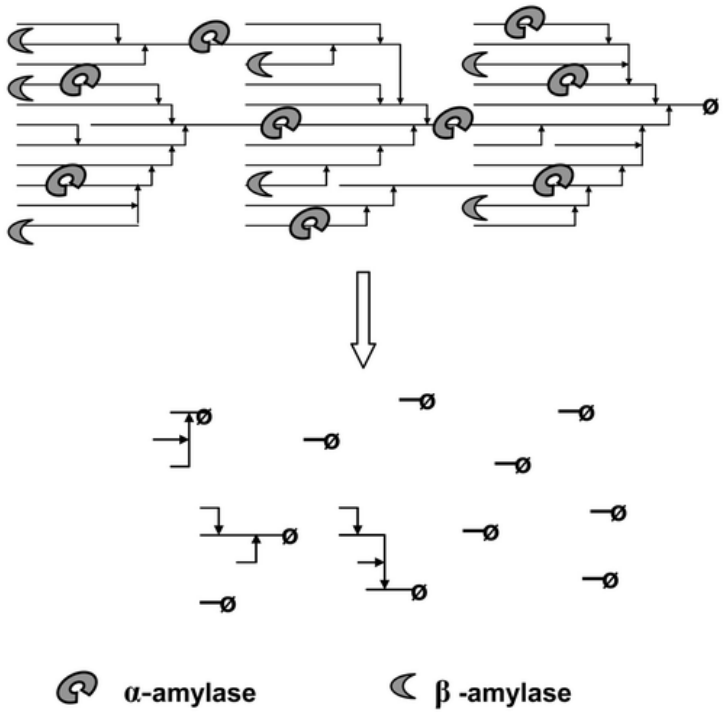


Fig. 11.6. Action of both α- and β-amylase on starch, showing mainly maltose formation and, in addition, some branched dextrins. The solid lines represent α-1,4-linked glucose units; arrows indicate α-1,6 linkages. Both amylopectin and α-limit dextrins have only one reducing end (ϕ). (Courtesy A. Bijttebier)

In most cases, nonalcoholic beers are produced by removing the alcohol from beer after it is brewed. The most popular method to remove the alcohol is reverse osmosis.

BEER FINISHING

In the first step, the chilled beer is filtered through diatomaceous earth. It is aged or lagered at low temperature (typically 0°C) under a counterpressure of typically 0.4 bar of carbon dioxide. The aging period varies. In former times, a lagering time of up to 12 weeks was common practice. During the lagering period, more settling occurs, and the taste changes to become more mellow. The mellowing results from the formation of esters from the alcohols and acids produced during fermentation. As a result, the beer aroma becomes more pleasant and the flavor less yeasty and sharp.

Beer can develop a haze that appears as it is cooled and disappears as it is warmed. The haze is referred to as "chill haze." In general, the appearance of such insoluble haze is considered to be a serious quality defect, as the average consumer wants the beer to be crystal clear in appearance. The problem has been traced to a reversible loss of solubility of protein-proanthocyanidin (see above) complexes. To avoid the problem, a number of "chill-proofing" measures can be taken that either reduce the concentration of proanthocyanidins in beer or affect the protein constituents qualitatively or quantitatively. These include the use of proanthocyanidin-free hop extracts, polyvinylpolypyrrolidone, proteolytic enzymes, bentonite, and tannic acid.

As their name implies, the use of proanthocyanidin-free hop extracts reduces the concentration of proanthocyanidins in beer and hence that of protein-proanthocyanidin complexes. Polyvinylypolypyrrolidone is an effective adsorbent for proanthocyanidins. When beer is filtered over this agent, barley and hop proanthocyanidins are removed from the solution, and this equally contributes to beer colloidal stability.

The use of proteolytic enzymes reduces the molecular weight of protein-proanthocyanidin complexes and increases their solubility. Both bentonite and tannic acid treatments remove proteins from beer and hence equally increase its colloidal stability.

Before bottling, the beer is given a final filtration through cellulose fibers. In some cases, it is then pasteurized before bottling or canning, generally with high-temperature, short-time treatments. The treatment alters the flavor slightly.

Bottling is generally in brown bottles to protect the beer from light that would alter its flavor. Both bottling and canning are done cold and against a counterpressure of carbon dioxide. This avoids the loss of carbon dioxide and also protects against contamination by organisms or oxygen.

Distilled Products

Ethanol for whiskey is obtained by fermenting grain mashes. Industrial alcohol for fuel or as a chemical feedstock can also be obtained from grain.

To produce whiskey, maize, rye, barley, or other grain is ground, mixed with water, and cooked severely under pressure to gelatinize the starch and sterilize the mash. After cooling, barley malt is added as an enzyme source to convert the starch to fermentable carbohydrates. After mashing, which is similar to the process used in brewing, processes vary widely depending upon the type of whiskey that is being made. In all instances, yeast is added to produce alcohol. In sour mash whiskey, a bacterial inoculum is added to contribute to the flavor of the product. Fermentation generally lasts about three days. After the fermentation is complete, the product is distilled. Distillation may involve several steps and is often preformed in copper kettles. Following distillation, most whiskey is aged in wooden barrels. Some of the barrels have their insides charred. This produces a milder and smoother flavor (charcoal removes aromatic compounds). The aging process is usually for a number of years, during which the whiskey matures and develops the desired flavor.

Since water and ethanol form an azeotrope of about 95% alcohol and 5% water, it is not possible to obtain higher levels of alcohol by distillation. The product containing 95% alcohol is called "grain neutral spirits." It has little flavor, as most of the flavor compounds remain in the water. A distillate consisting of 50% alcohol is called 100 proof. The terminology comes from the fact that this is the minimum level of alcohol in water that will burn. Historically, igniting the whisky was the "proof" that was often demanded to show that the whiskey was not cut too far.

In industrial practice, the still is usually cut (i.e., a fraction is taken off) at about 160 proof, or 80% alcohol. It is then diluted with water to 80–100 proof for aging and bottling. The flavor of the product is determined by the grains used, the inoculums, if any, the method and degree of distillation, the conditions and length of aging, and, if it is a blended whiskey, the skill and taste of the blender.

CHAPTER 12: Yeast-Leavened Products

Wheat is unique among the cereals in that its flour can form dough when mixed with water. In addition, wheat dough retains the gas produced during fermentation or by chemical leavening and thus gives a leavened product. These two characteristics of wheat flour dough are responsible for the popularity of wheat products.

The present chapter deals with dough-based yeast-leavened products. By its very nature, the discussion is restricted primarily to wheat flour systems. It is unusual to find yeast-leavened products made from other cereal flours anywhere in the world, except for those based on rye flour. Indeed, rye flour is also used to make yeast-leavened products in some parts of the world. However, in general, yeast-leavened products made solely from rye flour are rare. Rye tends to be used as a flavoring agent in wheat-flour-based recipes rather than as the most important dough ingredient.

The most popular yeast-leavened product by far is bread. The amount of bread consumed in the world is truly staggering, as is the wide array of sizes, shapes, textures, and tastes that bread comes in. Breads vary in size from small bread sticks to loaves weighing several pounds or kilos. Crust color and texture can vary from the thin, white crust of Chinese steam bread to the thick, black crust of pumpernickel. The reasons for the existence of such variety are complex and difficult to sort out. Many of them have to do with tradition, the other foods consumed, and the proportion of bread in the diet. Two factors of great importance in the industrialized world are convenience and economics. Supermarket bread is more convenient and generally less expensive than bread from retail bake shops. However, it may not reach the supermarket shelves within the first 24 h after baking and thus is not as fresh. In addition to meeting the consumer demand for convenience, in the industrialized world, the breadmaking industry needs to provide products that remain soft, and thus desirable, for many days after production. In some parts of the world, bread is consumed within a few hours and most certainly within the first day after it is produced. Much of such bread is truly inedible the day after baking. Another factor is the difference in quality of the bread wheats grown in North America, Australia, Argentina, Russia, Hungary, the Middle East, and the Punjab area of India on the one hand and the quality of, for instance, the typical European wheats on the other hand.

In what follows, different aspects of breadmaking processes, the raw materials used, and the roles of their specific components are discussed, as are some quality aspects of the products obtained. Although the focus is mainly on bread, other products are also considered.

Quality of Breadmaking Flour

When dealing with flour quality, one always must consider its end use. Flour suitable for breadmaking may not be good for, for instance, cookies (biscuits) and other products such as those described in Chapter 13. In this section, the discussion of flour quality is confined to its use in breadmaking and focuses on loaf volume as a primary quality parameter when flour is processed into bread.

Breadmaking flour is usually produced from hard wheat (North American terminology is used in this chapter; see Chapter 1) of relatively high protein content. However, in various parts of the world, breads are made from either soft or durum wheat. Therefore, kernel hardness is not an absolute requirement for breadmaking. The protein content requirement is more important. In practice, it appears to be impossible to make a good-quality loaf of bread from flour that contains a low level (e.g., 8%) of protein. Clearly, the level of protein in flour is important for its breadmaking functionality. However, the protein content itself does not always ensure good bread quality. Therefore, both a certain concentration and a certain quality of wheat flour protein are needed to produce a quality loaf.

The protein in flour can be quantified with good accuracy by several techniques. However, protein quality cannot be determined so easily. In fact, the most reliable test for evaluating breadmaking quality is still a breadmaking test. The choice of breadmaking test is, of course, critical. It must not be limiting in any factor, so that the true ability of the flour to retain gas and give a large volume is fully expressed. A number of such tests exist in the literature.

Figure 12.1 shows typical regression lines relating bread volumes determined by a breadmaking test for flour samples of different protein content from two different wheat cultivars. Line A represents samples from an excellent-breadmaking wheat cultivar, i.e., one that yields high loaf volumes. Line B represents samples from a poor-breadmaking wheat cultivar. The plot clearly shows the effect of both the level of protein and its quality. Such lines are essentially straight above about 8% protein, and they reveal an obvious correlation between protein content on the one hand and loaf volume on the other. Their slope, which reflects the increase in loaf volume per unit of protein, is a measure of flour quality. By processing wheat flours with a suitable breadmaking procedure and knowing their protein contents, one can obtain a rapid estimate of the protein quality of a cultivar. For flours from different cultivars that produce bread loaves of different volumes, one can indeed use this type of plot to determine which has the better protein quality. In the case of the

conceptualizedFigure 12.1, flour from cultivar A with 12.0% protein (in a standardized breadmaking test using 100 g of flour) results in a loaf volume of 1,040 cm^3, while flour from cultivar B with the same protein content under the same conditions results in a loaf volume of 800 cm^3. The plot clearly shows that flour from cultivar A has the larger slope and hence this cultivar is better suited for breadmaking applications than cultivar B.

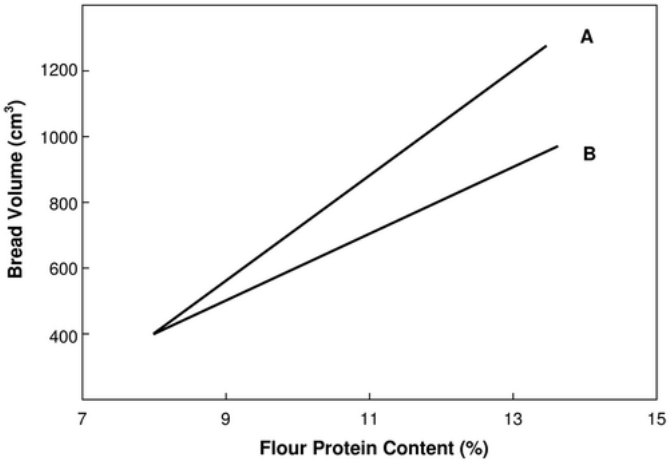


Fig. 12.1. Conceptualized graph showing the effects of flour protein concentration and quality on the volume of a bread loaf produced from 100 g of flour. Flour A is clearly of better quality than flour B. (Courtesy A. Bijttebier)

An interesting aspect of the plot is that the regression lines intersect at about 8% protein. It follows that protein quality is not an important factor when flour protein content is low and that the ratio of loaf volume to protein content is not a true measure of breadmaking quality because the linear relationship between protein content and loaf volume does not hold all the way to 0% protein. In fact, a bread loaf made from 100 g of flour with no protein would still have a loaf volume of about 400 cm^3. Because the regression lines all intersect at about 8% protein, it takes only a single sample of known bread volume and protein content to determine the slope of the line and thereby estimate the protein quality of the sample. Of course, the estimate is much better when based on breadmaking results of more samples of varying protein content.

As useful as the plot of loaf volume as a function of protein content is, it does not prove the dependence of loaf volume on protein content and quality. It is only a statistical relationship. Proof that the protein is responsible for differences in loaf volume came from studies that fractionated good- and poor-quality flours into gluten, starch, and water-extractables. The fractions were then reconstituted into either the original flours or flours in which the gluten from the good-breadmaking flour was reconstituted with the starch and water-extractables from the poor-breadmaking flour and vice versa. This showed unequivocally that the gluten protein fraction controls the mixing requirement of flour and the resulting volume of the loaf of bread.

Breadmaking Formulas and Systems

Bread's ingredients can be categorized as either essential or nonessential. Many different procedures can be used. The details of a particular procedure depend upon many factors, including tradition, the cost and type of energy available, the type and quality consistency of the flour available, the type of bread desired, and the time between breadmaking and consumption.

BREADMAKING FORMULAS

The minimum formula for bread consists of flour, yeast, salt, and water. If any one of these essential ingredients is missing, the product is not bread. Other ingredients, all of which are nonessential but often present in the formula, are sugar, various enzyme preparations (including malted grain and endoxylanase), surfactants, oxidants, fat, sugar, and additives to protect against molds.

Essential Ingredients

The flour, of course, is the major component. In combination with water, it is responsible for the structure of the bread. Together, they are responsible for forming viscoelastic dough that retains gas. Water serves as both plasticizer and solvent. Without water, dough cannot be formed, and fermentation does not take place.

Yeast is needed to convert fermentable carbohydrates into carbon dioxide and ethanol. The gas that results from this conversion provides the lift that produces a light, leavened loaf of bread. In addition, yeast has a very marked effect on the rheological properties of dough. The role and impact of yeast are discussed in more detail later in this chapter.

Salt is generally used at levels of about 1–2% based on flour weight. Its maximum level in many parts of the world is regulated by law. It contributes to taste and affects the dough's rheological properties. Salt makes dough stronger, presumably by shielding charges on the dough proteins.

Nonessential Ingredients

As outlined in Chapter 8, where allowed by law, flour can come from the mill containing some nonessential ingredients. In general, where permitted, nonessential ingredients can be added to flour at the mill, at the bakery, or both.

When sugar is added, this is generally done at the bakery. Sugar is fermentable by yeast and, at the right levels, provides a sweet taste to the bread. With the proper enzymes in the dough, sufficient maltose is produced from the damaged starch in the flour to maintain fermentation, and added sugar is not necessary for gas production. However, under many production conditions, added sugar is used for fermentation.

As described in Chapter 8, sound (unmalted) wheat flour contains only low levels of α-amylase, and it is common practice to add α-amylase to bread flour, mostly at the mill. In addition, some amylases, including α-amylase or maltogenic amylase (see Chapter 2 and below), can be added at the bakery to improve the shelf life of bread.

As also discussed in Chapter 8, endoxylanases (see Chapter 4) can be added as bread volume enhancers. In many instances, they are added at the bakery, irrespective of earlier addition at the mill.

Various emulsifiers, sometimes referred to as "surfactants," are added at the bakery and function as dough stabilizers when they interact with the gluten protein in the dough and as crumb softeners when they complex with the gelatinizing starch during baking (see below). Some emulsifiers also can change the size of the bubbles formed during mixing by changing the interfacial tension, γ, of the system, and thus they affect the grain, i.e., the appearance of the sliced surface of bread. Examples of dough stabilizers include sodium stearoyl lactylate, ethoxylated monoacylglycerols (also referred to as ethoxylated monoglyceride), and diacetyl tartaric acid esters of mono- and diacylglycerols (also referred to as diacetyl tartaric acid esters of mono- and diacylglycerides) (Fig. 12.2). They are used at about 0.5% of the flour weight. The mechanism or basis of their dough-strengthening effect is not completely understood. It has been suggested that the emulsifiers form liquid, lamellar films between the gluten and the starch, thus improving the film-forming properties of the gluten.

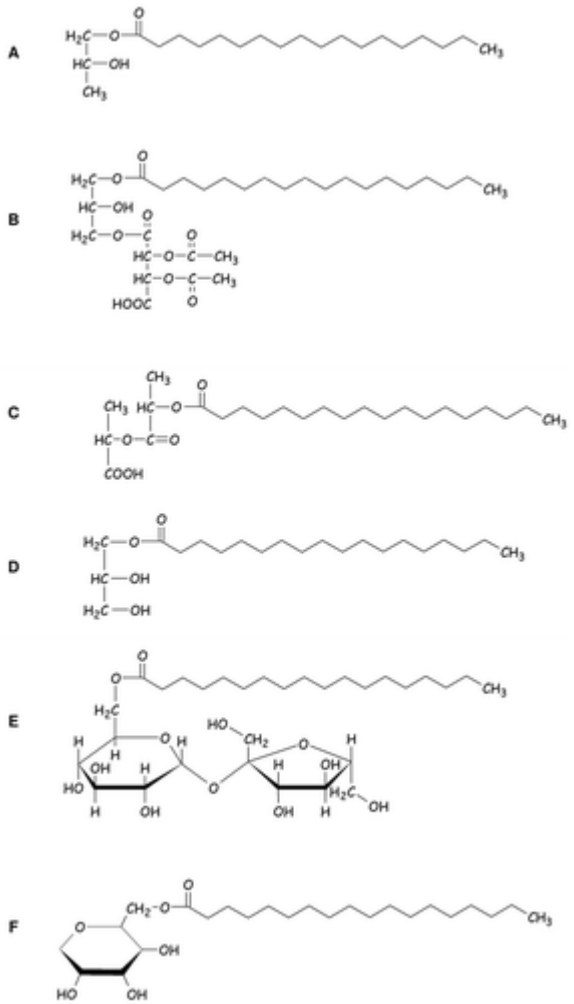


Fig. 12.2. Structures of emulsifiers commonly used in cake mixes (**A**, propylene glycol monostearate) or breadmaking (**B**, diacetyl tartaric acid ester of 1-glycerol monostearate; **C**, stearoyl lactylates; **D**, 1-glycerol monostearate; **E**, sucrose monostearate; and **F**, sorbitan monostearate). (Courtesy M. Verswyvel)

Components that act as oxidants (see below) in breadmaking include ascorbic acid, potassium bromate, azodicarbonamide, and calcium peroxide. They are added at the mill, at the bakery, or at both the mill and the bakery. Used at levels of parts per million, they improve dough strength and result in bread with better loaf volume and texture. Their action is discussed further later in this chapter.

Fat or shortening is added at the bakery. It plasticizes dough. Thus, an increase in the level of shortening in the dough requres a decrease in the level of water, and vice versa, to maintain an equal dough consistency. In addition, shortening increases bread volume, typically by 10%. Finally, the addition of fat in the formula makes bread stay soft and more palatable for a longer period of time (Fig. 12.3).

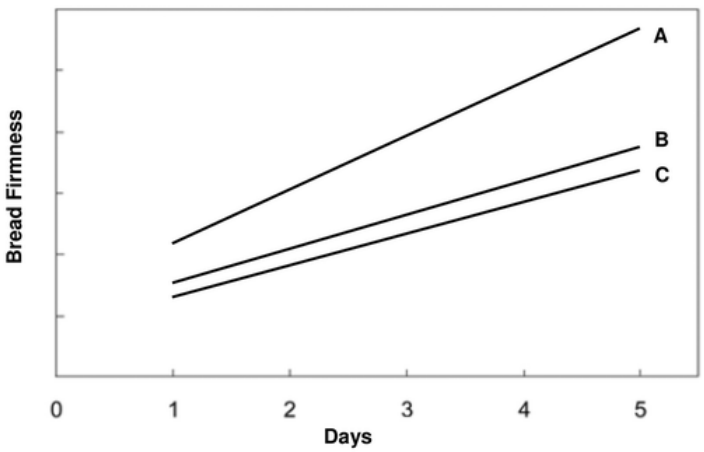


Fig. 12.3. Conceptualized graph comparing the firming rates of control bread (A), bread containing shortening (B), and bread containing both shortening and monoacylglycerols (C). (Courtesy A. Bijttebier)

To increase bread softness, and hence its shelf life, bread formulas usually contain surfactants. These may or may not be the same as those discussed above as dough strengtheners. Most common compounds for this usage at the bakery are monoacylglycerols (Fig. 12.3), also referred to monoglycerides. A common level of usage is 0.5% based on flour weight.

Finally, the most commonly used additive to control mold growth is calcium propionate.

BREADMAKING SYSTEMS

The processes involved in creating bread can be divided into three basic operations: mixing or dough formation, fermentation, and baking. Different procedures can be used. In this section, the straight-dough, sponge-and-dough, liquid-sponge, and short-time breadmaking systems are briefly described.

Straight-Dough System

The simplest breadmaking procedure is the straight-dough system (Fig. 12.4). Such a procedure is quite commonly used in many parts of Europe. In this system, all the formula ingredients are mixed into a developed dough that is then allowed to ferment. During its fermentation, the dough is usually punched at least once. After fermentation, it is divided into loaf-sized pieces, rounded, molded into the loaf shape, and, in many cases, placed into the baking pan. The dough is then given an additional fermentation, also referred to as a "proof," to increase its size. After it reaches the desired size, it is placed in the oven and baked. In the straight-dough system, the fermentation time may vary quite widely, from essentially no time to as long as 3 h.

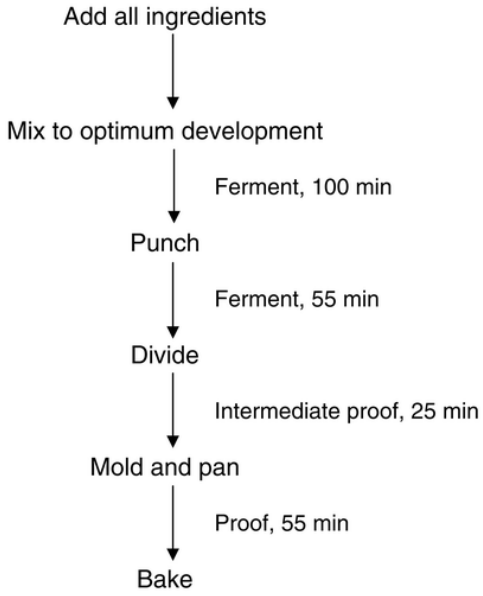


Fig. 12.4. Outline of a straight-dough process.

In general, straight-dough bread is chewier than is bread made by other procedures. It has a coarser cell structure, and it is generally considered to have less flavor. The quality of the product obtained is quite sensitive to the timing between individual process steps. With larger batches, which are common in commercial practice, this time sensitivity can be a problem. Thus, if the first part of the batch receives optimum fermentation, it follows that the last part is overfermented.

Sponge-and-Dough System

The most popular baking process in North America is the sponge-and-dough procedure (Fig. 12.5). In this procedure, about two-thirds of the flour, part of the water, and the yeast are mixed just enough to form a loose dough, which is referred to as a "sponge." The sponge is allowed to ferment for up to 5 h. It is then combined with the rest of the formula ingredients and mixed into developed dough. After mixing, the dough is given an intermediate proof for 20–30 min. This is referred to as the "floor time." The floor time allows the dough to relax. It is then divided, molded, and proofed as is done in the straight-dough procedure. The sponge-and-dough procedure gives soft bread with a fine cell structure. It is generally considered to have well-developed

flavor. One of the great advantages of the sponge-and-dough procedure is its tolerance to variations in fermentation and processing time. It is thus more amenable to industrial production methods.

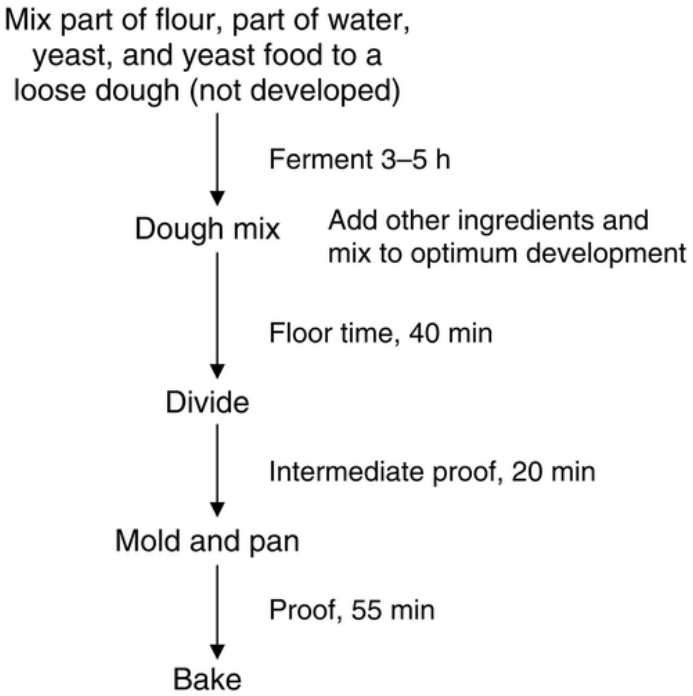


Fig. 12.5. Outline of a sponge and dough process.

Liquid-Sponge System

Many other breadmaking systems can be viewed as modifications of one of the above two procedures. These include the liquid-sponge, or preferment, systems, where the fermentation is done as a liquid in a tank instead of as a sponge. In this case, part or all of the flour is held out of the fermentation step.

Short-Time Breadmaking Systems

Short-time breadmaking systems are popular in the United Kingdom and Australia. In the United Kingdom, the Chorleywood procedure is used for about 80% of total bread production. It mixes the dough under a partial vacuum (see below) and then essentially proceeds as a no-fermentation-time straight-dough system. It is economical and produces bread that is popular in the United Kingdom. The Australian short-time procedure differs from the Chorleywood process in that it uses more oxidants for dough development.

Straight-Dough Breadmaking

The phenomena that occur during breadmaking can be very well described by discussing the different phases of the straight-dough process, as used in the production of white pan bread. These phases are dough formation, fermentation, molding, proofing and baking. Where appropriate, some elements of short-time breadmaking procedures are discussed as well. Attention is also paid to several measures that can be taken to increase the quality of bread. Finally, staling of bread and the phenomena that form the basis of bread firming are discussed.

DOUGH FORMATION

In most food systems containing wheat flour, production of a product begins by mixing flour, water, and various other ingredients to form dough. Dough is more than just a flour-water system. When wheat flour and water are mixed in various proportions, they form everything from slurry when water is in great excess to a dry but slightly cohesive powder when flour is in great excess. At intermediate levels, they produce a cohesive dough mass. The main steps involved in dough formation include mixing and full hydration of the flour particles. At the same time, care must be taken not to overmix the dough.

Diffusion of Water in Flour Particles

Wheat flour obtained by roller milling for the purpose of breadmaking is typically sieved through sieves of 132-µm openings (see Chapter 8). Its particles are quite dense and large compared to starch and protein. In comparison, starch granules (5–10 and 25–40 µm, see Chapter 2) and, especially, protein molecules are much smaller.

When water is added to such dense flour particles, the particle surfaces rapidly hydrate. Indeed, a lot of water is available to moisten the surface area of the particles. In contrast, water penetrates the particles slowly. The only driving force for the water to move to the center of the particle is diffusion, which is slow.

Mixing of Flour and Water

When mixing begins, it provides an additional mechanism for interaction of flour and water. As the hydrated particles rub against each other, the mixer bowl, or the mixer blades, the hydrated surfaces are removed, and a fresh layer of the particles is exposed to the excess water in the system. As this is repeated many times, the flour particles slowly become completely worn away and hydrated. As more and more of the free water hydrates the protein and starch, the system's resistance to extension is increased progressively. Thus, the height of a mixing curve produced with a mixograph (see Chapter 5) gradually increases to a peak (Fig. 12.6).

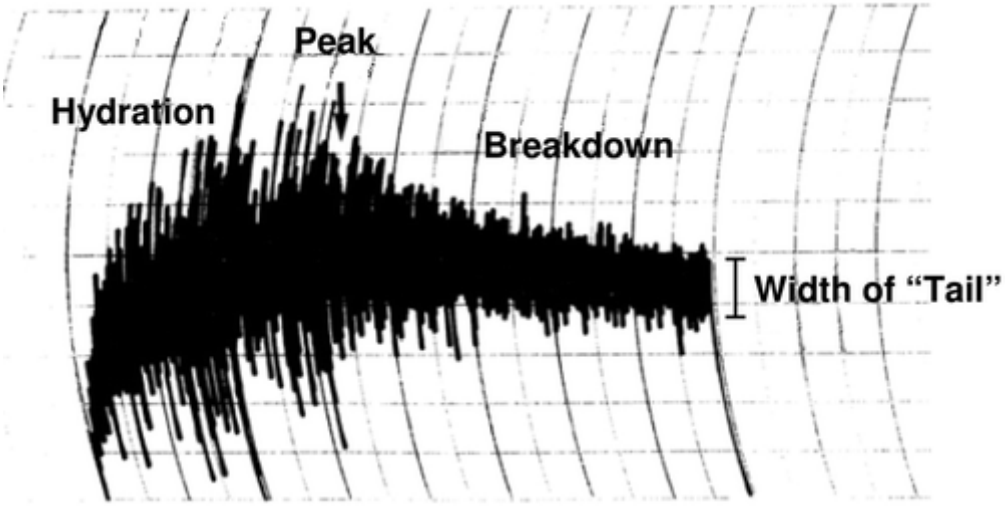


Fig. 12.6. A mixogram curve, hydration, peak development, and breakdown. The width of the "tail" of the curve is also indicated.

Dough that has been mixed to a peak is referred to in breadmaking jargon by a number of terms, e.g., "mixed dough," "dough with minimum mobility," or "optimally mixed dough." All of these terms imply that an end point has been reached. They also imply that this is the point to which a dough should be mixed for producing a loaf of bread. It appears obvious that a peak or plateau occurs because all the flour particles are hydrated. If they were not all hydrated, then continued mixing would give more resistance to extension and shift the point of maximum resistance to a longer mixing time and more resistance.

At this maximum, the dough is optimally mixed because all the protein and starch are now hydrated. Protein or starch that is not hydrated cannot interact in the dough in any beneficial way. Dough development is essentially the consequence of complete hydration of the flour particles. A scanning electron micrograph of optimally mixed and subsequently freeze-dried dough (Fig. 12.7) shows no intact flour particles but instead a random mixture of protein fibrils with adhering starch granules. The latter are present in the dough in the native state. During dough preparation, starch evidently absorbs water and probably acts as inert filler in the continuous protein matrix of the dough.

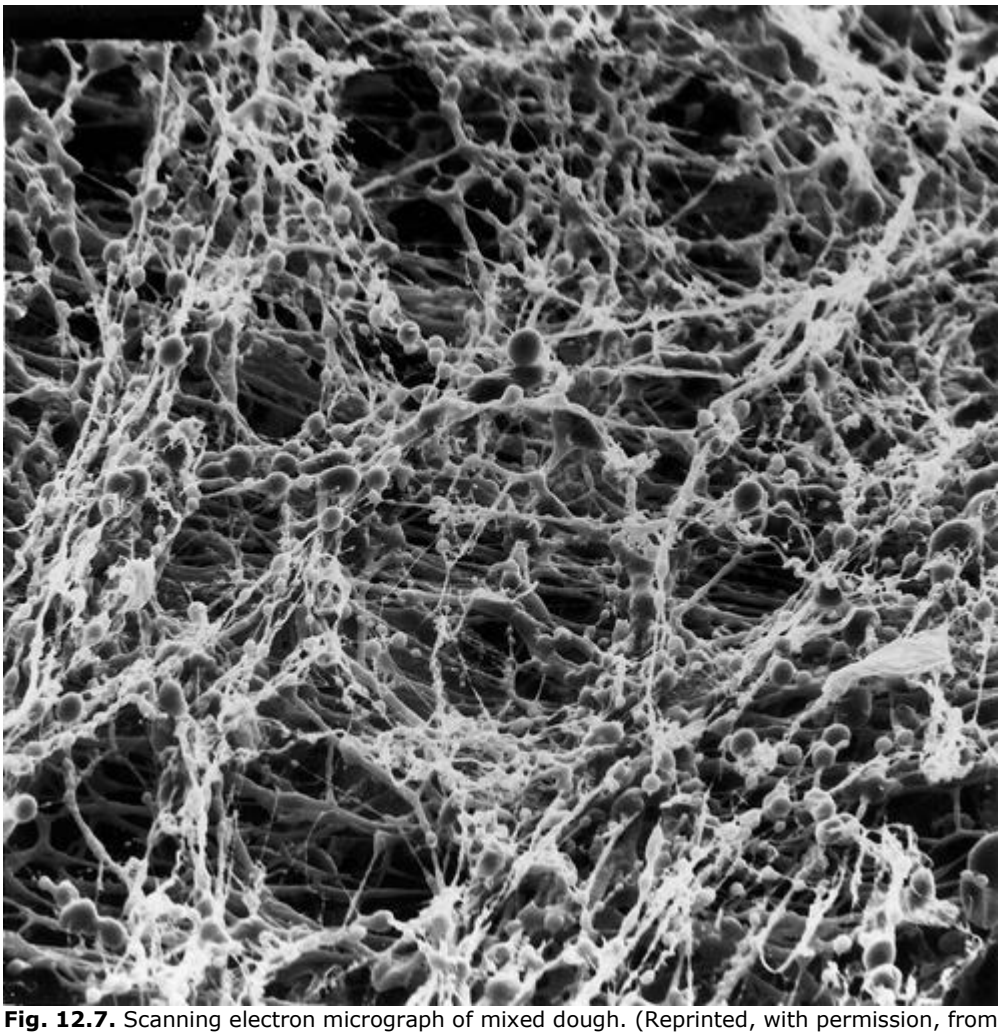


Fig. 12.7. Scanning electron micrograph of mixed dough. (Reprinted, with permission, from Hoseney 1978)

Developed dough has a tendency to relax. When mixed to optimum and then given time with no work being applied, some mixing is necessary to restore the resistance to extension of the dough to its original value. This shows that dough development is a reversible process. The fact that dough can be developed, allowed to relax, and then develop again implies that the bonding developed during mixing also includes hydrogen or hydrophobic bonding or both. The next section dscusses these elements.

Factors Affecting Mixing Characteristics

Figure 12.8 shows mixing curves of various flours. Each mixing peak occurs at a different time. Also, to reach optimum hydration, these different flours were not mixed to the same work input, as shown by the differences in the areas under the curves, which essentially measure the work required to mix the doughs. The differences are to a large degree associated with the dough-forming ability of the gluten protein fraction of wheat flour (see Chapter 3).

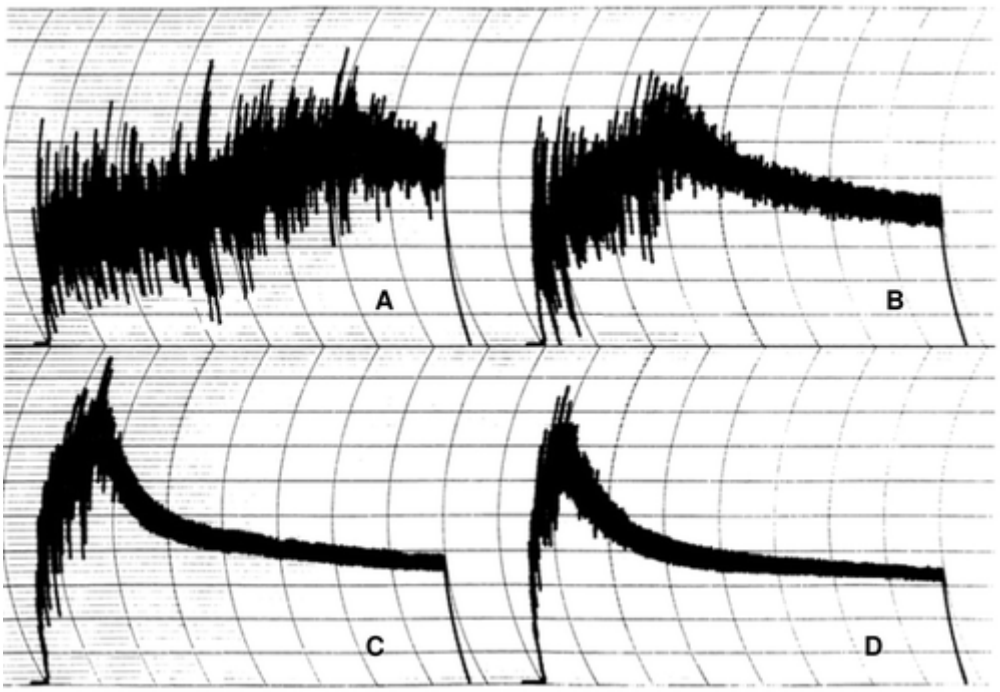


Fig. 12.8. Mixogram of hard winter wheats showing excellent (**A**), good (**B**), poor (**C**), and extremely poor (**D**) mixing properties. (Adapted from Hoseney and Finney 1974)

An important characteristic is that mixing leads to viscoelastic dough. A prerequisite for an elastic system is that it has continuity. Starch granules, of course, are not responsible for these dough characteristics, as they clearly remain discrete, discontinuous entities in the dough. While gliadin proteins are too small to impart continuity to the dough system, glutenin proteins can do that because of their high molecular weight and their entanglement with one another.

Several facts are important for understanding the role of glutenin in dough formation. First, agents such as cysteine, sodium bisulfite, and related compounds are quite effective in both shortening mixing time and reducing dough strength. They break disulfide bonds in the glutenin proteins by participating in thiol-disulfide exchange reactions, thereby making the proteins smaller (see Chapter 3). These smaller proteins hydrate more easily and thus lead to shorter mixing times. Second, several studies have shown that dough strength is related to the level of the high molecular weight glutenin fraction.

In this context, more particularly, much work has concentrated on the high molecular weight subunits that make up glutenin (see Chapter 3). It has been found that the absence of these subunits leads to very weak dough and that certain subunits are linked to better strength than others are.

However, not only the high molecular weight of glutenin and its ability to entangle and the viscous properties of gliadin are responsible for dough viscoelasticity. A first additional factor is the high amide content of gluten proteins because of the predominance of the amino acid glutamine (see Chapter 3). Because this amino acid can form hydrogen bonds, this suggests substantial hydrogen bonding in the system. Evidence for substantial hydrogen bonding stems from the observation, on the one hand, that mixing flour with deuterium oxide (D_2O) instead of with H_2O (Fig. 12.9) produces much stronger dough and, that, on the other hand, mixing flour with solutions of urea instead of with water produces much weaker dough (Fig. 12.10). Indeed, while deuterium oxide increases hydrogen bonding, urea breaks such bonds.

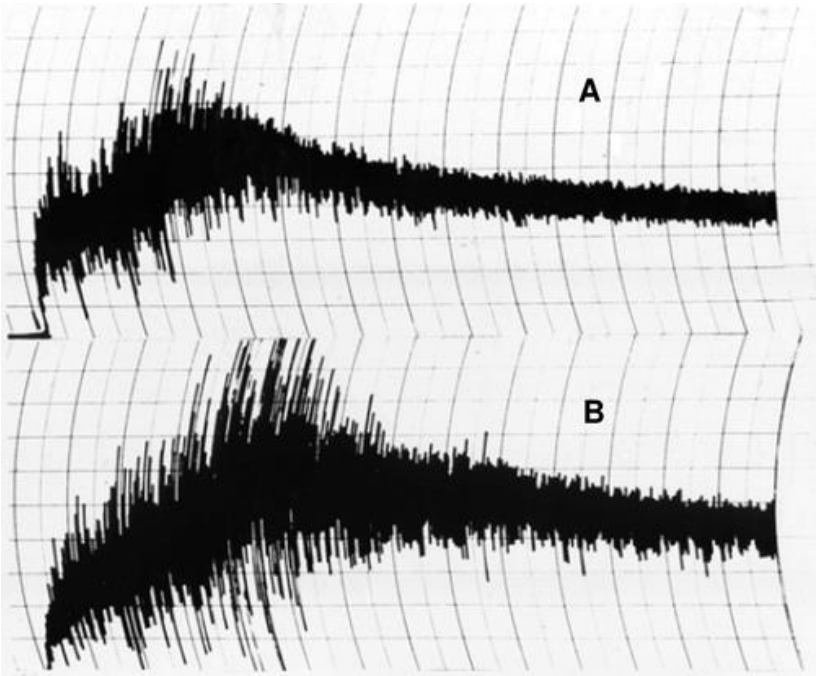


Fig. 12.9. Mixograms of wheat flour mixed with water (**A**) or deuterium oxide (D_2O, **B**). (Reprinted, with permission, from Hoseney 1979)

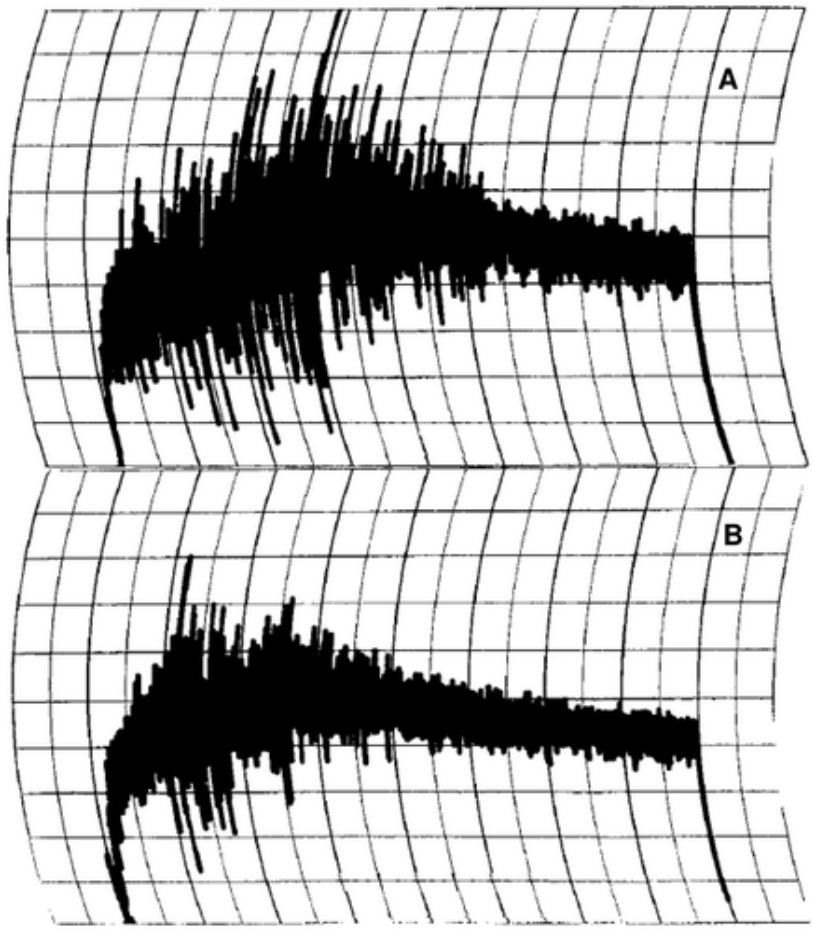


Fig. 12.10. Mixograms for control flour (**A**) and the same flour containing 1.5% urea based on flour weight (**B**). (Reprinted, with permission, from Hoseney and Rogers 1990)

A second factor is the absence of substantial charges on the gluten proteins, which suggests that there is little charge repulsion between the chains.

A third additional factor is that their hydrophobic amino acids may well contribute to hydrophobic interactions.

Taken together, these factors clearly suggest that the strength and elasticity of fully hydrated dough are linked to the presence of high molecular weight glutenin, which forms huge mass entities through entanglement with itself and interactions with gliadin and other glutenin fractions through hydrogen bonding and hydrophobic interactions. In this model, gliadin acts as a plasticizer and weakens interactions between glutenin chains. This increases the dough's flow properties.

Overmixing

After reaching optimum development, continued mixing produces wet, sticky dough with an overmixed sheen. This is generally referred to as the dough being broken down. Once the gluten proteins are hydrated as a result of mixing, the resistance to extension of the resulting dough is such that disulfide bonds in the gluten are, increasingly, broken by the mechanical mixing action. The resulting highly reactive thiyl radicals are then available either for renewed formation of disulfide bonds or for reactions with other components. While random renewed formation of disulfide bonds probably does not impact dough strength, reactions with α,β-unsaturated carbonyl compounds, such as fumaric acid, maleic acid, or ferulic acid, lead to breakdown of the dough structure. In line with the above, the effect of activated double-bond compounds on dough breakdown during overmixing is reversed by lipoxygenase (e.g., in enzyme-active soy flour, see Chapter 4), presumably because the enzyme creates additional free radicals in the gluten proteins. Mixing in a nitrogen atmosphere also prevents overmixing; this implies that oxidation is involved. The nature of the oxidation is not clear.

It follows from all of the above that shear-thinning as a result of continued mixing of the long protein molecules and lining them up in the direction of flow to offer less resistance to mixing is not the reason for dough overmixing, as it would not depend on the presence of oxygen in the system.

Air Incorporation During Dough Mixing

Another important aspect of dough mixing is the incorporation of air. As elegantly demonstrated in Figure 12.11, as dough becomes cohesive, it starts to incorporate air bubbles and thus decreases in density. The size of the bubbles incorporated depends on the interfacial tension, γ, in the system, which can be affected by the use of surfactants (see above). At the point of optimum mixing, typically half the total level of air that can be incorporated has been incorporated. This air, particularly its nitrogen content, is important in most baked products because it produces the cells into which the carbon dioxide subsequently diffuses. Indeed, because nitrogen is not very soluble in water (and thus also not in the dough's aqueous phase, while both carbon dioxide and oxygen are), nitrogen provides the necessary nuclei. As outlined below, the carbon dioxide produced by yeast must diffuse into preexisting gas cells. Because of this fact, if the dough did not contain air cells, the grain of the final bread would be very coarse, with only a few large cells. Stated in different terms, the nitrogen gas trapped during mixing provides the nuclei for subsequent gas expansion or leavening of the dough.

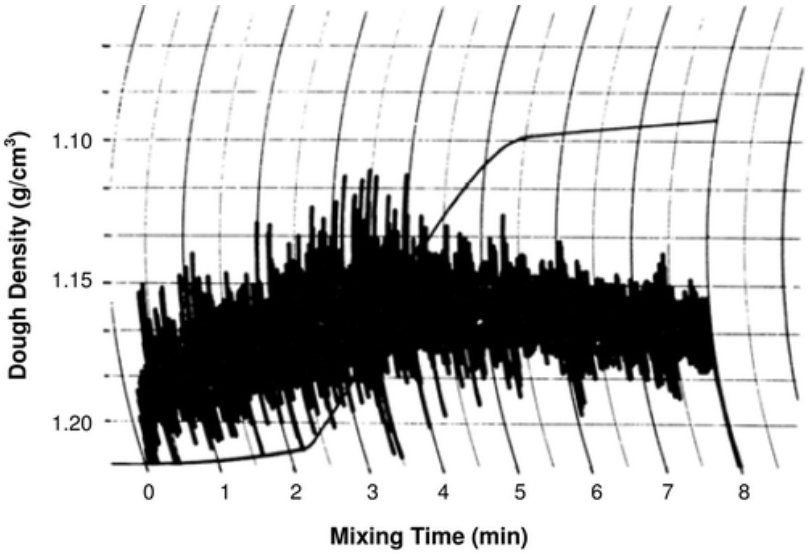


Fig. 12.11. Mixogram showing the decrease in dough density as a function of dough mixing time. (Reprinted, with permission, from Junge et al 1981)

In breadmaking systems such as the Chorleywood procedure (see above), mixing is under partial vacuum. At first glance, this would appear to be detrimental to bread quality as it would limit air uptake. However, the partial vacuum is beneficial because the small bubbles created expand under the reduced pressure and thus can be subdivided into more bubbles as the mixing proceeds. The more bubbles created, the finer the grain of the baked product will be.

FERMENTATION AND GAS RETENTION

As a result of the fermentation process, dough leavens and increases in volume. Several aspects of this phenomenon must be discussed in order to make clear the phenomena that occur. The main aspects concern the action of yeast; the reasons for gas retention; and the roles of gluten, nonstarch polysaccharides, and lipids in the phenomenon. Also important is the fact that yeast affects dough rheological properties.

Fermentation

Yeast is a living organism that is inactive during storage. The inactivity is caused either because the yeast has been dried, i.e., in the case of active dry yeast, or because it is stored at low temperature, i.e., in the case of compressed or crumbled yeast. Commercially produced yeast is always contaminated with bacteria, mainly lactobacilli. These do not appear to be important in regular breadmaking processes, as the fermentation times are too short for these organisms to exert an impact.

When yeast is incorporated into dough, the conditions are suitable for it to become active. Bread fermentation is an anaerobic process. Thus, little growth of yeast occurs during dough fermentation. In fact, the oxygen in dough is rapidly consumed by the yeast and bacteria as fermentation starts. Thereafter, the fermentation is anaerobic unless we add oxygen to the system by remixing. As outlined in Chapter 11, the fermentation reaction for glucose is

$$C_6H_{12}O_6 \rightarrow 2\ CO_2 + 2\ CH_3CH_2OH + 66.5\ kJ/mol$$

Yeast can also readily ferment the nonreducing sugar sucrose because it possesses a very efficient invertase system, which rapidly hydrolyzes sucrose into glucose and fructose, both of which are readily fermentable.

Under conditions of maximum yeast activity, glucose is utilized at a rate of about 0.75–3.0 g of sugar per hour per gram of yeast solids. Using this data to estimate its consumption in a typical straight-dough breadmaking process comprising 3 h of fermentation and a 55-min proof with compressed yeast (29% solids) added at 2.0% of flour weight, one can estimate a glucose consumption of 1.74–6.96 g/100 g of flour. Estimates of sucrose consumed, based on the fermentation products and the volume of carbon dioxide necessary for dough leavening, have been reported as about 3.50 g/100 g of flour utilized during the 4-h fermentation and proof. This value, however, does not consider loss of carbon dioxide to the atmosphere. Others have estimated that, during fermentation of a straight-dough, about 2.0% sugar (based on flour weight) is consumed from mixing to the end of proof. That value accounts only for the disappearance of sucrose and does not include fermentable carbohydrates naturally present in the flour.

The major products of yeast fermentation thus are carbon dioxide and ethanol. As carbon dioxide is produced, the dough's pH decreases, and its aqueous phase becomes saturated with carbon dioxide. Indeed, dough just out of the mixer usually has a pH of about 6.0. During fermentation, the pH drops to about 5.0. A rapid drop is caused at first by carbon dioxide dissolving in water. A second factor is the slow production of organic acids by the bacteria in the dough. The flour itself and, if present, either milk or soy proteins in the formula are good buffers and therefore help to control pH. At the end of fermentation, most of the leavening gas is present as carbon dioxide (CO_2) and little of it is bicarbonate (HCO_3^-) or carbonate (CO_3^{-2}) (see also Fig. 13.1).

Gas Retention

It takes a time before the volume of fermenting dough begins to increase. The initial lag found in a gas "production" curve for bread dough is because the dough's aqueous phase must become saturated with carbon dioxide before its evolution or loss can be measured. Carbon dioxide solubility in the aqueous phase is inversely related to the temperature and is affected by pH. Thus, the carbon dioxide is available to leaven the system only after the aqueous phase has become saturated. Once the aqueous phase is saturated, the leavening gas diffuses to preexisting gas cells. It does this because it cannot create new gas bubbles. Bubble mechanics indeed show that the pressure (P) in a bubble is related to the radius of the bubble (r) and the interfacial tension (γ) by the following relationship:

$$P = 2\,\gamma/r$$

Thus, in a system where the interfacial tension γ does not change, if *r* approaches zero, then the pressure *P* required to start a new bubble is infinite. It follows that a single carbon dioxide molecule cannot create a gas bubble and that, once the dough aqueous phase is saturated, the molecule must diffuse to a preexisting gas cell or to the atmosphere surrounding the dough piece.

Yeast and Dough Rheology

In addition to its gas-producing capabilities, yeast also affects dough rheology. Measurement of the width-to-height ratio (i.e., spread) of a dough piece following fermentation (Fig. 12.12) gives an indication of its viscous-flow and elastic properties. The spread ratio of dough that has more viscous-flow properties is higher than that of more-elastic dough. Figure 12.13 shows that flour-water dough gives a large spread ratio after 3 h. This indicates that the viscous-flow properties predominate in flour-water dough. When yeast is added to such dough, the spread ratio is reduced. The dough goes from one with a large viscous-flow component to one that is elastic, as a result of 3 h of fermentation. The trend toward dough with more elastic properties is the same trend as that found when oxidants are added to dough. Thus, yeast clearly has an oxidizing effect. Spread tests with either control dough or dough in which supernatant isolated from fermenting yeast cells served as dough water have shown that it is yeast itself, and not its fermentation products, that causes the changes in dough rheology. Also, the change in pH as a result of fermentation (see above) has little effect on the dough's spread ratio.

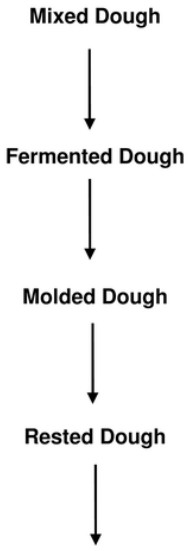


Fig. 12.12. Experimental scheme for determining the "spread" of wheat flour dough. The dough is mixed, fermented, and molded. Following a rest period, the spread is measured as the dough piece width over its height (*W*/*H*). (Adapted from Hoseney et al 1979)

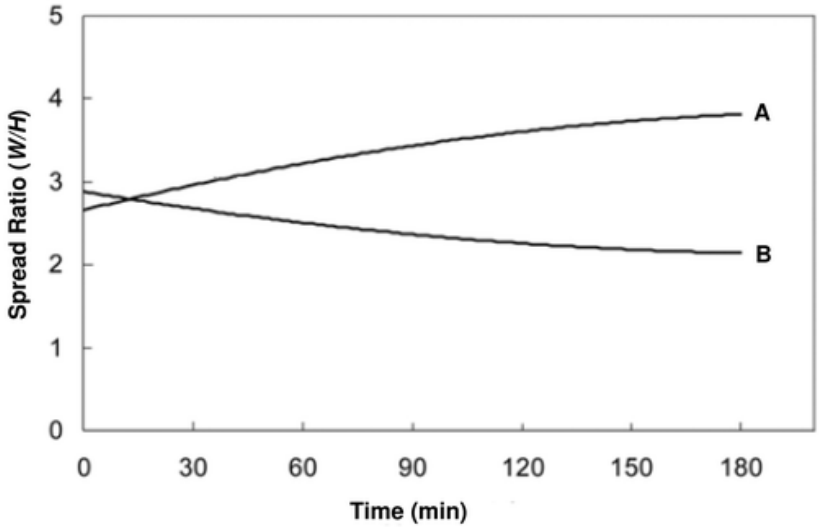


Fig. 12.13. Conceptualized graph showing the spread ratio (width [*W*]/height [*H*]) as a function of time for dough consisting of water and flour (A) or flour, water, and yeast (B). (Courtesy A. Bijttebier)

Role of Gluten and Arabinoxylan in Gas Retention

A long-accepted viewpoint in cereal chemistry is that the carbon dioxide is retained by the hydrated gluten proteins, which form a sheet or membrane. The model that is often used is that of a rubber balloon. Thus, in this view, hydrated gluten membranes form closed, gas-holding balloons (the air cells), which prevent carbon dioxide loss. This concept must be questioned because there is no reason to assume that such hydrated cell membranes would be semipermeable and that they thus would let carbon dioxide diffuse into the cell and at the same time prevent the gas from leaving the cell. In fact, no barrier is needed, as the carbon dioxide in the bubble is not likely to diffuse out extensively because the aqueous phase surrounding the bubble is saturated with carbon dioxide. In addition, yeast constantly produces more leavening gas. Gas retention, then, is not a mystery but only an application of the laws of diffusion, and the differences in gas retention capacities of different wheat flours (seeFig. 12.1) probably can be ascribed to the degree to which they (alone and/or following interaction with lipids and arabinoxylan) slow down gas diffusion.

Water-extractable arabinoxylan (see Chapter 4) probably functions somewhat as does gluten during fermentation. Because of its viscosity-enhancing effect, it slows down the diffusion rate of carbon dioxide out of the dough and thus contributes to gas retention, even if its concentration in flour is typically only 0.5%. While, at first sight, the concentration of water-unextractable arabinoxylan in flour (typically 1.5%) seems too low for it to exert an action in breadmaking, one should realize that it typically occurs at levels that are about 15% of those of gluten in bread. Apart from the fact that it has high water-holding capacities, its role at the fermentation stage seems rather limited.

Punching and Remixing

As fermentation proceeds, it is customary to punch or remix the dough, depending upon which baking system is being used, and to then continue with fermentation. There are two reasons for this practice.

First, punching or remixing subdivides the gas cells, resulting in many more but smaller cells. In the process, a large portion of carbon dioxide is lost to the atmosphere, but the important aspect of the process is the creation of the new gas cells by subdivison. Thus, in addition to air cells being incorporated at the dough-making stage (see above), new gas cells are created by punching or remixing.

Another important benefit of punching or remixing is redistribution of the dough ingredients. Yeast cells are not mobile in dough. Therefore, they depend upon the sugar diffusing to them. As fermentation proceeds, the diffusion distances become large, and the concentration of the nutrient diminishes, along with the rate of fermentation. Punching or remixing brings the yeast cells and fermentable sugars together again. In zero- or short-time breadmaking systems, punching is not practical, as the dough is not given sufficient time to expand. The net result is usually a coarser grain (or, stated differently, fewer cells) in the bread. A partial solution to this problem is to mix under partial vacuum, which expands the dough and allows the gas cells to be subdivided without the need for the dough to expand (see above).

Summary

To sum up the above, in mixed bread dough, an insoluble but highly hydrated gluten protein system constitutes the continuous phase, with starch and air bubbles as the discontinuous phases (Fig. 12.14). Dough's viscous flow properties are to a large extent controlled by gliadin, while its elasticity is controlled by glutenin. Also dispersed throughout the aqueous system are yeast cells, which ferment sugar and produce, among other things, carbon dioxide. The carbon dioxide is produced in the aqueous phase and saturates the water. Once the water is saturated, newly produced carbon dioxide must migrate elsewhere. Because it cannot form new bubbles, the preexisting air bubbles are the only alternative. The carbon dioxide enters the bubbles and increases their pressure. The dough's viscous-flow properties allow the bubble to expand and thereby equalize the pressure. As a net result, the total volume of the dough mass is increased or, in other words, the dough is leavened.

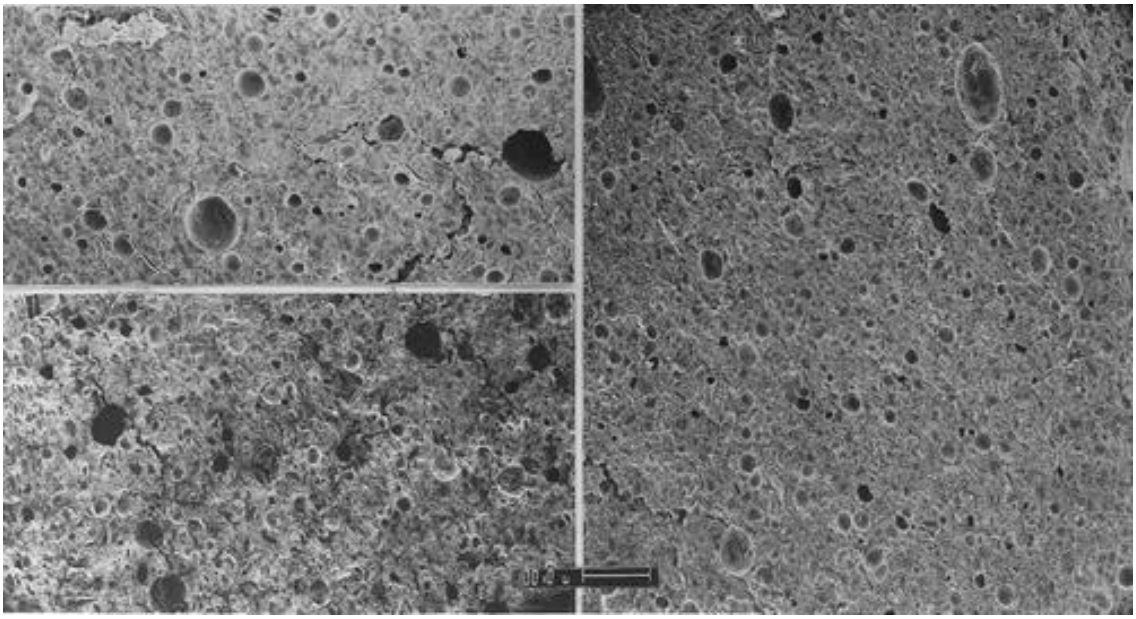


Fig. 12.14. Scanning electron micrograph of cyro-fractured freeze-dried, flour-water doughs. **Right**, dough containing 0.5% sodium stearoyl lactylate; **upper left**, control dough; **lower left**, dough containing 3% shortening. (Reprinted, with permission, from Junge 1981)

MOLDING AND PROOFING

Mechanical punching or sheeting of dough during fermentation results in the gluten fibrils becoming aligned (Fig. 12.15). After fermentation, the dough is divided into individual loaf-sized pieces and given a floor time, i.e., it is allowed to rest at room temperature. After the dough has relaxed, it is ready for molding, which is essentially sheeting followed by curling, rolling, and application of additional pressure. As dough is sheeted by being passed between multiple sets of rolls, it is sheeted in different directions. Continued machining in one direction would align the protein fibrils and result in dough that is strong in one direction but weak in the direction at a 90° angle to the sheeting direction. After being molded, the loaf is panned, with the final lap facing down in the bottom of the pan (Fig. 12.16).

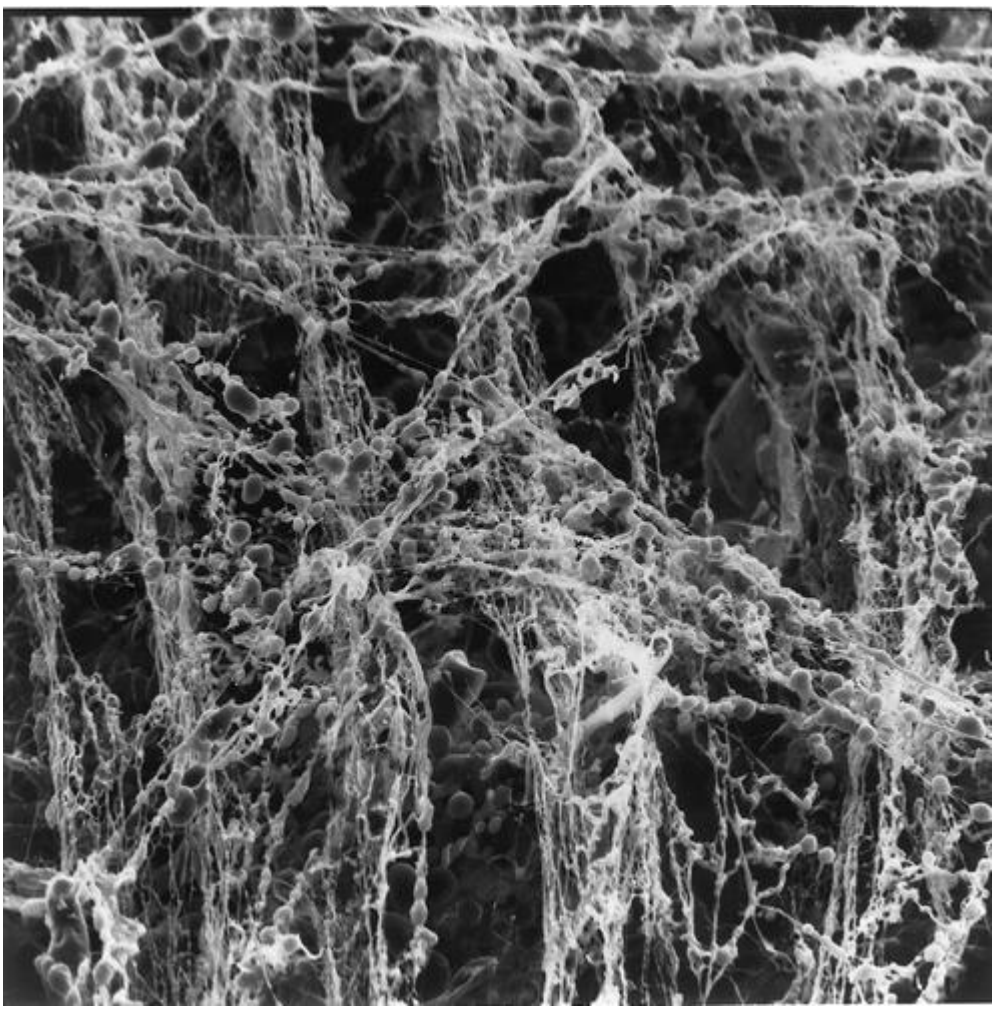


Fig. 12.15. Scanning electron micrograph of dough after fermentation. Note the alignment of the gluten fibrils. (Reprinted, with permission, from Hoseney and Seib 1978)

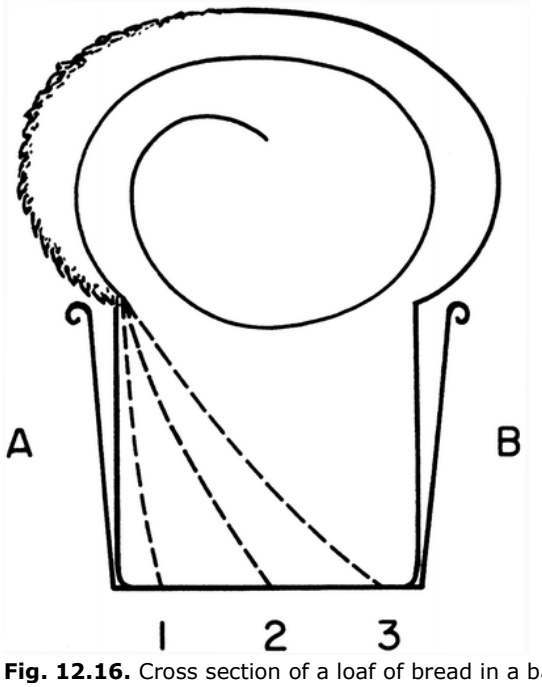


Fig. 12.16. Cross section of a loaf of bread in a baking pan. The solid spiral line represents the dough-to-dough interface in the upper part of the loaf that results from the dough molding operation. The dotted lines represent three different dough-to-dough interfaces in the lower part of the pan resulting from placing the crease of the

dough roll at three different positions. The break and shred is on side A. (Reprinted, with permission, from Shogren and Finney 1984)

The dough is then ready for proofing. This final fermentation step is usually at 30–35°C and 85% relative humidity. Because the oxidized dough now has only limited viscous-flow properties (see above), it no longer flows under the force of gravity but fills the pan by expansion due to leavening. Proofing usually takes about 55–65 min, during which the dough increases greatly in volume.

The amount of carbon dioxide present in fully proofed dough is only about 45% of the total produced by fermentation. The balance of the gas is lost during fermentation, punching, molding, and proofing.

BAKING

The rate of baking of bread is generally quite constant. The rate at which a loaf bakes is determined by the rate of heat penetration into the dough, which is difficult to change. Increasing the oven temperature speeds up the rate of baking only slightly. The higher temperature results in larger temperature and moisture gradients in the loaf but does not greatly change the time required to raise the center of the loaf to the desired temperature. It is instructive to classify the changes that occur during baking of a loaf of bread as either visible or cryptic. Once both have been dealt with, it is useful to discuss what determines the end of the loaf expansion in the oven, i.e., the ovenspring (see below), and to deal with the structure of the crumb in the final product. Equally instructive is a discussion of the role of gluten, arabinoxylan, and lipids as factors determining the final product volume.

Changes to the Exterior

When proofed dough is placed in the oven, most of the heat that is absorbed by the product comes through the baking pan. Therefore, the rate at which the dough temperature increases depends upon the heat transfer from the air and the baking surface of the pan. Dough conducts heat less efficiently than the metal pan. Therefore, a well-defined temperature gradient forms from the outside to the center of the baking loaf.

Once the loaf is in the oven, three large changes are evident, two of which rapidly become apparent. The first is the almost immediate expansion of the dough; the second is the drying of the surface. The third is the crust browning.

Thus, when the proofed dough is placed in the oven, it expands rapidly. This is the well-known phenomenon of ovenspring. Once completed, the ovenspring is a nonreversible phenomenon because the dough does not shrink to approximately its original size when the loaf is removed from the oven. However, when one removes the loaf from the oven during the ovenspring, the dough does shrink back.

Several factors are responsible for the ovenspring. First, as the temperature rises, the yeast becomes quite active before it is killed at about 55°C; thus, for a time, it produces more carbon dioxide. Second, the carbon dioxide in the aqueous phase becomes less soluble as the temperature is raised, causing more carbon dioxide to move into the air bubbles. Third, the carbon dioxide in the air bubbles expands, as do all gases, as the temperature is increased. Finally, vaporization of the water-ethanol azeotrope (with a boiling point of 78°C) during heating in the oven may well contribute greatly to the overall expansion of the dough, provided that such azeotrope is formed in the dough. If it is not formed, then the vaporization of both water and ethanol is important. Generally, the ovenspring stage lasts less than 8 min. The remaining baking time then ensures that the center of the loaf approaches 100°C.

The surface of the dough that is exposed to the oven atmosphere skins over and rapidly forms a crust. The crust forms because the surface of the dough is dried. The moisture on the surface of the dough vaporizes very rapidly, because it is in contact with dry, high-temperature air. However, the crust remains cool because of the heat needed to vaporize the water. Thus, much of the starch in the crust retains its birefringence in the finished loaf. If a thicker, heavier crust is desired, steam is generally added to the oven. The steam slows the rate of water vaporization, and the surface cooks to a greater extent, producing a thicker crust. The formation of a crust or skin is not responsible for the loaf's retention of gas, as this is controlled by the properties of the interior dough and not by the surface.

The later stages of baking are when all the crust browning occurs. It is the result of Maillard reactions between reducing sugars such as glucose and fructose on the one hand and free nitrogen groups on proteins, peptides, or amino acids on the other hand. Browning occurs late in baking because it takes place much faster in a dehydrated system and requires higher temperatures. In baking, at the crust, these conditions are reached only after the rate of vaporization of water at the surface has diminished greatly. That only the crust and not the crumb undergoes browning is because the crumb does not dehydrate sufficiently for Maillard reactions to occur.

When bread is removed from the oven and allowed to cool, it does not collapse. This alone shows that the system now is gas-continuous. If it were still only a gluten-continuous system and not also a gas-continuous system, the pressure differential that would develop when the gas cooled would cause the loaf to collapse.

Changes in the Interior

The simple experiment of attempting to force air through dough and bread shows that, in dough, gluten is the continuous phase and the gas cells are the discontinuous phase. As a result, dough can be used to blow a bubble such as is done in the alveograph (see Chapter 5). In contrast, a slice of bread has an open-celled sponge-like structure and offers no resistance to the passage of air. The air freely passes through, showing that bread is not only gluten-continuous but also gas-continuous. Therefore, when dough is transformed to bread, it is no longer capable of retaining gas.

The internal structures of doughs that have been baked for various periods of time (Fig. 12.17) show a sharp demarcation between the dough and the bread crumb regions of each loaf. This line of demarcation is consistent with the gradient of temperature that develops during baking. Thus, one can conclude that temperature is responsible for the transformation of dough to bread.

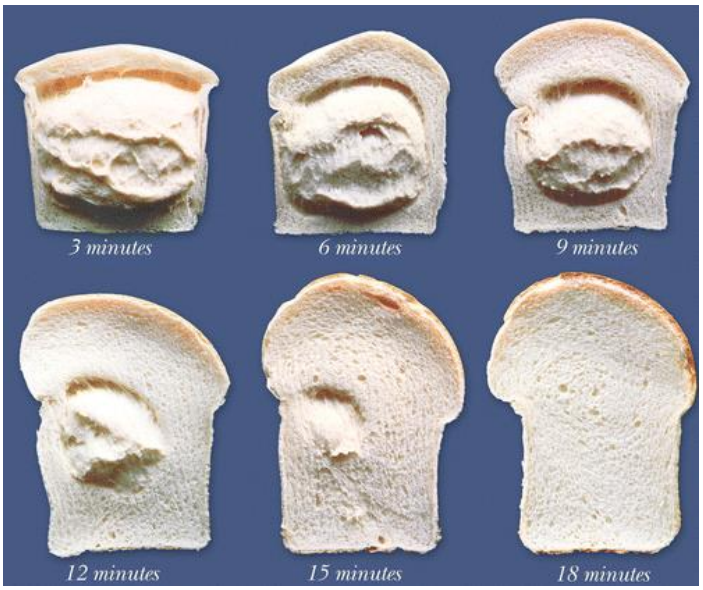


Fig. 12.17. Cross-sections of dough during baking. (Courtesy TNO Institute for Cereals, Flours and Bread, Wageningen, The Netherlands; photography by Piet Sluimer)

Among the changes caused by heating dough systems, the most prominent is starch gelatinization. During baking, the starch in the bread dough starts to gelatinize (i.e., its crystals melt) at about 65°C. This is also the temperature at which the demarcation between dough and bread crumb described above occurs. Figure 12.18shows that the melting of the amylopectin crystals (see Chapter 2) extends over a broad temperature range. It is also important to note that, at the water levels present in dough, starch swelling occurs over a wide temperature range. During gelatinization and swelling under these conditions, the granular identity of starch is largely retained. Part of the solubilized amylose forms inclusion complexes with either certain added lipids (not with triacylglycerols) or some of the endogenous wheat polar lipids, as evidenced by the V crystal type (see Chapter 2) of fresh bread crumb. The gelatinization process makes the continuous, primarily protein, walls of the air cells stronger because it withdraws water from the system. While high levels of β-amylase are present in flour (see Chapter 2), this enzyme is inactive on intact starch and is inactivated by heat before the starch gelatinizes. In contrast, there is a window of activity for both malt and fungal α-amylases. These enzymes are active in the time between the gelatinization of starch and their own denaturation. The window is larger for malt than for fungal α-amylases. Bacterial amylases are also active when the starch gelatinizes, but they are not always denatured in the baking process. Malt or fungal α-amylases, in contrast, are partially active during the initial phases of gelatinization baking but are inactivated later in baking.

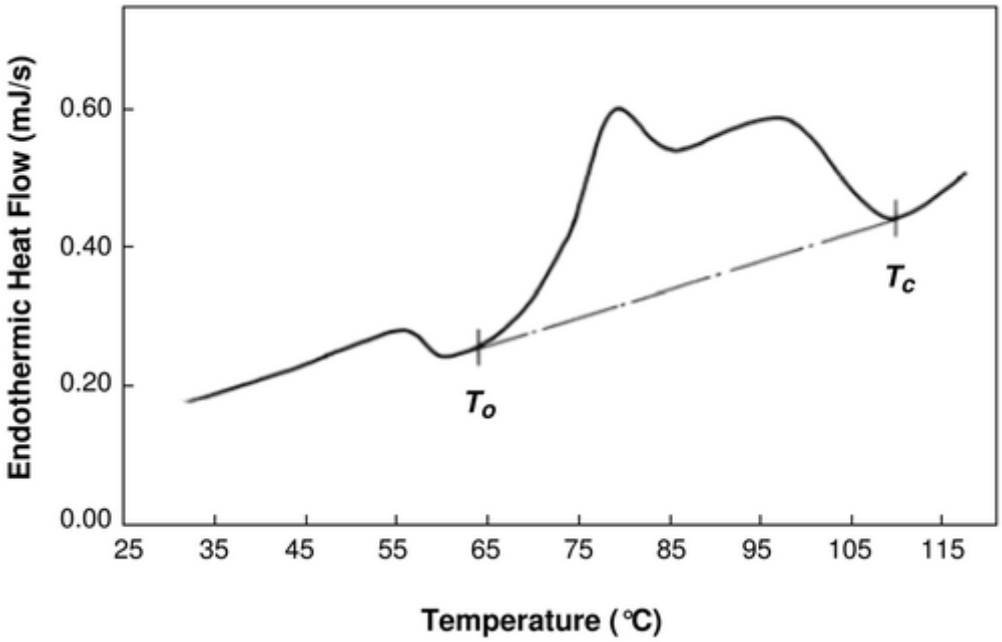


Fig. 12.18. Differential scanning calorimeter thermogram of bread dough without yeast, with indication of the onset (T_o) and conclusion (T_c) temperatures of the endothermic transitions. The total endothermic heat flow for the dough corresponds to about 3.75 J/g. The thermogram shows that starch crystal melting begins at about 65°C and that, because of the limited water level in dough, it extends over a broad temperature range. (Adapted from He and Hoseney 1991)

During baking, drastic changes also occur in the gluten proteins. First, as a result of starch gelatinization, water is withdrawn from the gluten proteins. The reduced amount of plasticizer changes gluten properties. Second, the gluten undergoes strain hardening, i.e., the force necessary to extend it increases as it is stretched thin to cover the expanding gas cells. Finally, heat causes the gluten proteins to become increasingly cross-linked through the formation of new disulfide bonds (Chapter 3). At first, only glutenin-glutenin cross-linking occurs, but, at temperatures exceeding 90°C, disulfide bonds form and link gliadin and glutenin.

At the same time, the pressure inside the gas cell continues to increase as a result of the temperature increase (see above) until the cell wall ruptures and the system becomes gas-continuous, i.e., a sponge structure is formed. Scanning electron micrographs (Fig. 12.19) show that dough/bread heated to below 70°C has no tears in the cell walls, while dough/bread heated to above 88°C show tears or failures in its cell walls. At the end of baking, i.e., at about 95°C, the bread has lost its ability to flow under the force of gravity and is now more elastic than the dough was.

End of the Ovenspring

When bread dough is baked with ohmic heating in an electrical resistance oven, there are essentially no temperature gradients, and the dough heats uniformly. When one bakes dough by this method, little carbon dioxide is lost until the dough temperature reaches about 72°C. At that temperature, large amounts of carbon dioxide are released from the then partially baked bread. At this point, the dough loses its ability to retain carbon dioxide and no longer expands (Fig. 12.20).

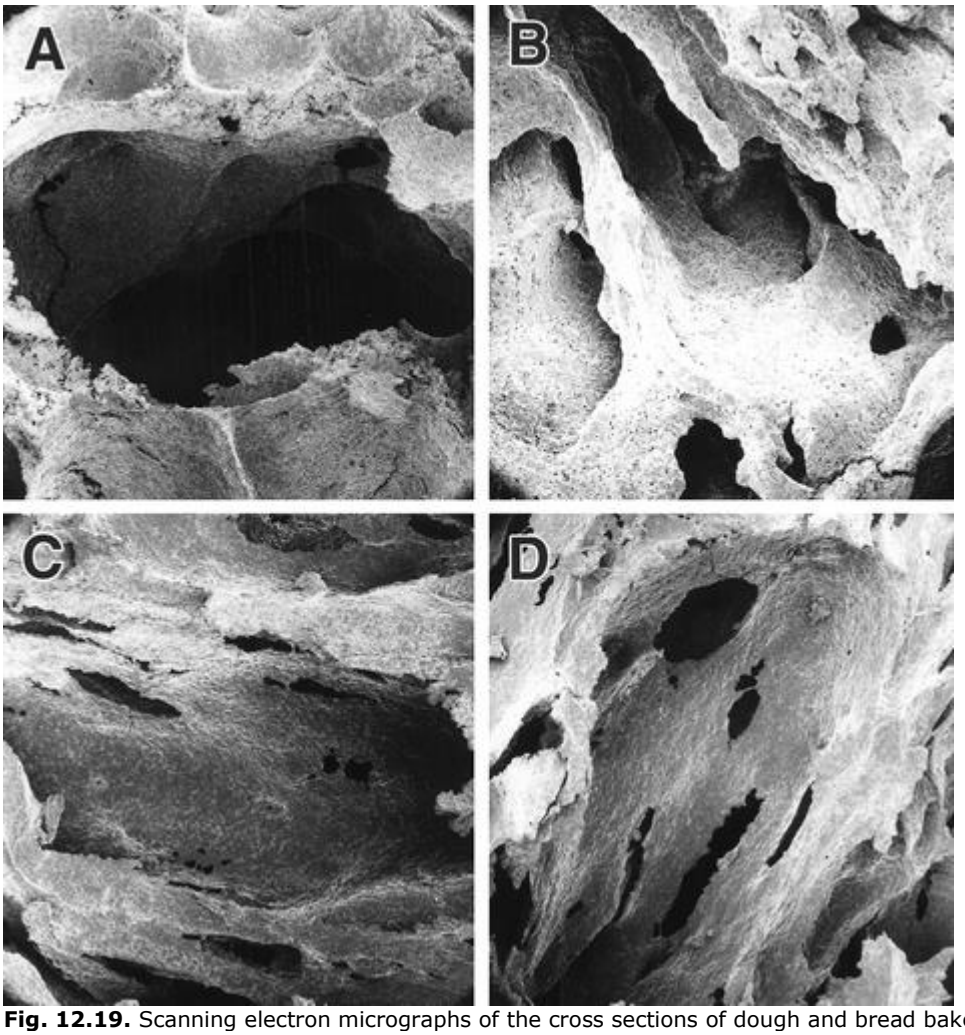


Fig. 12.19. Scanning electron micrographs of the cross sections of dough and bread baked to 28°C (**A**), 70°C (**B**), 88°C (**C**), and 95°C (**D**). (Reprinted, with permission, from He and Hoseney 1991)

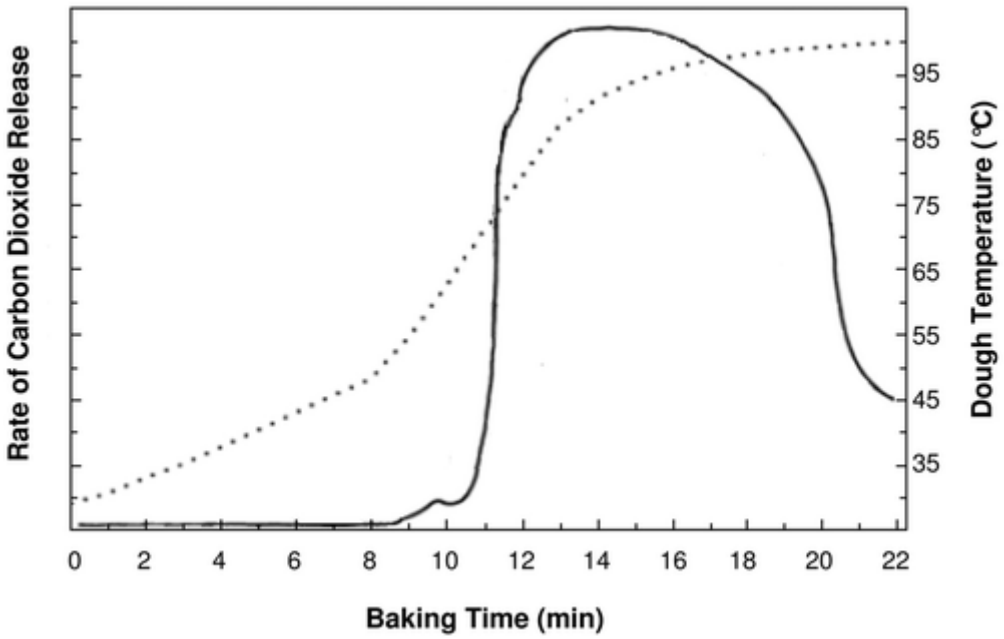


Fig. 12.20. Rate of carbon dioxide release (full line, arbitrary units) as a function of temperature (dotted line) during baking of fermented bread dough in an electrical resistance oven. (Adapted from He and Hoseney 1992)

However, in conventional baking, there is a pronounced temperature gradient in bread during baking. Thus, the changes in the starch and gluten described earlier occur from the outside of the loaf toward the center, with the result that the expansion stops early in the outer layers but continues in the loaf center. The fact that the outer layers have become gas-continuous and the cell walls have become strong results in them no longer expanding in response to the pressure from the center of the loaf. Instead, the increase in pressure from the inside now results in the break and shred, i.e., the area on the loaf exterior where new dough is exposed to oven temperature as the loaf expands. As the loaf breaks, this allows more loaf expansion and a continuation of ovenspring. The ovenspring stops when the transformation from dough to bread occurs deeper in the loaf so that the pressure generated in the center of the raw dough is insufficient to cause more shred or when the transformation has reached the center of the loaf and pressure is no longer being generated.

Crumb Structure

The crumb structure or grain of a loaf of bread is not a random collection of cells but instead an organized system that can tell us much about the loaf. In an aqueous environment with no added stress, gas cells are round because this shape gives them the minimum surface area and, therefore, the least free energy. Such cells are evident in cakes or in bread made with continuous breadmaking systems (Fig. 12.21). One can therefore infer that the external forces on the cells are uniform in all directions in those systems. In conventionally made bread, many of the cells are elongated, indicating that the dough forces on the cells are not uniform (Fig. 12.21). The degree of elongation is, then, a measure of the strength of the dough and a measure of the chewiness of the bread.

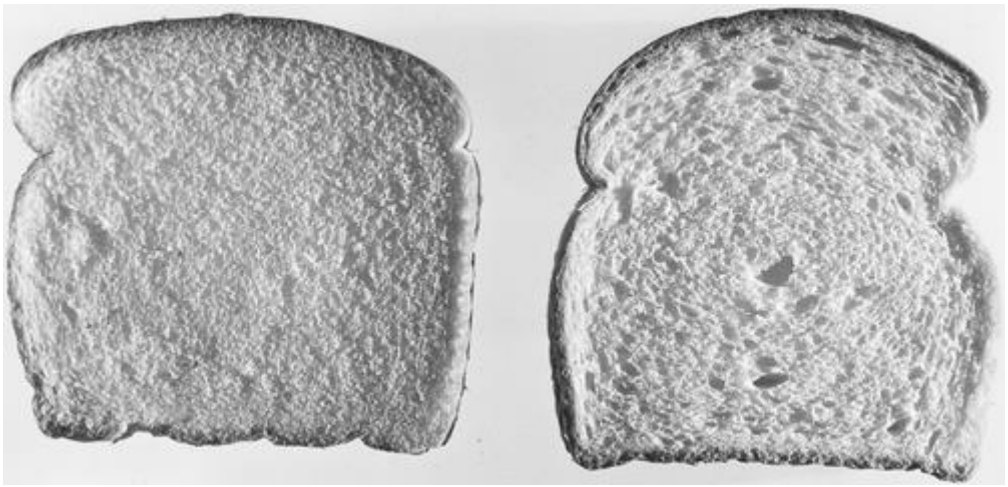


Fig. 12.21. Crumb grain of bread produced by the continuous baking procedure (left) and a sponge and dough procedure (right). (Reprinted, with permission, from Hoseney and Seib 1978)

During molding (see above), the dough is sheeted and then rolled into a cylinder. The cells are elongated around the cylinder. If the dough is strong, the elongation persists through the proof stage. During baking, the crust on the exposed surface of the dough breaks at one or both sides where the crust meets the pan. With strong dough, the break tends to occur on the side of the last lap. As the break occurs, the loaf expands in that direction, giving a "break and shred" (see above) and a nice, well-defined slip plane, i.e., an area where the elongated cells slide past each other as the dough expands in the interior. If the loaf breaks on the other side, the grain is much less organized and more difficult, if not impossible, to judge. In bread made from fully oxidized and developed dough, one would expect a large number of the cells to be elongated, with a distinct slip plane. In underoxidized dough, also referred to as "green," many small, round cells with thin cell walls are evident, and the slip plane is not distinct. Overoxidized dough results in loaves with larger, round cells with thick cell walls and a very prominent slip plane.

Gluten and Bread Volume

Gas cell walls in bread dough contain gluten. At fermentation temperatures, gas retention is the result of the restricted diffusion of the leavening gas, which in turn results in increasing dough volumes. Under such conditions of gas production and loss, the net effect is that less gas diffuses out of the system than is produced by it. Once the dough is in the oven, the pressure in the individual gas cells increases greatly, and, because of cell expansion, the gas cell walls become thinner and at the same time harder until they rupture. The relationship between flour protein content and bread volume (Fig. 12.1) is reasonable, as the protein determines the cell wall thickness at any point in the breadmaking process. Flour protein quality is therefore linked to the way the protein allows the gas cell walls to expand. Insufficiently elastic gluten leads to low bread loaf volume as gas diffusion is rapid. Increased elasticity leads to greater loaf volume up to a point, but overly elastic gluten impedes the expansion of gas cells, resulting in lower loaf volume. Hence, dough can be too weak

or too strong. Excessively strong dough is termed "bucky" and produces loaves with poor loaf volume, crumb grain, and symmetry. In practice, gluten properties can be modified to produce reasonable bread by the use of oxidizing and/or reducing agents.

Effect of Oxidizing and Reducing Agents on Gluten

The most prominent linkages in gluten are disulfide bonds, which link the glutenin subunits. Hence, oxidizing and reducing agents with large effects on the dough thiol-disulfide system can affect the degree of polymerization of glutenin subunits and thereby change the mechanical and rheological properties of the dough.

Low concentrations of endogenous glutathione (glutathione-SH) weaken dough and increase extensibility through thiol-disulfide interchange with polymeric gluten (gluten-S-S-gluten) as follows:

$$\text{gluten–S–S–gluten} + \text{glutathione–SH} \rightarrow \text{gluten–S–S–glutathione} + \text{gluten–SH}$$

Chemical oxidizing agents, such as potassium iodate and potassium bromate ($KBrO_3$) react with low molecular weight thiol compounds such as reduced glutathione in the flour and form disulfide compounds that are not active in changing dough rheology. It is also possible that they form intermolecular disulfide bonds in gluten proteins and thus contribute to dough strength. Potassium bromate, the slowest acting of all commonly used oxidants, has historically been one of the most common bread improvers in the United States and certain other countries. However, its use has been greatly reduced by toxicological studies suggesting that it could be carcinogenic. Potassium bromate can be, and still is, used in the United States, albeit much less than in the past. However, if used, it must be in small amounts such that not more than 20 ppb is present in the finished product, and its use must be declared on the label. The overall reaction of gluten and potassium bromate is expressed as follows:

$$KBrO_3 + 6\ \text{gluten–SH} \rightarrow 6\ KBr + 3\ \text{gluten–S–S–gluten}$$

Potassium bromate is a slow-acting oxidant that acts during fermentation and baking. At least part of potassium bromate's time-dependent effect may be because of the change in dough pH during fermentation, as it reacts faster at lower pH. In contrast, potassium iodate is a fast-acting oxidant that has its action during mixing.

Azodicarbonamide is often used as an alternative oxidant. Upon dough formation, it is rapidly and completely converted to the metabolically inert, nontoxic biurea, which is stable in bread. Calcium peroxide is also used as an oxidant. It forms hydrogen peroxide, which acts as an oxidant and is believed to also cause polymerization of water-extractable arabinoxylans. Polymerization dries the dough and allows higher levels of water to be added. Another source of hydrogen peroxide and, therefore, an oxidant in bread is the enzyme glucose oxidase (EC 1.1.3.4).

Ascorbic acid (often denoted as AH_2) also improves bread volume. Ascorbic acid has both a rapid and a time-dependent effect on dough rheology. The vitamin C effective stereoisomer l-*threo*-ascorbic acid is the isomer that most strongly enhances the strength and the handling and baking properties of dough. The other three stereoisomers of ascorbic acid have only minor oxidizing effects on dough. This stereospecificity suggests that at least one enzyme contributes to its effect in breadmaking. The enzyme involved in the conversion of l-*threo*-ascorbic acid is ascorbic acid oxidase. It uses molecular oxygen (O_2) as substrate. The oxidized ascorbic acid (A) acts as an electron acceptor in the oxidation of endogenous glutathione by wheat flour glutathione dehydrogenase and drastically reduces the level of reduced glutathione, which otherwise would weaken the dough through reaction with disulfide bonds in gluten. The reactions involved are the following:

$$2\ AH_2 + O_2 \rightarrow A + 2\ H_2O$$
$$A + 2\ \text{glutathione–SH} \rightarrow AH_2 + \text{glutathione–S–S–glutathione}$$

Reducing agents such as L-cysteine, glutathione, and sodium metabisulfite may be added to weaken the dough structure. This is beneficial in the case of bucky doughs.

Arabinoxylan and Bread Volume

It is assumed that, during the initial phases of baking, the water-extractable arabinoxylan (see Chapter 4) affects breadmaking by its impact on the system's viscosity and, thus, on gas diffusion. The water-unextractable arabinoxylan, in contrast, reduces bread quality. As outlined above, the concentration of water-unextractable arabinoxylan is typically 15% of that of the gas-cell-wall-forming gluten, and it presumably interferes with the gas cell walls. In this context, it is useful to repeat (see Chapter 8) that those endoxylanases that hydrolyze and thus dissolve water-unextractable arabinoxylan are especially useful in breadmaking. Also, the fact that such enzymes consistently are better able to increase the volume of bread made from low-protein flour than that of bread made from flour of high protein content is in line with their impact on gas cell wall rupture.

Lipids and Bread Volume

Defatting flour with petroleum ether in a way that does not damage gluten results in a flour that still produces a reasonable, but smaller, loaf of bread. When the lipids are added back to the flour, the resulting bread volume is restored to the original size. Research has shown that the polar lipid fraction and particularly the glycolipids are most important in this phenomenon.

The use of lipases (see Chapter 4) in breadmaking is quite recent. In particular, 1,3-specific lipases, which preferentially remove fatty acids from the 1- and 3-positions, improve dough rheological properties and may provide an alternative to the use of chemical dough-strengthening emulsifiers. Part of the released polyunsaturated fatty acids is oxidized by the wheat lipoxygenase and yields hydroxyperoxides and free radicals. These compounds can oxidize other constituents, such as proteins and carotenoids, thus affecting dough rheological properties and crumb color.

The functionality of lipids presumably is also related to their effect on the stability of the gas cells. In this respect, the positive influence of the polar lipids is attributed to their ability to form lipid monolayers at the gas-liquid interface of the gas cells, thus increasing the gas retention of the dough. Finally, it is of note that addition of small levels of shortening to bread dough improves loaf volume and leads to a fine, more uniform crumb structure with thin cell walls. None of the numerous hypotheses discussed in literature provides an acceptable explanation for the mechanism of the latter effect.

BREAD STALING

During storage, bread gradually loses its desirability. The undesirable changes that occur with time are collectively called "staling." They include toughening of the crust, firming of the crumb, a loss of flavor, an increase in the opaqueness of the crumb, and a decrease in soluble starch levels.

Bread Firming

The temperature at which bread is stored affects bread firming. When bread is stored below its glass transition temperature, T_g (see Chapter 6), its firming is halted. At temperatures just above the freezing point, firming is faster than it is at higher temperatures.

Changes in the Crust. The changes that occur in the crust differ from those in the crumb. When bread is freshly baked, the crust contains only 2–5% moisture. Under these conditions, it is friable. As water diffuses from the crumb, the crust loses its friability and becomes tough, going from a glassy state to one that is leathery or rubbery.

Changes in the Crumb. The changes that occur in the crumb are much more complex. It was shown about 170 years ago that the firming of bread crumb is not due to drying. Firming occurs even when no moisture is lost.

Because the amylose that can crystallize has already crystallized by the time the bread has cooled, amylose contributes only to the initial crumb firmness and not to crumb firming. Amylose is an essential structural element of bread; flour that is derived from waxy wheat and that therefore contains no amylose yields bread with very poor crumb characteristics. Addition of emulsifiers that complex with amylose to form amylose-lipid complexes (see Chapter 2) produces softer bread, presumably because, during baking, starch swelling is reduced and thus the swollen starch contributes less to the overall rigidity of the structure (see below).

The amylopectin component of starch retrogrades (see Chapter 2) over the same general time span as that of bread firming. Its outer chains form double-helical structures and crystallize. It is generally assumed that the

crystallization is both intermolecular and intramolecular. Retrogradation probably is also responsible for the increase in opaqueness of the crumb, presumably because of changes in the refractive index.

However, in spite of the logical assumption that firming and retrogradation are the same phenomenon, no firm proof has been offered that the two are causatively linked. Indeed, the extent or quality of starch crystallinity in bread is often poorly correlated with crumb firmness. When one realizes that firmness is a long-range rheological property, the formation of a structured network is most likely a more important factor in the increase of bread rigidity than the extent or quality of crystallinity. It is also highly likely that the gluten continuous phase in bread is involved in the network, perhaps along with the starch molecules amylopectin and/or amylose, which increasingly interlink multiple crystalline and amorphous regions.

In this context, a logical model is that the crystallization of the amylose increases granular rigidity and formation of the structured network consisting of interlinked crystallites and gluten. Such a network then dictates the bread's initial firmness.

During storage, comparable phenomena as a result of amylopectin crystallization would contribute to crumb firming. Evidence for this view is that stale bread can be temporarily refreshed by heating it to at least 50–60°C. This results in the melting of the amylopectin crystallites. However, bread crumb continues to lose firmness as it is heated further (Fig. 12.22). This strongly argues that firming involves more than the mere retrogradation of amylopectin.

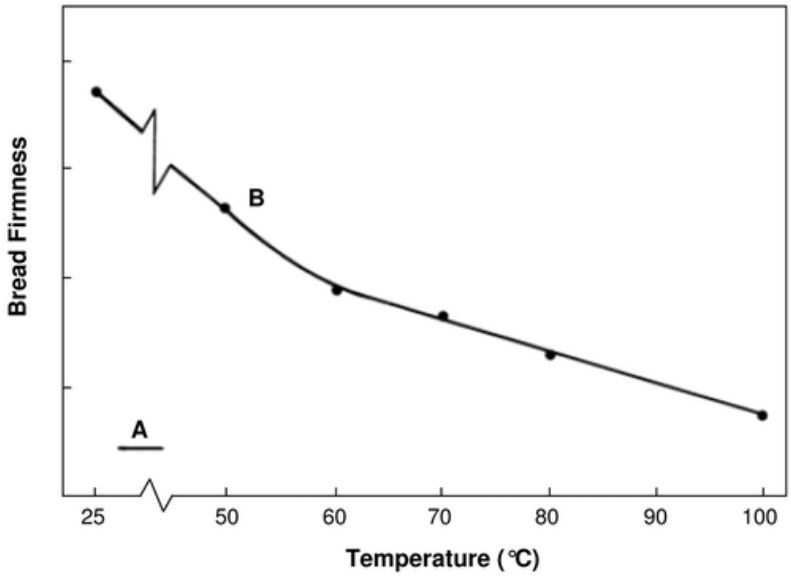


Fig. 12.22. Effect of heating for a specified time at different temperatures on the firmness of bread first stored for five days at room temperature (B). The graph shows that, by reheating the five-day-old bread to 100°C, the firmness can be reduced to almost that of the fresh bread (A). (Adapted from Ghiasi et al 1984)

Amylases as Antifirming Agents

In the absence of amylases, gluten and gelatinized starch are effectively cross-linked. As noted above, during bread cooling, the molecular reorganization of the amylose leads to a network consisting of interlinked crystallites, which is then responsible for the initial bread firmness. During storage, comparable phenomena resulting from amylopectin crystallization contribute to crumb firming.

Certain amylases exert an antifirming effect and thus retard the firming of baked goods. Several authors have suggested that dextrins of a particular size, created by the action of amylases during starch degradation, exert an antifirming effect by interfering with the reassociation and retrogradation of amylopectin and/or the formation of starch-protein cross-links in the aging bread. Other researchers believe that the antistaling effect of amylases is the result of the starch structure, which is modified as a result of the enzyme action and which has different retrogradation properties.

In this case, insight into the bread-firming process can be gained from studying the effects of either a maltogenic amylase from *Bacillus stearothermophilus* or those of an α-amylase from *B. subtilis*. While both enzymes are effective antifirming agents, in contrast to the second enzyme, the first one results in very resilient bread crumb and hence desirable eating qualities, which makes it a much-used enzyme system.

The maltogenic amylase has some unusual structural and starch-degrading properties when compared to those of α-amylases. During baking, following starch gelatinization, it produces mainly maltose from starch, and, in addition to its main exoactivity, it also has some endoactivity, as shown by its action on wheat amylose and β-limit dextrins. The enzyme is believed to have its main effect on amylopectin outer chains through its exoaction. Because of the much higher level of nonreducing ends in amylopectin than in amylose, amylopectin is its predominant substrate. Shortening the amylopectin outer chains by amylase action seriously impedes their recrystallization and hence clearly can explain its antifirming effect. At the same time, the enzyme's endoaction is believed to enhance the crystallization of amylose, probably because it increases amylose mobility. This results in increased initial bread firmness. One way to explain the excellent resilience of bread treated with maltogenic amylase is to invoke the fact that, when the outer chains of amylopectin no longer crystallize during storage, they no longer withdraw water from the amorphous gluten phase for incorporation into the crystal structure. Hence, the gluten remains well plasticized.

In contrast to the *B. stearothermophilus* maltogenic amylase, during baking, the *B. subtilis* α-amylase mainly hydrolyzes starch in an endo-fashion. It thus shortens the amylopectin outer chains to a lesser extent and does not seriously impede their recrystallization. However, its endoaction can still clearly explain its antifirming effect, as it degrades the macromolecular amylopectin structure. Nevertheless, as stated above, the enzyme leads to poor resilience of the resulting bread, as it does not prevent the crystallization of the outer chains of amylopectin and the accompanying withdrawal of water from the amorphous gluten phase for incorporation into the crystal structure.

Other Types of Leavened Products

In addition to the classic white pan bread, many other types of leavened products exist. These include nonwhite wheat breads, rye breads, sourdough-based breads, gluten-free breads, puff pastry and other sweet dough, and, finally, frozen dough. In the following sections, some general information on these systems is provided.

NONWHITE WHEAT BREADS

Breads made from 100% whole wheat, as well as breads from combinations of whole wheat and white flour, are rapidly growing in popularity. Most nonwhite wheat bread contains partly whole-wheat meal and partly strong white flour. Wheat gluten can also be added to the recipe to improve the volume. The formula, other than the type of flour and the addition of wheat gluten (see Chapter 9), does not vary greatly from that used for white bread. Such bread has an acceptable loaf volume and is quite palatable.

RYE BREADS

Rye flour is second only to wheat flour in its ability to retain gas and produce a light loaf of bread. The gas-retaining ability of rye flour appears to result from the arabinoxylan (see Chapter 4) that rye flour contains rather than from the proteins.

In Europe, some bread is made from 100% rye flour. However, this type of bread is rarely seen in North America. Most rye bread sold in North America is made with white wheat flour with enough added rye flour to attain a desired flavor and appearance. Rye flour is generally produced either as light or dark flour. Light rye is just short patent flour, whereas the dark flour is more likely a straight-grade flour to which lower-grade flour streams have been added. The different flour types are used to produce the color and flavor desired. The types of rye bread vary widely, from white wheat loaves containing only small levels of rye to much darker and denser loaves. Rye flour does not have the type of gluten found in wheat and therefore produces a low-volume, dense loaf. Two strange practices are associated with rye bread production in the United States. Formulas for most North American rye breads contain caraway seed, either whole or ground. An equally strange practice is adding caramel as a source of color to white bread that contains just enough rye to be so labeled and then marketing the resulting product as dark rye bread.

SOURDOUGH-BASED BREADS

Before baker's yeast became commercially available, the sour system was the only leavening agent available. Sours are mixtures of naturally occurring organisms that are found in flour or in the atmosphere. They are predominantly bacteria but also contain a number of wild yeasts. The yeasts generally produce gas, and the bacteria are responsible for acid production, although some bacteria also produce gas.

Sours can be started by several techniques. Using old dough is the simplest. As dough becomes old, the yeast becomes inactive, as the pH is low. At the lower pH, bacteria are still quite active. With time, the food available for the organisms becomes limited; however, as new flour is added and the "starter" is fed or rebuilt, the bacteria become more predominant. One must guard against getting the pH too low, because below pH ~3.7,

putrefaction bacteria take over and the odors are quite bad. Generally, this is not a problem, as flour is a relatively good buffer. The desirability of a sour depends upon the flavor produced and the rate of gassing obtained. In general, the gas-producing ability of sours is lower than that of commercial yeast. Consequently, the proof time of sourdough bread is often long, on the order of several hours. Sourdough bread is often produced as round loaves and baked in ovens with steam to give a heavy crust.

GLUTEN-FREE BREADS

A number of reports purport to show that bread can be produced in the absence of gluten. One can argue that such products are not bread. Clearly, they have a texture and grain quite different from what we expect from wheat-flour-based bread. Two different phenomena appear to be responsible for the ability of gluten-free systems to retain gas. The first is the use of agents to materially increase the aqueous viscosity of the system; the second is the use of emuslfiers to enhance a starch-continuous system. Some reported systems have contained locust bean gum or xanthan gum, whereas others have used surfactants. The reported data clearly show that those reagents do indeed result in the retention of gas by a gluten-free starch system. It appears the common thread in these systems is that the additives slow the diffusion of gas.

SWEET DOUGHS

This section concerns doughs with sugar levels exceeding 10% of flour weight. In such a system, the yeast invertase rapidly converts sucrose to glucose and fructose, which increases the osmotic pressure in the dough. While the yeast is fairly osmotic-tolerant, it ferments at a markedly slower rate at such high sugar levels. This is why higher levels of yeast are generally used in sweet-dough preparations. Other than the sugar's effect on yeast, most sweet doughs do not present any particular problems. They tend to be sticky, particularly if they are warm. Keeping the dough temperature low is an advantage. Specific more-osmotic-tolerant yeasts have been developed for use with these sweet doughs.

Puff pastry, croissants, and Danish doughs are made up of layers of dough and layers of shortening or butter. Puff pastry dough differs from other sweet dough as it contains no yeast. To obtain the layers, the dough is worked to a given size; then two thirds of the dough is covered with fat, and the dough is folded to give three layers of dough separated by two layers of fat. The dough is then repeatedly sheeted and lapped. This gives rise to the many, many alternating layers of dough and fat. For the system to work correctly, the fat layer must maintain its continuity. Therefore, the fat must have the correct softening point and rheological properties. Because the fat properties change rapidly with temperature, the dough temperature is carefully controlled. A common practice is to sheet the dough several times and then return it to a cold room to allow it to rest and cool before it is subjected to an additional series of sheetings.

FROZEN DOUGHS

The use of frozen dough, particularly in in-store bakeries, has several advantages. For example, highly trained personnel are not required for the bake-off. In addition, the aroma of freshly baked bread in the supermarket is a definite advantage, and the frozen dough can be held until it is needed and then thawed and used, reducing waste. Other advantages include the production of large amounts of dough using trained personnel at a central location and the ease of shipping the relatively dense frozen dough over long distances. Disadvantages include the shipping of the water in the dough and the need for good temperature control during shipping and storage.

The major disadvantage of frozen dough is the variable performance of the product after frozen storage. In general, dough frozen with no fermentation before freezing performs better than dough frozen after fermentation. Even after a relatively short fermentation time before freezing, the resulting frozen dough takes extended times to proof. Products of fermentation thus appear to be detrimental to the yeast in frozen dough applications. It is also of importance that, under normal industrial conditions, the yeast probably does not freeze. The water around the yeast freezes, but the yeast cytoplasm probably just supercools as it does not freeze until about −35°C.

Another problem with frozen dough is the growth of ice crystals in the dough. As the ice crystals grow during storage, water is removed from the protein. Upon thawing, this water does not go back into the protein but instead results in wet, sticky dough with a coarse structure. Remixing or sheeting of the dough eliminates the problem, but this is usually not a viable option in a bake-off operation.

A rapid rate of freezing is probably desirable, as it limits fermentation time. However, this is difficult to realize. Bread dough, with its gas cells, is a reasonably good insulator, and it is therefore difficult to change either the freezing or thawing rate at any point except on the surface of the dough.

Good industrial practice to obtain optimal product quality includes measures to maintain a constant frozen temperature, to eliminate fermentation before freezing, to use strong wheat flour and/or vital wheat gluten in the recipe, and finally, to use ascorbic acid as an oxidant. Indeed, for reasons that are not clear, ascorbic acid appears to give much better results than do other oxidants in frozen dough systems.

CHAPTER 13: Chemically Leavened Products

The diversity of chemically leavened wheat products made from wheat flour is truly amazing. Such products include cookies (biscuits), cakes, crackers, and pretzels, with wide variation within each of these groups. Cookies not only vary in appearance and taste but also in the type of processing needed to produce desirable products.

In North America, chemically leavened products are, for the most part, made from flour from soft wheats (North American terminology is used in this chapter; see Chapter 1). However, small levels of yeast may be used in some pretzel formulas. In Europe, where no wheats as soft as the typical North American soft wheats are available, wheats of harder texture are the logical raw material. However, the factors that make hard wheat hard apparently have an effect upon the texture of the products made from flour from such wheat. Thus, cookies made from flour from hard wheats are almost invariably harder in texture than the same products made from flour from soft wheats.

Chemical Leavening

The four gases that are capable of leavening wheat products are air, water, carbon dioxide, and ammonia. Air, a mixture of gases, assists in leavening baked products. Water is also present in all baked products, but its leavening effect is quite limited, mostly because it has a relatively high boiling point. Water vapor is an effective leavener only when the product is heated at a very fast rate, as for saltine crackers. In contrast to bread (see Chapter 12), the products described in this chapter are leavened by carbon dioxide produced by chemical reactions of either bicarbonate or carbonate with acids or by the decomposition of ammonium bicarbonate (NH_4HCO_3).

The most common sources of carbon dioxide are sodium or ammonium bicarbonates. Sodium bicarbonate ($NaHCO_3$) reacts with an acid (HA) as follows:

$$NaHCO_3 + HA \rightarrow NaA + CO_2 + H_2O$$

Ammonium bicarbonate, when heated, releases three gases in the following reaction:

$$NH_4HCO_3 \rightarrow NH_3 + CO_2 + H_2O$$

Ammonium bicarbonate can be used only in products that are baked to a moisture content of 5% or less. If products produced with ammonium bicarbonate had higher water content after baking, they would retain ammonia, which would make them inedible. Thus, the use of ammonium bicarbonate is limited to the production of dry cookies and some snack cracker products. In such products, it has the advantage that it leaves no residual salt after it reacts. Residual salts can affect the flavor or the dough rheology or both. Potassium bicarbonate is also a potential source of carbon dioxide for leavening. However, it is generally not used because it tends to be hygroscopic and to impart a slight bitterness to the products.

The most popular leavening agent by far is sodium bicarbonate (baking soda). Its popularity is based upon a number of advantages it offers. It has a relatively low cost and high purity, is easy to handle and nontoxic, and gives a relatively tasteless end product. Sodium carbonate could also be used as a source of carbon dioxide but is not. Its major disadvantage is its high alkalinity, which increases the danger of getting a localized region of high pH that might be detrimental to the product.

To understand the use of carbon dioxide as a leavening gas, one must understand its chemistry. It reacts with water to form carbonic acid (H_2CO_3):

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Carbon dioxide can exist as the free CO_2 or as one of two ion species, bicarbonate (HCO_3^-) or carbonate (CO_3^{-2}). The relative proportion of each is determined by the pH and temperature of the solution. Figure 13.1 shows the effect of pH in determining which species can exist. No leavening gas (CO_2) is available if the pH stays above 8.0. Many soft wheat products end up with a pH near 7.0, where only a part of the CO_2 is in the gaseous state.

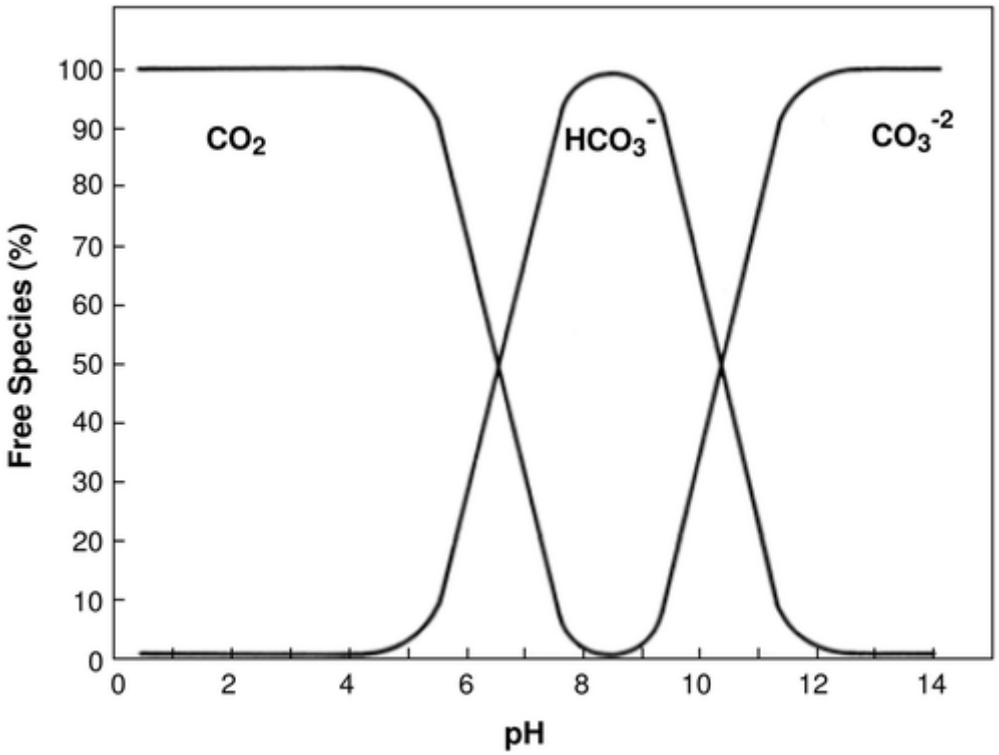


Fig. 13.1. Graphical presentation of the percentages of carbon dioxide (CO_2), bicarbonate (HCO_3^-), and carbonate (CO_3^{-2}) species vs. pH. The graph shows that, below pH 4.0, only carbon dioxide is present, that bicarbonate is the only species present at pH 8.5, and that, above pH 12.0, bicarbonate is the only form. (Courtesy Orion Research Inc., Cambridge, MA)

Sodium bicarbonate ($NaHCO_3$) is quite soluble in water and dissolves rapidly when batter or dough is mixed. This, of course, raises the pH of the system to the point where no carbon dioxide is released. Heating of sodium bicarbonate in an aqueous system causes it to disproportionate into carbon dioxide and sodium carbonate (Na_2CO_3), as follows:

$$2\ NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

When acids are added to batter or dough systems in combination with $NaHCO_3$, a larger yield of carbon dioxide is obtained and the rate of its evolution can be better controlled. Many ingredients used in baking are sources of acid. Acidic fruits or buttermilk are obvious examples.

If the formula does not contain the acid, then a combination of baking soda and an acid (i.e., baking powder) must be used. Baking powders consist of mixtures of baking soda, one or more acid salts, and a diluent. In the United States, by law, a baking powder must yield not less than 12% available carbon dioxide. That regulation effectively establishes the level of soda. The acid or acids used are determined by their neutralization values (see below). The inert diluent is usually dried starch. Its primary function is to physically separate the soda and acid particles and prevent their premature reaction.

Baking powders are either single- or double-acting. A double-acting baking powder is one that contains two acids, one that reacts because it is soluble already at room temperature and another that reacts when the product is heated.

The amount of acid required in a formulation depends upon the amount of soda and the neutralization value of the acid. Because the acids used are acidic salts, the stoichiometry of their reactions is often not clear. Therefore, the concept of neutralization value was developed.

$$\text{Neutralization value} = \frac{\text{g of } NaHCO_3 \times 100}{100 \text{ g of acidic salt}}$$

Generally, the final pH of the product should not be affected by the leavening reaction. However, if the correct amount of acid is not used, the properties and taste of the product will change. For example, an excess of soda generally gives the product a soapy flavor. The color of many products is highly dependent upon the pH.

Several leavening acids are used in the baking industry. In general, the acids vary in their rate of reaction at various temperatures (Fig. 13.2). Table 13.1 lists the properties of the most common leavening acids.

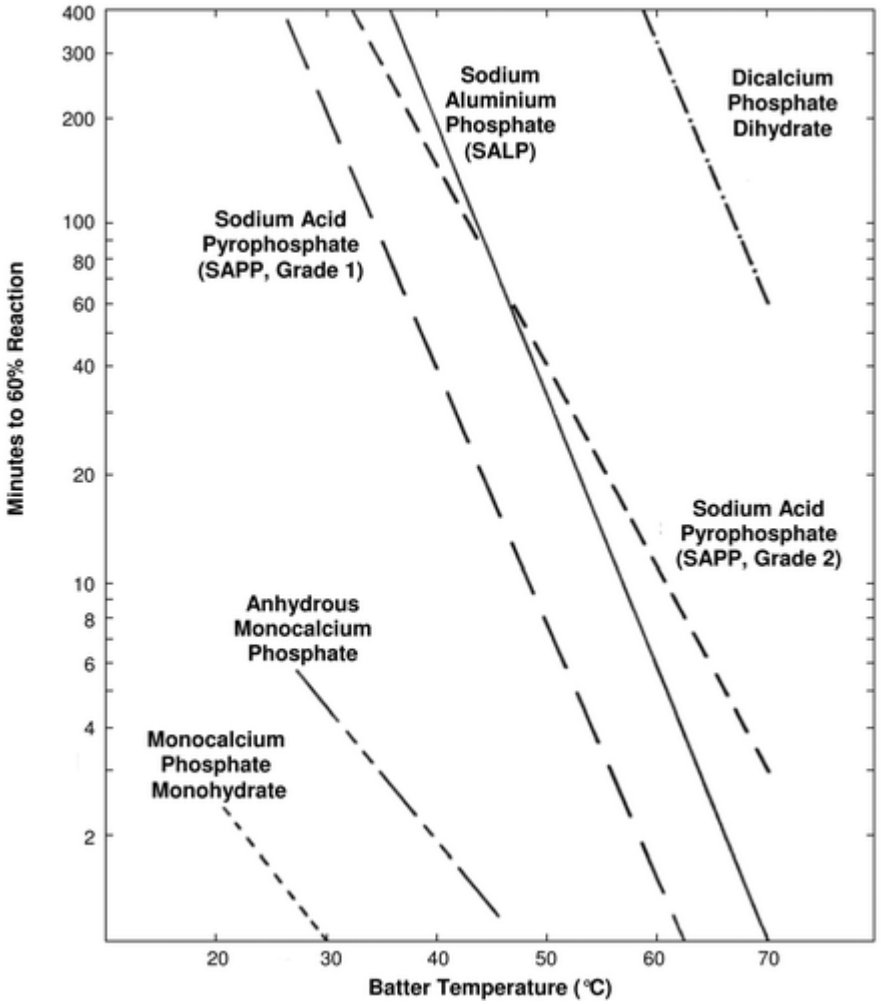


Fig. 13.2. Time (in min) after which the reaction of various leavening acids in a batter has occurred to an extent of 60%, plotted as a function of temperature. Different grades of sodium acid pyrophosphate (SAPP) exist. The higher the temperature, the faster the leavening acids react. (Adapted from Kickline and Conn 1970)

TABLE 13.1
Properties of Common Leavening Acids

Leavening Acid	Formula	Neutralization Value	Relative Reaction Rates[a]
Cream of tartar (monopotassium tartrate)	$KHC_4H_4O_6$	45	1
Monocalcium phosphate monohydrate	$CaH_4(PO_4)\ H_2O$	80	1
Anhydrous monocalcium phosphate	$CaH(PO_4)$	83.5	2
Sodium acid pyrophosphate (SAPP)	$Na_2H_2P_2O_7$	72	3
Sodium aluminum phosphate (SALP)	$NaH_{14}Al_3(PO_4)_8\ 4H_2O$	100	4
Sodium aluminum sulfate (SAS)	$Al_2(SO_4)_3\ Na_2SO_4$	100	4
Dicalcium phosphate dihydrate	$CaHPO_4\ 2H_2O$	33	5[b]
Glucono-δ-lactone (GDL)	$C_6H_{10}O_6$	50	…[c]

[a] Relative rate: 1 = reactive at room temperature, 5 = requires oven temperature for reaction.
[b] Generally reacts too slowly to be a leavening acid; used to adjust final pH.
[c] Reaction rate depends on many factors in addition to temperature.

Cream of tartar, i.e., the monopotassium salt of tartaric acid, the original leavening acid, was obtained as a co-product from wine production. It reacts readily at room temperature. Because it is relatively expensive, it has been largely replaced by monocalcium phosphate in most applications. Monocalcium phosphate also reacts readily at room temperature and is widely used as the fast-acting component in double-acting baking powders.

Several sodium acid pyrophosphates (SAPPs) are on the market. They vary in their reaction rates, depending upon how they are made. SAPPs are used widely in canned biscuits and in cake doughnuts, both of which have unique leavening requirements that are handled only by the SAPPs. The major problem with SAPPs is the aftertaste that they leave in the mouth. The so-called "pyro" taste that they induce is quite noticeable in these products. It apparently comes from the exchange of calcium from the teeth for the sodium in the disodium phosphate that results from the leavening reaction and is the result of the enzyme action that splits the pyrophosphate. Attempts to limit the effect of the disodium phosphate by adding various forms of calcium to the formula have been only partially successful.

Sodium aluminum phosphate (SALP) is the newest of the leavening acids. It is widely used as the second (higher-temperature) acid in double-acting baking powders and also in commercial baking mixtures. It not only is a good leavening acid, it also gives strong products with a strong crumb texture.

Sodium aluminum sulfate (SAS) was the most common second acid in baking powders before SALP was available. It is still used in some formulations. The major problems with SAS are its weakening effect on crumb texture and its slightly astringent taste.

Dicalcium phosphate is not an acidic salt and thus would not be expected to give a leavening reaction. However, at higher temperatures, the salt disproportionates and gives an acidic reaction. Generally, this happens at too high a temperature for the salt to be useful as a leavening acid, but it is useful to adjust the final pH of the product.

The internal ester glucono-δ-lactone produces an acid as it is hydrolyzed. Its usefulness in baked products is somewhat limited, as the hydrolysis occurs over a wide temperature range. It also tends to produce products with a slightly bitter aftertaste. Its major advantage is that it does not produce the inorganic salts found with other leavening acids.

Besides their obvious effects upon the amount and rate of gas production and, in some cases, their effect upon the product's taste, the salts produced by the leavening reaction can affect the rheology of the product. In general, di- or trivalent ions tend to increase the elasticity of the product, and sulfate ions tend to decrease its elasticity. These ions presumably act by forming ionic cross-links with the proteins in the batters.

In the United States, cookies are products made from flour from soft wheat. They are characterized by a formula high in sugar and shortening and relatively low in water. Similar products made in Europe and the United Kingdom are called "biscuits." The "biscuits" made in the United States are more accurately defined as chemically leavened bread. The diversity of cookie products is quite wide. They vary not only in formula but also in type of manufacture. Even then, several products do not fit the above definition of cookies but are still called "cookies" mainly because they don't fit elsewhere.

In commercial practice, cookies are baked in long tunnel ovens. Typically, the baking zone of such an oven is 1 m wide and between 30 and 150 m long. The cookies are generally baked on a solid steel band that conveys the product through the oven at a rate that produces the desired bake time (Fig. 13.3). Cookies can be classified according to the properties of their doughs. Hard doughs are related to bread dough since they have a developed gluten network, but they are of a stiff consistency. Short doughs, on the other hand, are much more like cake batters but contain much less water. Their consistency can be compared to that of wet sand, and, as a consequence, when pulled or under pressure, their structure breaks; i.e., it is short. These doughs have only limited, if any, gluten development. Perhaps the best way to classify cookies made from short doughs is by the way the dough is placed on the baking band. Such a classification allows us to divide cookies into four general types.

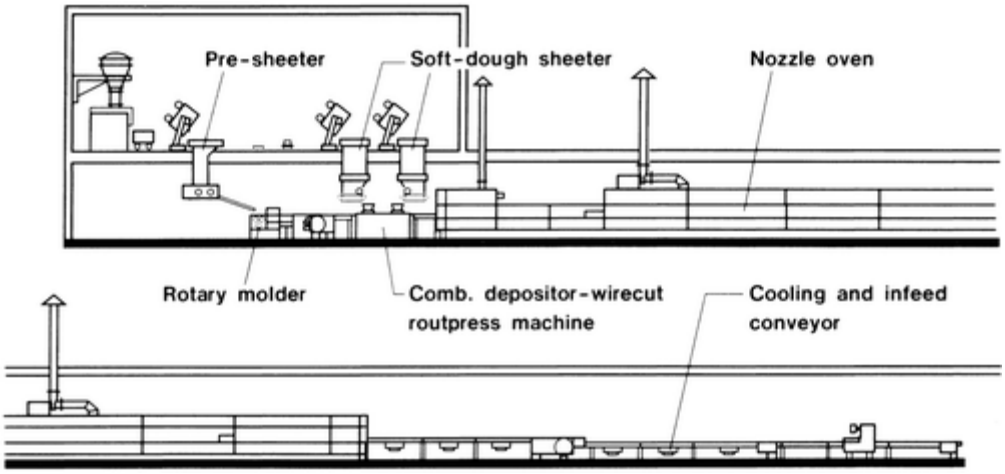


Fig. 13.3. Illustration of a typical cookie line that can be adapted to produce several types of cookies. (Courtesy Werner and Pfleiderer, Stuttgart, Germany)

ROTARY-MOLD COOKIES

For this type of cookie, the dough is forced into molds on a rotating roll. As the roll completes a half turn, the dough is extracted from the cavity and placed on the band for baking. The consistency of the dough must be such that it will feed into the cavity with no voids but still be extracted from the cavity without being distorted. During baking, the cookie should neither rise nor spread. Any significant movement will distort the design embossed on the cookie.

Formulations for rotary-mold cookies (Table 13.2) are characterized by fairly high sugar and shortening levels and very low levels of water in the recipe (<20%, based on the flour and including the moisture in the flour). The typical dough is crumbly, lumpy, and stiff, with virtually no elasticity. The gluten in the dough should not develop during mixing. Much of the cohesiveness of this type of dough comes from the plastic shortening used. The cookie does not spread during baking.

TABLE 13.2
Typical Formula for Rotary-Mold Cookies

Ingredient	Parts	Ingredient	Parts
Flour (soft wheat)	100	Condensed milk	6.0
Sugar	20	Whole egg	3.5
Shortening	25	Butter	1.2
Cream of tartar	0.5	Lecithin	0.3
Sodium bicarbonate	0.5	Malt	1.4
Salt	1.5	Water (variable)	~10.0

Rotary-mold cookies are economical to produce. A small amount of water is added to the dough and, therefore, less energy is required to remove it during baking. A rotary mold is generally used if it can make the desired product. Typical examples of American cookies made on rotary-mold equipment are Oreo and Hydrox cookies.

CUTTING-MACHINE COOKIES

The process for this type of cookie includes both rotary-cut and stamped doughs. The dough is made into a continuous sheet, and the product is cut out from it (Figs. 13.4 and 13.5). Typical examples are animal cookies, gingerbread men, etc. The formula contains much more water than do formulas used with a rotary mold. The sugar content is relatively low compared to that of most cookies. Because of the high water level and low sugar level, and since the dough has been sheeted, the dough is developed in this system. The gluten development stops spread and distortion during baking of this type of cookie.

Fig. 13.4. Photograph showing continuous production of cookie dough pieces by rotary cutting of a dough sheet. The dough scrap is removed by lifting it away. (Courtesy D. Ortiz, Kellogg Company, Battle Creek, MI)

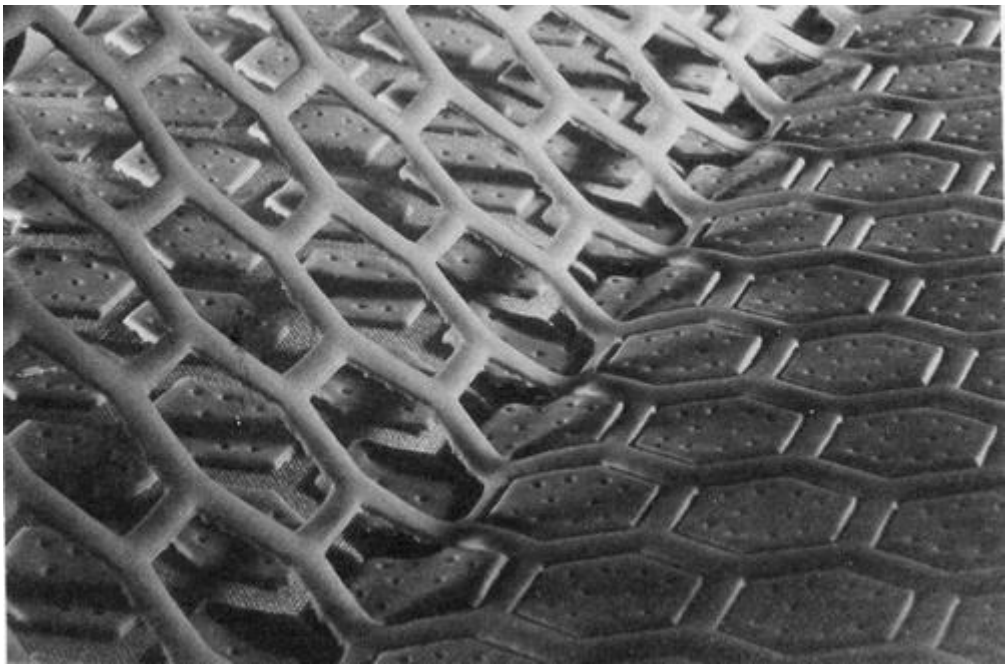


Fig. 13.5. Rotary-cut pieces from sheeted dough, with the scrap being lifted away. (Courtesy Werner and Pfleiderer, Stuttgart, Germany)

WIRE-CUT COOKIES

Relatively soft dough is extruded through an orifice and cut to size, usually by a reciprocating wire. The dough must be cohesive enough to hold together, yet short enough to separate cleanly when cut by the wire. A typical formulation, based on flour weight, may contain 50–75% sugar, 50–60% shortening, and up to 15% eggs, or, when no eggs are used, 40–60% sugar, 15–50% shortening, and 8–35% water. Wire-cut machines can handle a range of cookie dough types, and a wide variety of products can be made. Wire-cut cookies rise and spread as they are baked. In addition to common cookies including sugar snap, chocolate chip, and oatmeal cookies, fig or date bars can be coextruded and wire-cut.

SUGAR WAFERS

This type does not really fit our definition of cookies, but it does not fit elsewhere. Ice-cream cones and sugar wafers differ from other cookies. The dough formula (Table 13.3) contains no sugar, essentially no fat, and a large excess of water.

TABLE 13.3
Typical Formula for Wafers or Ice Cream Cones

Ingredient	Parts
Flour	100
Water	135
Sodium bicarbonate	0.375
Salt	0.5
Lecithin	1.5
Coconut oil	1

The flour is usually of a short extraction (see Chapter 8) and, in the United States, is generally from a white wheat. The bran specks from red wheat would show up in the product. If the flour has too little gluten, excessively dense products generally result. If the flour is too strong, the wafers are hard and flinty. The ingredients are generally mixed to produce a lumpfree batter. Overmixing, or for that matter, simply holding

the batter too long, causes the gluten strands to separate from the aqueous mixture. Therefore, a common practice is to make small batches and use each batch in a relatively short time.

Even though sodium bicarbonate is in the formula, its major function is to adjust the pH, not to act as a leavening agent. The primary leavening in this product is the steam produced from water. Baking is usually done in a closed-plate system that resembles waffle irons (Fig. 13.6). Sets of plates travel on an endless chain through the heating chamber. The plates open automatically and are filled with batter. Products that stick to the plate and go through another cycle present major problems. The double shot of batter often springs the plates so that they no longer operate correctly. Wafers are also produced in continuous ovens.

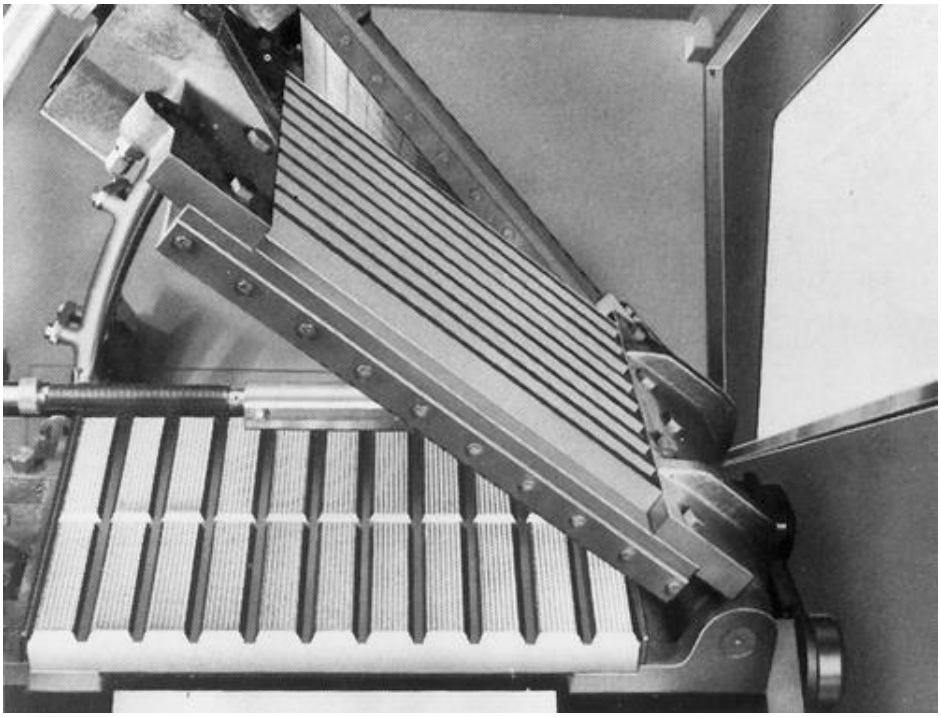


Fig. 13.6. Sugar wafer baking unit, showing the plates. (Courtesy Hass Machinery of America, Inc., Richmond, VA)

After baking, the product is cut into "books" and the filling placed between the various layers. The filling generally consists of fat, sugar, flavors, and ground scrap product. The breakage is quite high for this type of product, particularly for ice cream cones.

Cookie Flour Quality

As with all quality determinations, one must first define what constitutes good quality. In general, cookie quality can be summarized in three general terms.

The first is the size of the cookie, both the width and the height. The importance of cookie size can be appreciated if one considers that the cookie box, with its appropriate labeling, including net weight, has standard dimensions. With many cookie recipes, the size of the final cookie very much depends on how the cookie dough spreads in the oven. If cookies spread too much in the oven, they do not fit in the box without breaking. If the spread is too little, then the box is not completely filled and the net weight is in error. The problem is avoided with rotary-mold or rotary-cut cookies, which have no spread in the oven, but not all types of cookies can be produced on that equipment.

The second is how the cookie bites. Good quality cookies must have a tender bite.

The third concerns the cookie surface. Cookies having shallow, narrow cracks are considered to be the most desirable. This quality is not strictly determined by the cookie flour quality.

The nice, tender bite associated with good-quality cookies comes from two major factors. The use of fat, or shortening, as it is usually called, produces a short product, i.e., a product that lacks long-range interactions and has little, if any, gluten development. The word *shortening* came from this usage. The second factor is the flour. Generally, good flour gives products with a tender bite.

COOKIE DOUGH PRODUCTION

The primary function of the mixing step in making cookie dough is to produce a uniform mixture and to incorporate air into it. For high-quality products, that often requires creaming, i.e., mixing the sugar and shortening, as a preliminary step. The advantage of creaming is discussed later in this chapter in the context of cake production. In general, gluten development during mixing is not desired. Development of the gluten leads to tough products and generally to cookies that do not spread. Therefore, following creaming, in a second step, the flour is added with minimal mixing. A small amount of gluten development is needed in dough that will be sheeted and cut. Sometimes the dough is allowed to equilibrate for (typically) 30 min to ensure a consistent product quality.

In general, the retarding of gluten development is not much of a problem. With the high levels of sugar and fat added in most cookie formulas and the relatively high pH because of the sodium bicarbonate, the gluten proteins do not develop very readily. Gluten cannot develop if it is not hydrated. Sugar has a drastic effect on gluten development, as discussed later in this chapter.

COOKIE BAKING

When cookie dough is heated in an oven, several events occur. They can be shown by heating cookie dough in a differential scanning calorimeter (DSC) (Fig. 13.7).

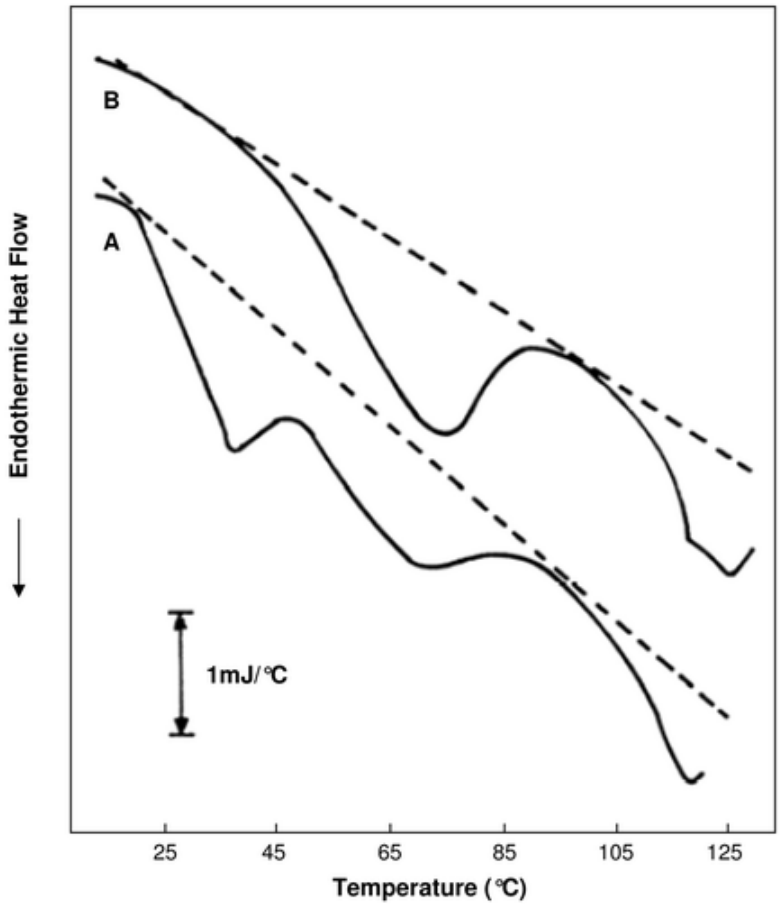


Fig. 13.7. Differential scanning calorimetry thermogram for cookie dough (A) and cookie dough containing no shortening (B). The dashed lines are the baselines. (Reprinted, with permission, from Abboud and Hoseney 1984)

Fat Melting and Sugar Dissolution

First, the shortening in the dough melts. Shortening gives the dough part of its plastic character, so the dough containing melted shortening is freer to flow under the force of gravity. The second thermal event is dissolution of the sucrose. With a typical cookie recipe, only about one-half the sucrose is dissolved during mixing. The remainder stays in a crystalline form until the dough is heated. It then dissolves as well.

When sucrose dissolves, it increases the volume of solution in the system. Each gram of sugar, when dissolved in 1.0 g of water, produces about 1.6 cm^3 of solution. One of the effects of this can be seen in Figure 13.8, where the addition of dry sugar turns a powder system into a suspension. The increase in total solution also has a pronounced effect on the cookie dough. The increased solvent makes it sticky. Thus, if one attempts to produce cookies from syrup rather than crystalline sucrose, sticky dough that does not machine well is obtained.

Fig. 13.8. Starch-water mixture (1:1, left) and starch-water-sugar mixture (1:1:1, right). (Reprinted, with permission, from Ghiasi et al 1982)

Absence of Starch Gelatinization

Continued heating of the cookie dough in the DSC gives an additional endotherm at about 115°C, presumably because of starch gelatinization. Because the moist cookie dough does not reach this temperature during baking, it can be assumed that the starch does not gelatinize during cookie baking. This is confirmed by grinding the dried cookie crumb and heating it in the DSC. An endotherm equal in size to that found in the unbaked cookie dough is found, which shows that starch is not gelatinized during cookie baking. However, there are many cookie formulas, and those low in sugar and/or high in water content may well have some starch gelatinization.

Underlying Mechanisms of Cookie Baking

Time-lapse photography has been used to monitor the development of cookie spread during baking of sugar snap cookies made from excellent- and poor-quality cookie flours. As demonstrated in Figure 13.9. the lateral and vertical dimensional changes of such cookies during baking are markedly affected by flour quality. During the first 2 min in the oven, baking behavior is similar for both poor and excellent cookie flour doughs. Both types of cookies expand in width and height due to the production of leavening gases. By the third minute of the baking cycle, the cookie baked from excellent cookie flour spreads more rapidly and continues to spread for a longer period during baking than the cookie from the poor cookie flour. Cookies made from excellent cookie flours cannot support their own weight against uncontrolled, structural collapse under gravitational force. The resulting expansion (increased cookie diameter) and decreased cookie height are accompanied by progressive structural collapse throughout the baking cycle, with the most dramatic phase of collapse occurring in the last minute of the 10-min baking cycle. In contrast, the cookie made from poor cookie flour withstands collapse during baking.

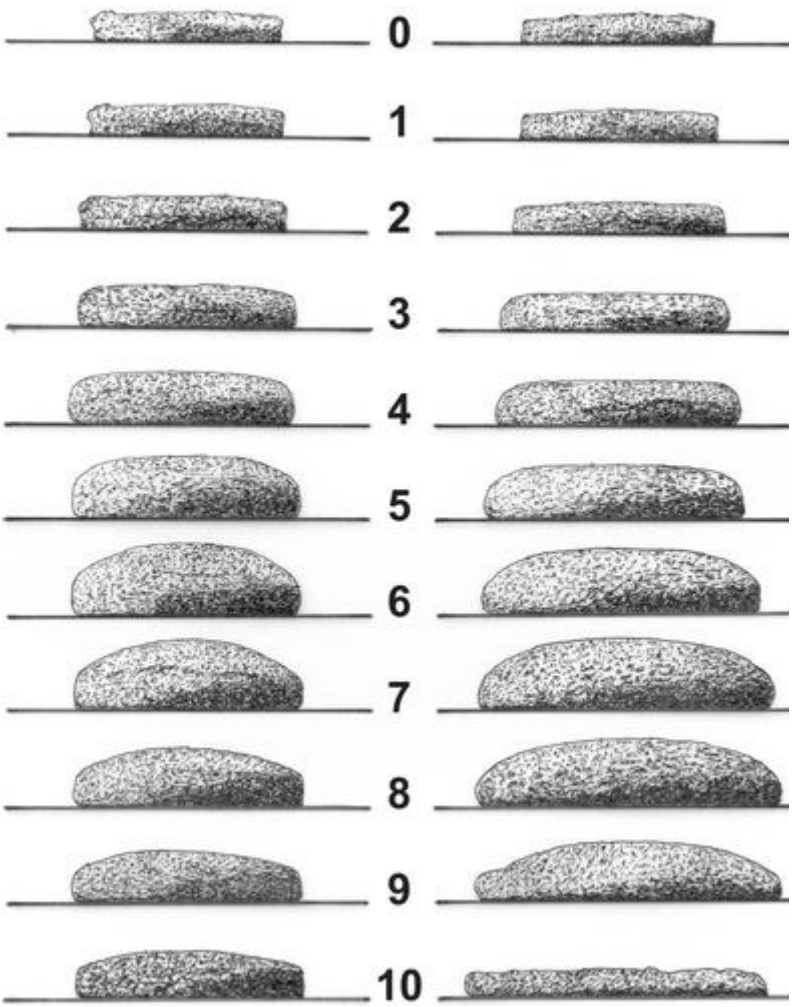


Fig. 13.9. Stylized time-lapse photographs demonstrating the development of cookie spread during sugar snap cookie baking for a poor quality (left) and excellent quality (right) cookie flour. The baking time (on the left side of the photograph, in minutes) increases from top to bottom. The lateral and vertical dimensional changes during baking are markedly affected by flour quality. During the first 2 min in the oven, baking behavior is similar for both poor and excellent cookie flour doughs. Both types of cookies expand in width and height due to the production of leavening gases. By the third minute of the baking cycle, the cookie baked from excellent cookie flour spreads more rapidly and continues to spread for a longer period during baking than the cookie from the poor cookie flour. Cookies made from excellent cookie flours cannot support their own weight against uncontrolled, structural collapse under gravitational force. (Adapted from Yamazaki and Lord, 1971)

Cookie expansion and lateral flow have been related to the viscosity of the system. At baking temperatures, cookie dough made from excellent cookie flour has a lower viscosity than cookie dough made from poor cookie flour and thus shows more expansion due to faster flow under gravity. The question then arises as to what the underlying mechanisms of the viscosity of cookie dough are. While starch and soluble starch in the wheat flour may affect cookie spread, starch gelatinization can be ruled out, as discussed above. It appears that the viscosity changes during baking are related to the wheat proteins. The wheat proteins in a sugar snap cookie formula are not developed into a continuous gluten network during mixing. When the dough is heated during baking, the wheat gluten proteins go through their glass transition (see Chapter 6), thereby gaining mobility that allows them to interact and to form a continuous gluten phase. The viscosity of this continuous gluten phase is sufficient to stop the flow of the cookie dough. In cookie doughs from poor cookie-quality flours, this continuous gluten network is formed earlier and appears to be sufficiently strong to account for the resistance to expansion and spread during baking and the prevention of structural collapse.

Apart from gluten structural effects on viscosity, sucrose as a major ingredient in the cookie system is likely to play a role in the differences of cookie diameter when flours of different quality are used for cookie baking. Sucrose can act as a plasticizer, but it is much less effective than water due to its larger molecular mass. Antiplasticizing agents increase the glass transition temperature (T_g, see Chapter 6). Therefore, in comparison with water, sucrose may have an effect by acting as an antiplasticizer. The T_g of a cookie dough made from excellent cookie flour is raised to higher temperatures than the T_g of a cookie dough made from poor cookie flour. Since setting (i.e., the stop of cookie spread) is possible when the cookie system goes through T_g and thus into the flexible/rubbery region (where gluten proteins can form a network that increases the viscosity to a

degree sufficient to stop flow of the dough), doughs from excellent cookie flour would have more time to spread, resulting in a larger cookie diameter.

Cracking Pattern Development

Certain cookies, e.g., gingersnaps, have a cracking pattern on the surface. This cracking pattern develops during baking. The phenomenon has been explained as follows. Moisture is lost from the surface of the cookie at a rapid rate during baking. The hot air in the oven has the capacity to hold a large amount of water. As the water from the surface is lost, it is replaced by water diffusing from the interior of the cookie, and the sugar, not being volatile, is concentrated. Sucrose is, of course, the most popular sugar used in cookies. One of the unique properties of sucrose is its tendency to crystallize. In fact, it crystallizes at the surface of the cookie during baking. After the sugar has crystallized, it no longer holds the water that gives a moist and moldable surface. Thus, the surface dries and breaks as the leavening system expands the cookie, producing the cracked surface. Small amounts of high-fructose corn (maize) syrup or certain other sugars, such as glucose, fructose, or maltose, interfere with sucrose crystallizing and thus destroy the cracking ability (Fig. 13.10). A casual examination of gingersnaps readily reveals which contain corn (maize) syrups and which do not.

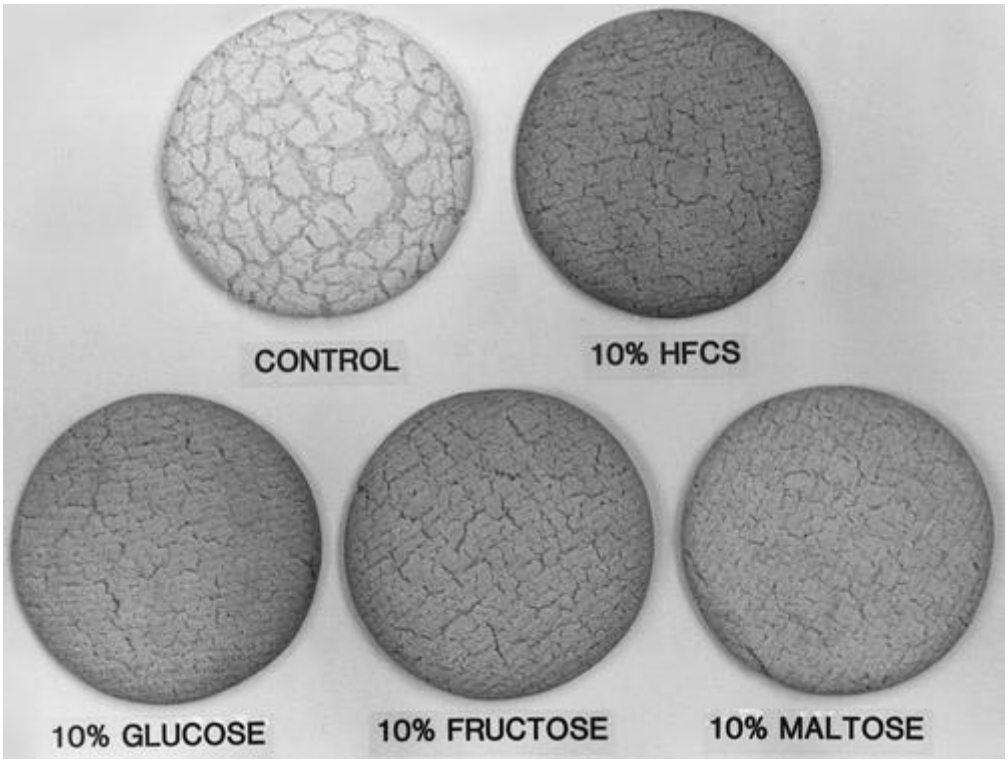


Fig. 13.10. Effect of small amounts of corn (maize) syrup and various sugars on the cracking pattern of cookies. HFCS = high-fructose corn syrup. (Reprinted, with permission, from Doescher and Hoseney 1985)

Cookie Texture Development

Essentially all cookies, except those that are dried to very low moisture content, are soft and quite flexible when they come out of the oven. With time, they become firm and often brittle. Some, such as sugar-snap or gingersnap cookies, give an audible snap when they are broken. This appears to be because of the crystallization of sucrose. When the sugar dissolves, the syrup gives the cookie flexibility. Indeed, if one wants to maintain a soft cookie, one can add a sugar or other substance that interferes with sucrose crystallization. If sucrose is allowed to crystallize, the water associated with the sugar is no longer controlled by the sugar and is free to migrate to other components. However, because the cookie has low moisture content after baking, i.e., 2–5%, its starch and protein are still glassy and therefore brittle. It is the brittle break that causes the snap in cookie. The change in texture, measured as the force necessary to fracture the cookie with time, has been shown with force deformation curves (Fig. 13.11).

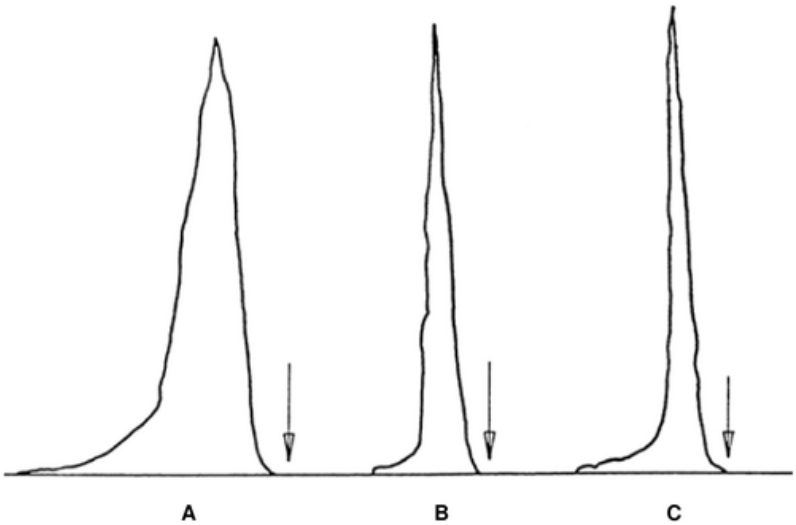


Fig. 13.11. Instron curves showing the force to compress sugar-snap cookies vs. time one day (A) and three (B) and five (C) days after baking. The arrows indicate starting points. The curves clearly show that sugar-snap cookies lose their potential to bend between days 1 and 3. The loss of the potential to bend is reflected in the development of the audible snap characteristic. (Reprinted, with permission, from Curley and Hoseney 1984)

Summary

As the cookie dough enters the oven and starts to heat, the shortening melts and gives the dough more fluidity. At the same time, the sugar dissolves and thereby increases the quantity of mobile phase. This also increases fluidity and allows the dough to spread as a function of gravity. The leavening system becomes active and expands the piece in all directions. The cookie continues to spread until the viscosity of the system becomes too large. Because starch is not gelatinized, the increase in viscosity is presumably a property of the flour proteins. In some cookies, a surface cracking pattern is detected as a result of sucrose crystallization, and the audible snap when one eats a sugar-snap cookie is also the result of sugar crystallization.

Crackers

As for cookies, a definition of crackers must be quite broad, as there are many types of crackers. In general, crackers contain little or no sugar but moderate to high (10–20%) levels of fat, based on flour weight. The doughs generally contain low levels of water (20–30%). The leavening is brought about either by water vapor or a chemical leavening system.

SALTINE CRACKERS

Saltine crackers are distinguished by their long fermentation time and their particularly light and flaky texture. They are made by a sponge and dough process with a formula similar to that given in Table 13.4.

TABLE 13.4
Typical Saltine Cracker Formula[a,b]

Ingredients	Sponge (%)	Dough (%)
Flour	65.0	35.0
Water	25.0	…
Yeast	0.4	…
Lard	…	11.0
Salt	…	1.8
Soda	…	0.45

[a] Ingredients based on flour weight.
[b] A "buffer" is often added to the sponge to inoculate the system.

Sponge Fermentation

The sponge fermentation is typically 16 h. During this fermentation, the pH drops from about 6.0 to about 4.0. An inoculum rich in bacteria is generally used to obtain this pH drop. The inoculum is called a "buffer" and is generally an old sponge. The quality of saltine crackers can vary widely, depending upon the activity and amount of buffer used. The bacteria play an important role in the changes occurring during fermentation. Flour contains only limited amounts of carbohydrates that can be utilized by either the yeast or the bacteria. Thus, in the sponge, the yeast and the bacteria compete for the fermentables. By using low levels of yeast and the added buffer inoculum, the bacteria are given the upper hand in the competition. If one uses too much yeast, it will win the battle for the fermentables.

During fermentation, the sponge becomes less elastic. Flour contains a proteolytic enzyme that has an optimum pH of 4.1. The action of this enzyme is thought to be important in modifying the dough's texture. This may also be the reason that the sponge must reach a pH of 4.1.

Dough Fermentation

After its fermentation, the sponge is mixed with the other dough ingredients and the dough flour. Included in the dough ingredients is sufficient sodium bicarbonate to bring the dough pH to above pH 7.0. For the correct taste and texture, the baked saltine should have a pH of about 7.2. Generally, baking reduces the pH by 0.1.

The dough fermentation period is typically 6 h. Because of the high pH, the yeast fermentation is predominant. Except for any changes brought about by the yeast, the dough is allowed to relax.

Dough Processing

Typically, 24 h after the sponge was set, the dough is ready to be processed (Fig. 13.12). The dough is laminated or lapped (Figs. 13.13 and 13.14) into eight layers of 0.3 mm each. After layering, the dough is passed through rolls to reduce its thickness from 2.5 cm to 0.30 mm. This is done in several steps and with a 90° "turn" involved. In this way, the dough is sheeted in both directions and is resistant to extension. After sheeting, the dough is cut and docked (Fig. 13.15). Cutting is usually done with a rotary cutter, which cuts (Fig. 13.15) the individual crackers to size but leaves them together in a continuous sheet. After cutting, the dough is docked. The purpose of docking is to attach the top and bottom surfaces of dough together, so it won't separate into layers. Docking is accomplished with docker pins that have a blunt end of about 0.15 cm diameter. The docking pins must create holes completely through the dough sheet. After docking, 2.5% salt (flour basis) is typically added to dough, and it is then baked.

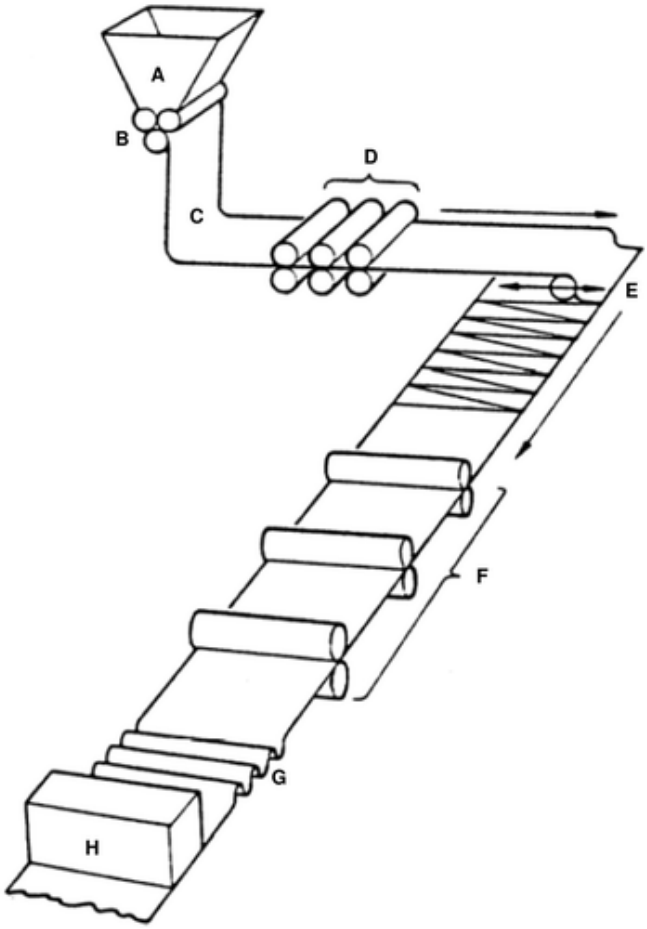


Fig. 13.12. Processing of a cracker dough. Dough hopper (A), dough-forming rolls (B), dough web (C), reduction rolls (D), lapper (E), final reduction (F), relaxing curl (G), and cutter-docker (H). (Courtesy Werner and Pfleiderer, Stuttgart, Germany)

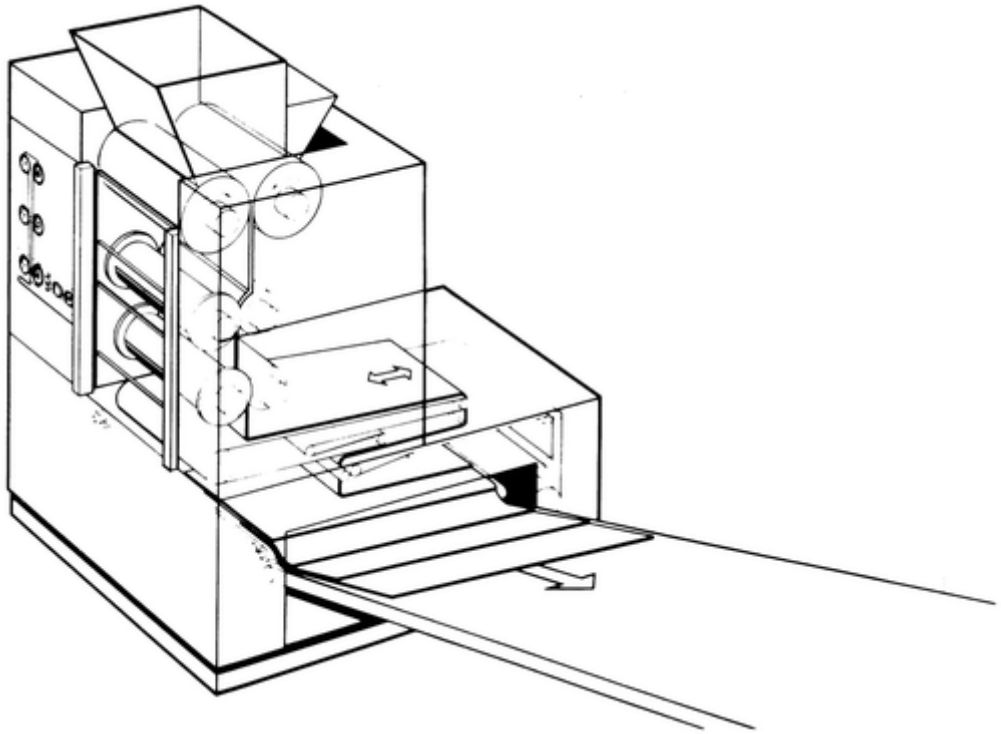


Fig. 13.13. A see-through view of forming rolls and laminator for cracker lines. (Courtesy Werner and Pfleiderer, Stuttgart, Germany)

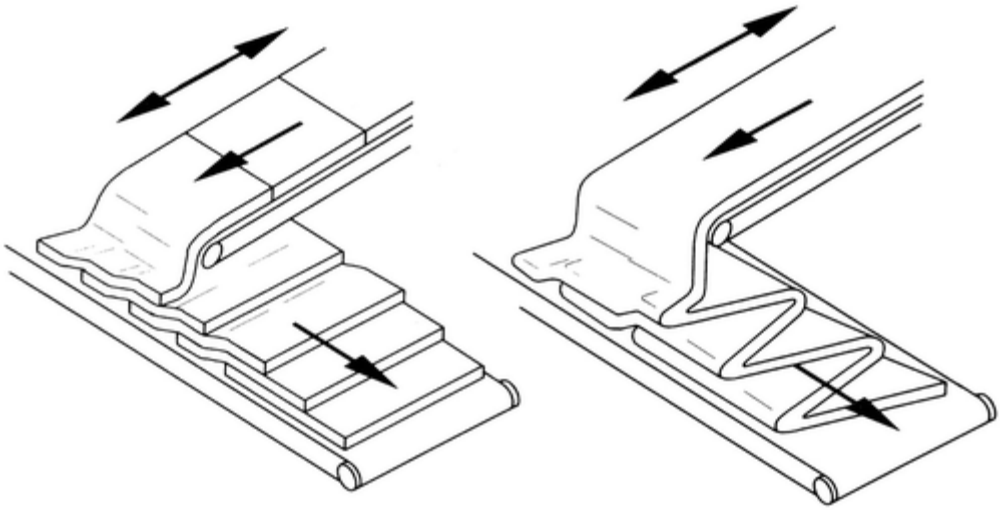


Fig. 13.14. Illustration of cutting lapping (**left**) and reciprocating lapping (**right**) of cracker doughs. (Courtesy Werner and Pfleiderer, Stuttgart, Germany)

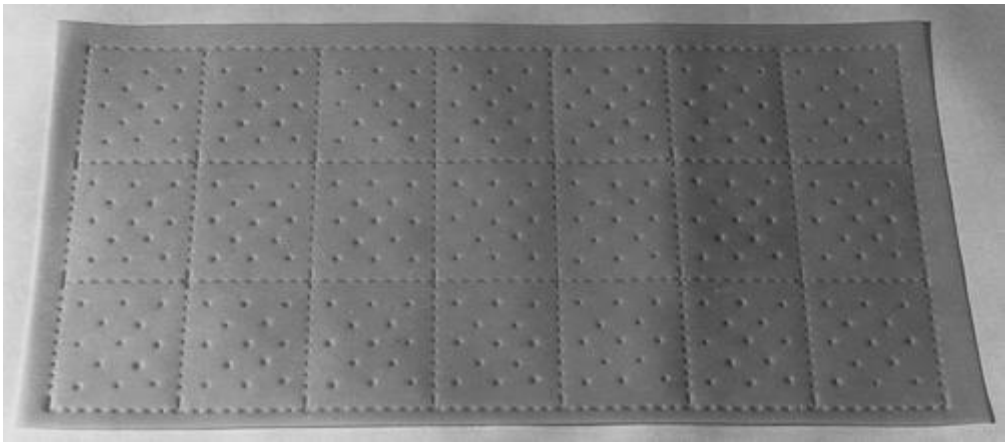


Fig. 13.15. Cracker dough after cutting and docking. (Reprinted, with permission, from Pizzinatto and Hoseney 1980)

Cracker Baking

Typically, the ovens' baking chambers are 100 m long and 1 m wide. The baking surface is a mesh band so moisture can be lost from the bottom of the cracker. If not, the cracker would curl during baking. Obviously, this is undesirable for a number of reasons.

Baking time is typically 2.5 min at 230°C. The rapid heating vaporizes water while it is still inside the dough and thus puffs the layers of the cracker between the points tied together by the docking holes (Fig. 13.16). Heating more slowly would just lead to loss of the water at the surface and no puffing. After baking, the crackers are cooled slowly so that they do not check; i.e., they do not develop tiny cracks that lead to breakage during shipping. The sheets of crackers are then mechanically broken into the individual crackers and packaged. Much of the texture and desirability of saltine crackers is a result of their low moisture content. When fresh from the oven, the crackers typically contain 2% moisture. They are packaged to maintain that low moisture, as even small increases in moisture decrease the desirability of the product.

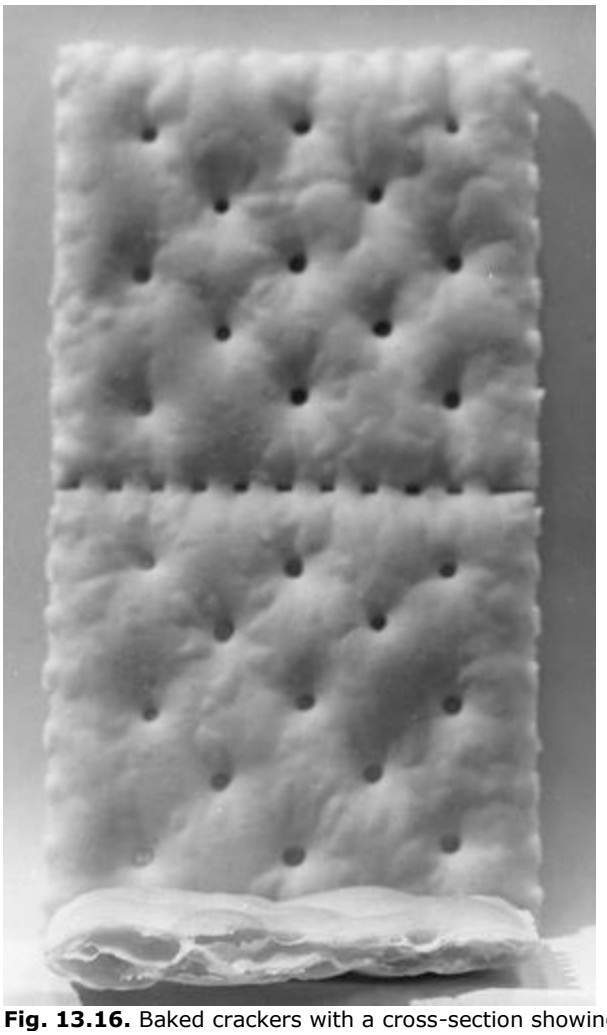


Fig. 13.16. Baked crackers with a cross-section showing the internal structure. (Reprinted, with permission, from Pizzinatto and Hoseney 1980)

SNACK CRACKERS

Traditionally, snack crackers were plain or flavored with cheese. However, in recent years, the types of flavors used to product snack crackers have expanded greatly. Whole meal, cracked wheat, and various vegetables and herbs are now used to flavor crackers. There has also been a trend to produce bite-sized crackers, which traditionally was not done because of the large amount of scrap dough produced. Many low or no-fat products are also on the market. The no-fat products have a firm bite and clearly show that shortening is important for controlling the texture of such products.

Snack crackers vary much more widely in formula than do saltines. In general, they contain more shortening and much higher levels of flavoring materials. They generally do not contain yeast and are not given an extended fermentation period. They are chemically leavened. The doughs are mixed once with all the ingredients, allowed to rest, sheeted and laminated, and then cut and docked. Cutting is usually in a more unique shape than found with saltines, and this gives rise to more scrap dough that must be added back to the doughs. In general, the texture of snack crackers is denser than that of saltines.

Cakes, like cookies, are characterized by high levels of sugar and fat in the formula. The difference between the two is that cakes also contain relatively high levels of water. Because the molar sugar concentration is much lower in cakes than in cookies, the starch gelatinizes during baking. Because of that difference, cakes set when baked, giving a light product. The set is caused, at least in part, by starch gelatinization and coagulation of egg protein. In cookies, the starch does not gelatinize or, if it does, such as in low-sugar recipes, it swells only to a limited extent and, therefore, the structure collapses.

Because the light structure of cakes is important, one must be concerned about how to obtain it. As was discussed in Chapter 12, no new cells can be created after mixing either by chemical leavening or by yeast. Thus, air must be incorporated into the batter in the form of small air cells (i.e., nuclei) during mixing. For bread, the number of cells can be increased with punches or remixes. However, for cakes, all the cells must be created during mixing and some cells are lost later in the process.

The setting of cakes in the oven appears to be partially the result of starch gelatinization and egg protein coagulation. As starch gelatinizes, it goes from an inert body that can bind about 30% of its weight of water to one that binds several times its weight. The setting of egg white is a complex process involving at least three phenomena: denaturation, aggregation, and gelation. The combination of the above increases the viscosity of the batter tremendously, which gives the batter a solid appearance and thus sets the cake. As discussed in Chapter 2, the sugar in the formula controls the temperature at which starch gelatinizes. The temperature at which egg protein denatures is also influenced by sugar concentration. Consequently, the formula controls at what temperature the cake batter transforms from a fluid to a solid. If this transformation occurs at a temperature below the boiling point of water, the cake sets into a solid system. If it occurs above the boiling point of water, the batter does not set, and the cake collapses into a fudge-like mixture.

Good cake batters must retain sufficient viscosity during heating to keep the starch suspended. If the starch, which is dense, settles, a tough rubbery layer forms at the bottom of the cake pan, and a very light fluffy foam is formed at the top. The higher viscosity also keeps the air bubbles from colliding with sufficient force to coalesce into larger bubbles. Large bubbles would have sufficient buoyancy to rise to the surface and be lost.

It is important to pick the correct baking powder for the cake. Generally, a double-acting powder is used. The first acid acts at room temperature to help nucleate the batter. The second acts during the oven stage. The leavening action must be timed so that the gas is produced while the batter can still expand but not so early that a major part of the gas may diffuse out. However, if the gas is released too late, not only can the batter not expand, but the cake's grain can be destroyed by the excess pressure that is developed. Besides the obvious effect of releasing gas, the choice of leavening acids can also have other effects. Di- and trivalent cations such as calcium (+2) and aluminum (+3) tend to impart a greater resiliency to the cake crumb. On the other hand, sulfate ions tend to weaken the crumb. Also, different leavening acids tend to buffer at slightly different pH levels. For example, monosodium phosphate buffers at pH 7.3, whereas aluminum phosphate does so at pH 7.1. This can change the appearance of the crumb. A change of only 0.2 pH units has a quite noticeable effect on the whiteness of the cake crumb.

Finally, generally, the finer the particle size, the better the cake flour. Therefore, most cake flours are pin-milled (see Chapter 8) to reduce the particle size. Pin-milling also increases the damaged starch in the sample, but this does not appear to affect the cake flour quality.

Different cake formulas are used in practice. An important cake type in the United States is the layer cake. A second type is the angel food cake, and a third is pound cake.

LAYER CAKES

Table 13.5 lists a typical formula for white layer cake. Because it contains more sugar than flour, it is referred to as a high-ratio cake. The flour used is chlorinated. Egg whites are important in that they contribute protein that helps trap air in the aqueous phase. Also, egg protein denatures and helps set a structure as a result of heating. As discussed below, shortening is important in multistage-mix cakes because it traps the air during the creaming step. Shortening is also important because it gives a more tender cake. Besides sugar's obvious function as a sweetening agent, it also has a tenderizing effect on the crumb, presumably because it delays gelatinization of starch. Reducing sugars are often added to the formula in the form of milk, which supplies lactose or fresh egg whites, which are a source of glucose, to give Maillard browning (see Chapter 12). Sucrose is nonreducing and, because the formula contains no yeast and therefore no invertase to hydrolyze sucrose to reducing sugars, it does not give browning. Also, because the pH of the system is basic, no chemical hydrolysis of sucrose to glucose and fructose occurs. Therefore, when sucrose is the only sugar in the formula, no browning takes place and the cake surface is quite white.

TABLE 13.5
Typical Formula for a Rich White Layer Cake

Ingredients	Percent, Flour Basis
Flour	100
Sugar	140
Shortening	55
Egg whites (fresh)	76
Milk (fresh)	95
Baking powder	1.3
Salt	0.7

Mixing Procedures

The mixing procedures for layer cakes fall into three different types, depending upon how the air is incorporated into the batter. Much of the confusion found in the literature on cakes is caused by not clearly defining what type of cake is being discussed.

Multistage Mixing. The first type of cake is made with multistage mixing. This is the classic procedure that starts with a creaming step. Fat and sugar are mixed together to form a cream. The purpose of the creaming step is to incorporate air into the fat. Two and even three subsequent mixing steps then incorporate the liquids and flour to form the final batter. Creaming steps are also used for certain types of cookies. An advantage of creaming is the formation of a large number of air cells, which lead to a fine texture. Also, the batter can sit for extended periods of time because the air is in the fat, where it is immobile and hence stable. As the cake batter is heated and the shortening melts, the air cells are released into the aqueous phase, where the leavening gases can diffuse into them and thereby leaven the cake. Cakes made by the creaming procedure generally have a very fine grain.

Single-Stage Mixing. The second type of cake is made with single-stage mixing. This type is bought as a box mix. To make cake mixes of the single-stage mixing type, the mix must be run through a cake finisher. This is essentially a grinder. Apparently, the purpose of the finishing is to bind the shortening to the flour. Microscopic examination of the finished mix shows no free fat in the mix even though it contains 20–25% fat. Presumably, free fat would destabilize the aqueous foam that is produced as a result of mixing.

The consumer just adds the liquids and mixes. In this case, the air is incorporated directly into the aqueous phase. This can be accomplished because the mix contains emulsifiers that lower the interfacial tension and allow the air to be incorporated directly. Propylene glycol monostearate (Fig. 12.2) is a common emulsifier used for this purpose.

When air is incorporated directly into the aqueous phase, the batter is not as stable as is a creamed batter. Gas can diffuse in a batter and, because the pressure in a small bubble is larger than the pressure in a large bubble (Chapter 12), there is a tendency for the small bubbles to disappear and the large bubbles to become larger. This phenomenon is controlled by diffusion. Gas diffuses out of the small bubbles into the aqueous phase and then into the larger bubbles. Because of the greater buoyancy, the larger bubbles overcome the high viscosity in the batter, rise to the surface and are lost. Thus, such cake batters should not be allowed to sit for long periods of time before being baked. Cakes made by single-stage mixing are generally quite delicate and not suitable for shipping. Therefore, they are not suitable for commercialization.

Mechanical Air Incorporation. In the third type of cake, the air is incorporated directly into the aqueous phase by mechanical means rather than by using emulsifiers. This type is made commercially, using high-speed mixing machines.

Flour

Flour for high-ratio cakes must be treated with chlorine gas (see Chapter 8). Use of unchlorinated flour gives cakes that collapse in the oven. The literature shows that chlorine reacts with almost all flour constituents. The rate of reaction is quite rapid with flour and much slower with starch. However, fractionation and reconstitution studies have shown that the reaction with the starch is responsible for the improvement in baking properties. The actual important effect of chlorine appears to be the formation of oxidized starch, which swells at a faster rate than untreated starch. This gives a more viscous batter at the same temperature than that with unoxidized flour. The increased viscosity of the batter keeps the cake from collapsing in the oven and, to some extent, after it is removed from the oven. The amount of chlorine gas used is critical. When chlorine reacts with organic material, hydrochloric acid is usually produced. Thus, the pH of the flour generally is a good measure of the extent of reaction and therefore of the amount of chlorine added. Generally, a pH of 4.7–4.9 is desired for most high-ratio cakes.

Egg Whites

Egg whites are added to cake to help build their structure. The proteins in egg white increase viscosity at room temperature by incorporating air bubbles. In addition, egg white proteins can set during heating and thereby greatly increase the viscosity at higher temperatures. Figure 13.17 shows that fresh egg whites are much more effective at doing this than are dried egg whites. It appears that the dried egg whites are denatured during the drying process, as they give no DSC denaturation peak (Fig. 13.18). Also, as outlined above, egg whites are a source of glucose, and, hence, contribute to Maillard browning.

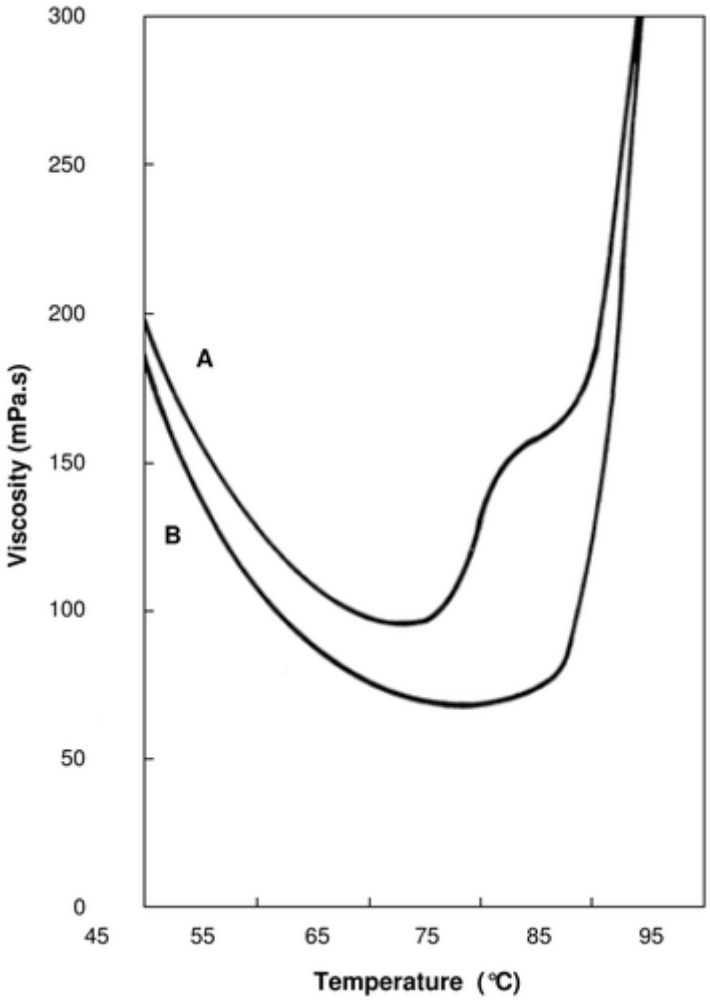


Fig. 13.17. Viscosity vs. temperature plots of cake batters containing fresh (A) or dried (B) egg whites. (Reprinted, with permission, from Shelke et al 1990)

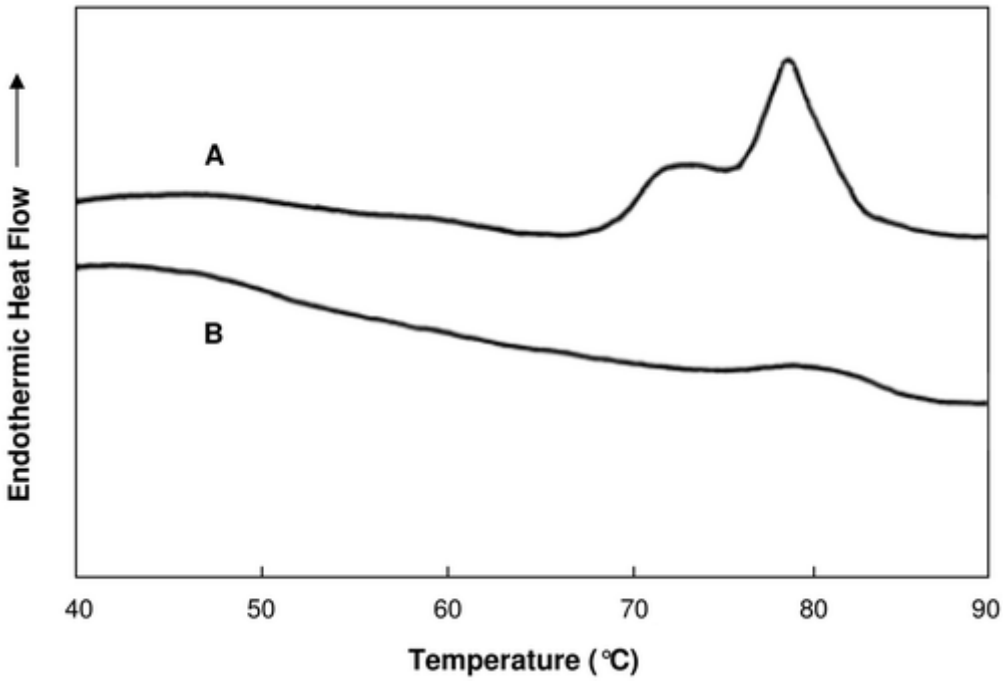


Fig. 13.18. Differential scanning calorimetric scans of fresh (A) and rehydrated dried (B) egg whites. (Reprinted, with permission, from Shelke et al 1990)

Shortening

Table 13.6 shows the effect of temperature and shortening emulsified with mono- and diacylglycerols on the viscosity of cake batters made with the AACC International white layer cake formula. Batter viscosity at ambient temperature increases with increased levels of shortening in the batter. However, the minimum viscosity of the batters when heated decreases with increased shortening levels. This suggests that, while the plastic shortening increases the viscosity, once it is melted to create a liquid phase it decreases viscosity in the oven. The viscosity of a cake batter is very important during the baking step. Too low a viscosity allows large bubbles to rise to the surface and escape. It also allows starch granules to accumulate at the bottom on the cake pan and produce a rubbery layer during baking (see above).

TABLE 13.6
Effect of Increasing Levels of Emulsified Shortening on AACC International White Layer Cake Batters

Shortening[a]	Viscosity (mPa·s)		Onset Temperature[b] (°C)	Onset Slope[c] (mPa·s/°C)	Cake Volume (cm^3)
	At Ambient Temperature	Of Heated Batter			
30	1,540 ± 20	108 ± 5	83 ± 0.5	81	995 ± 10
50[d]	1,950 ± 25	85 ± 5	83 ± 0.5	56	955 ± 10
80	2,250 ± 25	50 ± 5	83 ± 0.5	43	845 ± 5

[a] Percent based on flour weight.
[b] Onset of gelatinization.
[c] Rate of starch swelling.
[d] Control.

The level of shortening in the cake formula does not affect the onset of starch gelatinization (Table 13.6). However, high levels of shortening decrease the rate of viscosity increase. This suggests that the shortening decreases the rate of starch swelling.

Emulsifiers

The addition of certain emulsifiers to the formula of high-ratio, single-stage cake mixes is essential for incorporating sufficient air into the batter during mixing. The emulsifiers increase the batter viscosity. Presumably, this reflects the incorporation of additional air into the batter. The incorporation of air is also evident from the decreased specific gravity of the batter containing emulsifiers. Batters containing emulsifiers maintain higher viscosities throughout the heating period. Their presence also changes the rate of increase in viscosity. In this regard, their effect is comparable to that of shortening.

Sugars

Sugar increases the temperature at which starch gelatinizes. Thus, it is not surprising that the onset temperature of the rapid increase in viscosity increases as the level of sugar in the batter is increased. Perhaps less obvious is the effect of sugar level on batter viscosity. At ambient temperature, viscosity increases as the sugar level is increased. However, as the temperature is increased to the point where viscosity is at a minimum, that viscosity is much lower as the sugar level in the batter is increased.

The changes in viscosity can be explained as follows. At ambient temperature, much of the added sugar remains as a solid, as there is insufficient water to dissolve it all. The solid particles are responsible for the higher viscosity. As the temperature is raised, more of the sugar is dissolved, not only decreasing the number of solid particles but also increasing the amount and volume of mobile phase. Both of these factors decrease the viscosity.

ANGEL FOOD CAKES

Besides the more-standard layer cakes, it is useful to also consider foam or angel food cakes. Table 13.7 shows a formula for angel food cake. Only a low level of flour is used. The flour used is weak and is often diluted with wheat starch. The egg whites are the most important component in the angel food formula. Generally, the eggs and sugar are whipped to a protein foam, and the flour is folded in carefully so as not to disrupt the foam. The function of the flour appears to be to provide starch that will gelatinize and thereby remove excess free water. The cream of tartar (see above) is added to reduce the pH and thereby improve the whipping of the egg whites. The formula contains no leavening agent. The leavening is produced simply by the air trapped in the egg white foam. Care must be taken not to introduce any fat into the formula, as fat destabilizes the foam. In fact, one cannot use plastic containers because they retain enough fat to destroy the foam.

TABLE 13.7
Typical Formula for an Angel Food Cake

Ingredients	Percent Based on Flour Weight
Flour	100
Egg whites (fresh)	500
Sugar	500
Cream of tartar	20

POUND CAKES

Another type of cake that uses air for leavening is the "pound" cake, also called "Madeira" cake. The original formula for a pound cake was 1 lb (454 g) each of flour, butter, eggs, and sugar. This made a very heavy, rich, and expensive cake. Table 13.8 lists a more typical formula. It produces a lighter cake with better eating and keeping qualities.

TABLE 13.8
Typical Formula for Commercial Pound Cake

Ingredients	Percent Based on Flour Weight
Flour	100
Eggs (whole, fresh)	50
Shortening	50
Sugar	100
Milk (fresh)	50

Madeira cakes are often prepared with the creaming method. That way, air cells are incorporated into the fat. After the creaming step, the eggs are added. The sugar goes into solution, and a water-in-oil emulsion is formed, the air cells being dispersed in the fat phase only. Addition of flour changes the system into a multiphase structure. The flour particles are suspended in the aqueous phase of the now complete batter. The functions of the different ingredients are similar to those described for layer cakes (see above).

Biscuits

The American biscuit, actually a chemically leavened bread or bun, is unique to the United States. It has become quite popular, particularly in fast-food establishments. The use of chemical leavening gives dough that results in a rather thick cell wall and a coarse grain in the final product. The flavor is strongly influenced by the taste of the soda and the leavening acid. The production process is quite simple. The dough is mixed, sheeted to a desired thickness, cut, and baked.

A variation of the chemically leavened biscuit is the type sold refrigerated and packed in cans. The cans are actually foil-lined cardboard containers. The dough is mixed, sheeted, cut to size, and placed in the can. The volume of dough added to the can is much smaller than the volume of the can. The ratio of the two volumes must be carefully controlled. After the cans are sealed, they are placed in a proof box at a temperature high enough to trigger the leavening system but low enough not to hurt the dough properties. The dough then "proofs"; i.e., it expands to fill the can. The excess air that was in the can is expressed through the can, which is permeable to air but not to dough. The dough builds a pressure of about 0.1 MPa (1.0 bar) and in this condition is quite stable for typically 60–90 days. Because the dough is not sterile, organisms eventually destroy the quality of the biscuit. Once this starts, the pH drops, the pressure in the can increases to dangerous levels, and the dough becomes very short. These factors obviously limit the shelf life of the product.

The leavening acid for refrigerated biscuits must meet strict requirements. It must not react during mixing or sheeting of the dough but must react in the proof-room. This requirement is met only by some SAPPs.

CHAPTER 14: Pasta and Noodles

Pasta and noodles are wheat-based products formed from unleavened dough with different processes and raw materials. The formulations are generally very simple. For pasta, often only semolina and water are used. The ingredient list for oriental noodles is in many instances limited to flour, water, and salt(s) while, for North American noodles, the same ingredients and egg products are used. We here concentrate on the raw materials, the production processes, and the properties of these products.

Pasta, paste, and *alimentary pastes* are terms that describe a large number of products (Figs. 14.1 and 14.2). In this book, the term *pasta* is used to describe the extruded products that are generally made from durum wheats (*Triticum durum*Desf.; see Chapter 1).

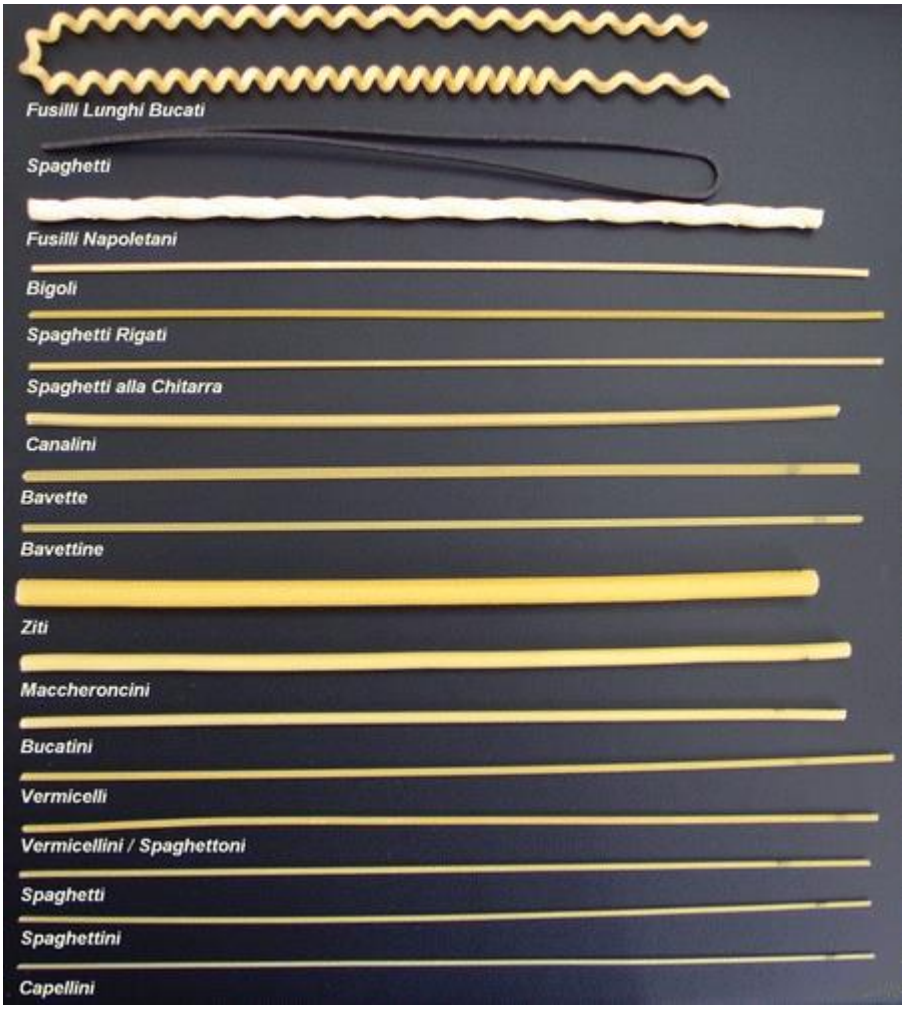


Fig. 14.1. Examples of long pasta products.

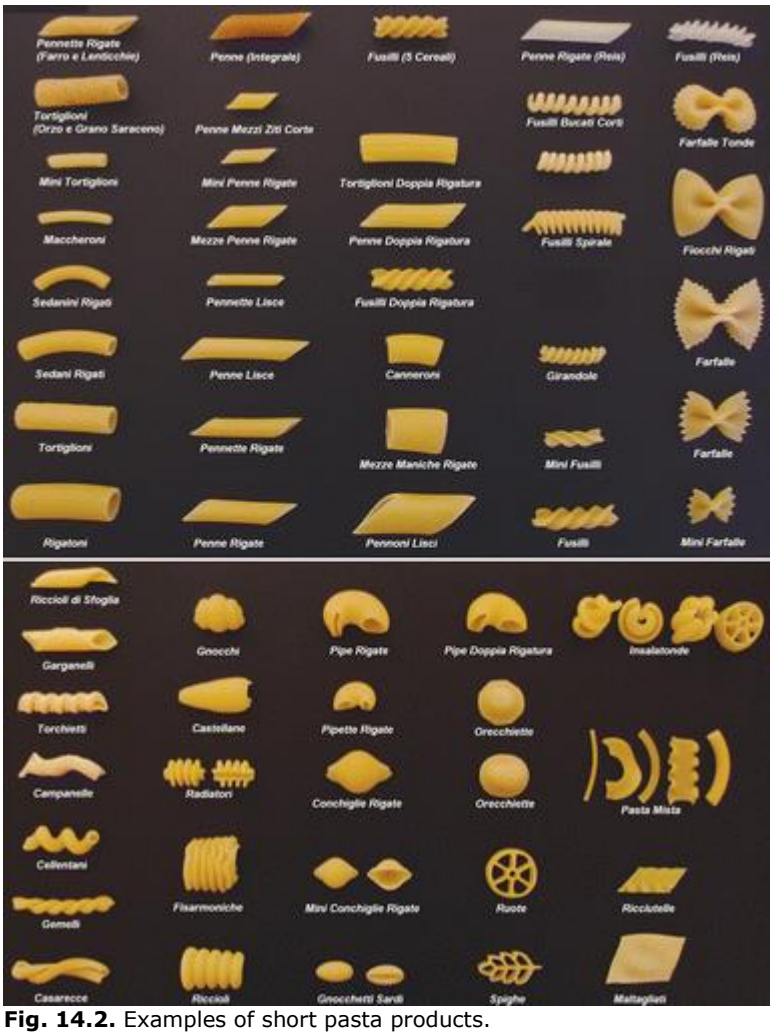


Fig. 14.2. Examples of short pasta products.

Italy is the largest pasta-maker in the world, with 3.5 million tonnes of pasta produced every year, half of which is exported all over the world. Although pasta is consumed worldwide, the annual consumption per person varies quite widely. In the United States, the consumption is about 9 kg per person per year, whereas that in Italy is about 28 kg per person per year. In other European countries such as Belgium, the average annual consumption is as low as 4–5 kg per year.

The most common types are macaroni and spaghetti. The U.S. Standards of Identity state that macaroni must be tube-shaped, hollow, and more than 0.11 in. but not more than 0.27 in. in diameter, while spaghetti must be cordshaped, not tubular, and more than 0.06 in. but less than 0.11 in. in diameter. Neither Italy nor the European Union has standards for shapes and names of pasta products. Although, based on its long tradition, Italy has many different types of pasta products, the country is very restrictive about the raw materials that can be used to make pasta. The basic composition of pasta is durum wheat semolina, and flour from bread wheat is not admitted at all. Today, the use of only durum wheat semolina is common practice in most Western European countries, as well as in the United States. However, in some Eastern European as well some Latin American countries, pasta is still produced with flour, although the trend there clearly is to increasingly adopt the Italian standard.

Defining pasta as an extruded product made with durum semolina effectively eliminates the various noodle products from being considered pasta. It also eliminates the couscous made in North Africa with durum semolina because, for couscous production, semolina is steamed and agglomerated into particles of about 2 mm in diameter. The product may be dried and resteamed before being eaten or may be eaten directly. Even with such restrictions, the number of products, shapes, and sizes of pasta made is astounding. Some manufacturers regularly make over 50 different products.

DURUM WHEAT AND PASTA QUALITY

It is generally believed that the ideal raw material for pasta is semolina from durum wheat rather than milling products from other wheat types. As outlined in Chapter 1, durum wheats are tetraploids, while common wheats (*T. aestivum* L.) are hexaploids. North American durums are mostly spring wheats. Although winter durums also exist, they are not grown commercially. In Europe and North Africa, durums are mostly planted for the winter cycle.

The durum wheat endosperm is high in carotenoid pigments (Fig. 14.3), which give the pasta its yellow color. Because of the relationship between the yellow color and consumer acceptance, the level of pigmentation has been used as a selection tool for good-quality durum.

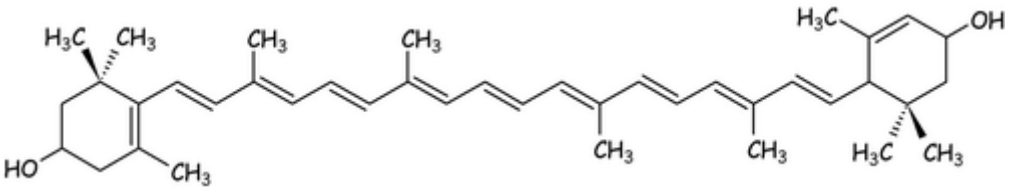


Fig. 14.3. Structure of a carotenoid pigment (α-dihydroxy carotene). (Courtesy M. Verswyvel)

Uncooked pasta should be uniformly yellow, as consumer acceptance has been strongly linked to a uniform translucent, yellow color. In addition, it should be mechanically strong and retain its size and shape during packaging and shipment. When cooked in boiling water, the product should maintain its integrity. The cooking water should be free of starch. After cooking, the pasta should give a firm "al dente" bite, and the surface should not be sticky. Finally, the pasta should be resistant to overcooking.

The use of durum wheats for breadmaking purposes seems to be limited mainly to North Africa and India. Durum gluten is usually weaker than that of common wheat. Nevertheless, cultivars with stronger gluten are more suited for breadmaking purposes than those with weaker gluten. Interestingly, the durum wheats with stronger gluten generally also give pasta with a stronger al dente bite.

Probably the most outstanding characteristic of durum wheats is their hardness. The grain is physically very hard, much harder than the hard common wheats (see Chapter 1). As outlined in Chapter 8, durum wheat is milled to give good yields of semolina and not milled to flour, as such milling inevitably would lead to excessively high degrees of starch damage. Flour is also produced as a co-product, but, in general, it is of lower value than the semolina. The flour is often used to make noodles but can also be used to make pasta. Durum flour generally gives excellent products. However, they are not as resistant to overcooking as are products made from semolina.

In many countries, when durum wheat is expensive, common hard wheat (North American terminology, see Chapter 1) farina, i.e., purified middlings from hard wheat (see Chapters 8 and 15), is often blended with durum or used by itself to produce pasta. In general, the hard-wheat farina produces good pasta. However, it does not have the yellow color because of lower levels of carotenoids in farina than in semolina and because it is not as resistant to overcooking as pasta produced from semolina.

PASTA PRODUCTION

Pasta production consists of hydration and mixing to obtain a homogeneous mass, which is then further kneaded, extruded through a die, dried, and packaged.

Hydration and Mixing

In essence, water is added to semolina to obtain about 31% moisture content. The level of water is therefore about one-half of the level used in bread dough. At such moisture content, the dough produced is very dry. When mixed, the dough made from durum wheat semolina and water forms into agglomerates (balls) of a homogeneous size, with an average diameter of a few centimeters. The size of the agglomerates is diagnostic for the correct level of water. Too much water gives larger agglomerates and eventually continuous dough, whereas too little water produces small agglomerates and a floury appearance, indicating insufficient hydration.

Mixing is performed in an airtight mixer in the absence of air. Air in the mixer is detrimental for two reasons. First, as the dough is forced down the barrel of the extruder, air is dissolved in the aqueous phase of the dough. When the pressure is removed as the dough exits the die, small bubbles can appear in the extruded piece. These small air bubbles make the piece appear opaque rather than translucent, which interferes with the perception of the yellow color. Also, the air bubbles cause points of weakness in the dried product. Second, all

semolina contains some activity of the enzyme lipoxygenase (see Chapter 4), which, in the presence of molecular oxygen, oxidizes the durum semolina's polyunsaturated free fatty acids and, in the process, co-oxidizes and bleaches the carotenoid pigments. Therefore, to control the bleaching action, the oxygen content is kept as low as possible.

Kneading and Extrusion

From the mixer, the dough enters an auger that kneads and exerts pressure on the dough as it moves down the barrel of the extruder to the die. The combined effects of kneading and pressure produce smooth, homogeneous dough that can be extruded. A considerable amount of unwanted heat is produced in that process. Therefore, the extruder barrel is jacketed and cooled with water. In general, the temperature of the dough is maintained at less than 45°C. Because both the temperature and the moisture content of the dough are low, essentially no expansion is obtained as the product exits the die, and no starch gelatinization occurs in the process.

The dies are normally made of bronze, although both stainless steel and Teflon-coated dies are also used. Bronze dies give excellent products but tend to wear out rapidly, as pasta products are abrasive and erode the soft bronze. As a result, worn-out bronze dies give misshapen products. Bronze dies must also be cleaned thoroughly or frozen when not in use. If not, the bacteria in the dough produce acids that pit the die, leading to inferior products. Both stainless steel and Teflon dies are smoother than bronze. They allow higher production rates and yield smoother and yellower products. However, the change in the surface character of the products also changes their cooking characteristics. The product cooks more slowly; water penetration is slower; and the surface tends to become mushy.

Drying as a Quality-Determining Factor

The extruded product still contains about 30% moisture. Its moisture content must be reduced to about 12% before the product is stable for shipment and storage. The drying process is a delicate operation as both drying too fast or too slowly lead to serious quality defects. When drying is too fast, only the surface layers dry and, because of moisture loss, undergo contraction. When, later on in the process, the inner layers also dry, they also contract. As a result, the outer layers crack and form fine, hairline fissures. This is called "checking." Checking makes the product appear opaque and also decreases its strength. If drying is too slow, long goods such as spaghetti stretch under their own weight. Also, if not dried sufficiently rapidly, products turn sour or develop mold.

In addition to the above, quality aspects such as the al dente bite, the stickiness and integrity of cooked pasta, and the loss of starch to the cooking water are all related to the drying procedures used. Ideal pasta clearly resists overcooking and does not readily lose starch to the cooking water.

It seems obvious that the level and quality of gluten proteins play a pivotal role in this respect. During drying, their properties are affected to a degree that depends on the process variables in general and on the drying temperatures used in particular.

When pasta is dried very gently, little protein polymerization occurs during the drying cycle, and, thus, a strong protein network is not present at the start of the cooking. In contrast, when pasta is dried at higher temperatures, protein polymerization occurs and, at the start of cooking, extensively polymerized protein is already present.

The optimum quality of the cooked pasta then depends on the properties of the protein during cooking and how it is able to prevent the starch from leaching. During cooking, the starch granules absorb water, swell, and hence increase in volume and exert pressure on the protein structures. Also during cooking, (further) protein polymerization reinforces the protein structure and make it better able to withstand the increased volume of the starch particles. The final product quality then depends on how the protein structure withstands the swelling of the starch.

When protein polymerization during cooking does not make up for insufficient polymerization during drying, excessive cooking losses occur. In contrast, the protein in pasta that has been dried at very high temperatures may well have polymerized to such a degree during the drying process that it has become too rigid to expand and retain the gelatinized starch during cooking, such that it also leads to pasta of inferior quality.

It follows that drying pasta is a delicate process. Standard drying procedures first rapidly dry the outer surface of the piece. This gives strength and decreases the chances of mold growth. Typically, 40% of the total water in the piece is removed over a 30-min period at a relative humidity of typically 58–64%, giving a relatively dry

area on the outside while the interior remains moist. This is sometimes referred to as "case hardening." The rapid drying period can be followed by a so-called "sweating period," in which the product is held in relatively humid air at 80–85°C and the moisture content is allowed to become more uniform. The sweating period is followed by a final drying to about 12% moisture. Usually, sweating and drying periods are alternated to permit moisture migration from the inside to the outside and then removal of the water that migrated to the surface. Usually, the overall drying cycle ends with a relatively long stabilization period, allowing the product to equilibrate at its final moisture level.

The use of microwave energy to dry pasta has the advantage, in principle, of heating the water in the piece uniformly, i.e., without a wet-to-dry gradient that can cause checking. In addition, it reduces the overall drying time. However, when heating too fast, water inside the product vaporizes and destroys the structure.

Noodles

Noodles are thought to have originated in China and are still a popular food throughout Asia. In all Asian noodles, a smooth surface is highly desirable. As with all foods, wide variations exist in the type of noodles preferred by different populations. In Korea and China, noodles with a chewy texture are preferred. In Japan, a fresh wet noodle (*udon*) with a soft texture is popular.

Noodles are generally made from flour from common wheat (*T. aestivum* L.; see Chapter 1), rather than from semolina or farina, and contain salt(s) in addition to flour and water. However, starch noodles, made principally from mung bean starch, are also produced throughout Asian countries. Such noodles are made by allowing a starch-water slurry to flow through a small orifice into boiling water. This results in vermicelli-sized strings. The noodles are then allowed to retrograde to gain strength. As starch noodles are consumed much less frequently than flour noodles, the discussion here focuses on the latter type of noodle.

In general, oriental noodles contain no eggs. As much as 40% of the wheat consumption in Asia is as noodles. There are many types of oriental noodles (Fig. 14.4). They vary in their ingredients, degree of cooking before sale, and/or degree of drying. In contrast, the U.S. Standard of Identity for noodles states that they must be made of wheat dough containing eggs. Dried noodles must contain less than 13% moisture and more than 5.5% egg solids. The discussion that follows does not cover North American noodles but instead focuses on the more popular Asian noodles.

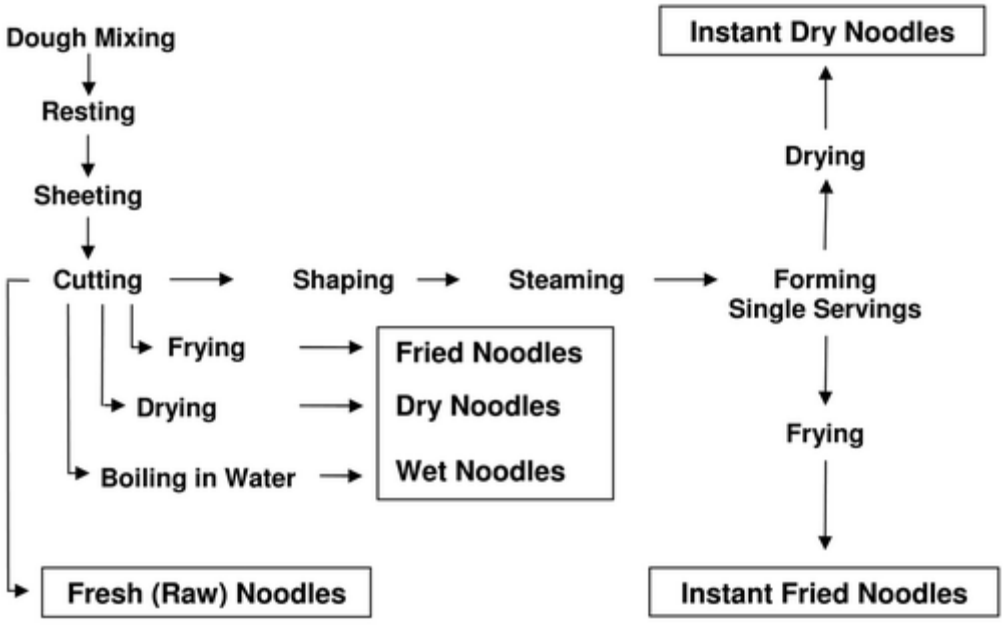


Fig. 14.4. Types of oriental noodles and their manufacturing processes. (Adapted from Moss 1973)

FLOUR FOR NOODLES

Because flour makes up 95–98% of the dry solids of noodles, its importance appears obvious. Although flour consists of many components, the present discussion concentrates on pigments, protein, starch, and enzymes and their importance in noodles.

Pigments

The two major types of pigment in wheat flour are carotenoids and flavonoids. Carotenoid pigments occur in the endosperm and give flour its creamy yellow color. The level of carotenoids varies widely among different cultivars of wheat. These pigments can be bleached rather easily and are destroyed by bleaching agents such as benzoyl peroxide (see Chapter 8) and enzyme-active soy flour (see Chapter 4; the active ingredient is the enzyme lipoxygenase).

Flavonoid pigments (Fig. 14.5) originate mostly from bran contamination of flour and are not bleached by the above bleaching agents. They are relatively stable and are colorless at acidic pH but give a yellow color at alkaline pH. They are the source of the yellow color in Chinese noodles containing *kansui.* However, when iron salts are also present at alkaline pH, the flavonoids often give rise to green and brown colors. Because of this, noodles are often made from low-extraction flour. Such flour has limited bran contamination (see Chapter 8) and hence limited flavonoid levels.

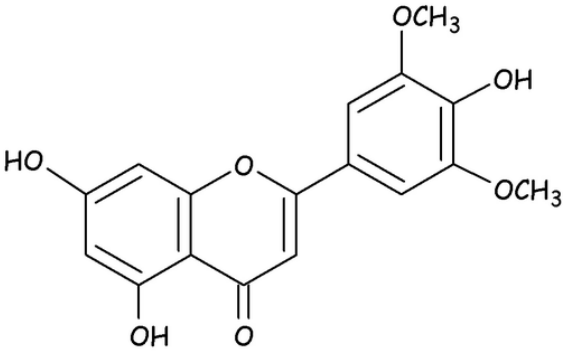


Fig. 14.5. Structure of the wheat flour flavonoid pigment tricin. (Courtesy M. Verswyvel)

Protein

As outlined earlier, the unique ability of wheat flour to form cohesive, elastic, and extensible dough is the result of its gluten proteins. Protein quantity and quality are important in noodle making. High levels (10–14%) of strong protein produce noodles with a chewy and elastic texture. Flour with too low a protein content gives noodles with poor cooking tolerance. When overcooked, the noodles are mushy and sticky.

Starch

During noodle cooking, starch changes from the raw granular form to the gelatinized form, which causes the noodle to set. Thus, the swelling properties of the starch are important. If the starch on the surface of the noodle is overcooked before the interior becomes cooked, the surface of the noodle becomes sticky. When a noodle is properly cooked, the starch on the surface is not sticky but gives a smooth mouthfeel.

Enzymes

Although flour contains only small levels of enzymes, those present can significantly affect noodle quality. Excessive levels of α-amylase (see Chapter 2) in flour, caused either by sprout damage or malt supplementation, cause rapid breakdown of the noodle structure. Polyphenol oxidase is another important enzyme affecting noodle quality. It is thought to be responsible for the darkening of fresh noodles during storage.

NOODLE PRODUCTION AND NOODLE TYPES

Noodle making is relatively simple. In essence, flour, salt or *kansui,* and (optionally) egg products are mixed. *Kansui* is a mixture of sodium and potassium carbonates but contains no sodium chloride.

The carbonates produce alkaline dough that gives a strong noodle with a bright yellow color, which is ascribed to the flavonoid pigments.

After a rest, the dough is sheeted, cut, and (optionally) dried in a fashion appropriate for the type of end product desired.

Dough Mixing and Dough Rest

The dry flour is placed in the mixer, and water and salt or *kansui* are added. Mixing the flour and the water (usually less than 35% based on flour weight) does not result in dough. Instead, spherical agglomerates are formed. Mixing generally takes 5–10 min with a mixer designed to cut dry flour into the water-rich agglomerates. After mixing, the dough is allowed to rest for 10–15 min. This contributes to a more even distribution of water throughout the system.

Dough Sheeting

After the rest, the crumbly dough is pressed between two large-diameter rolls to produce a dough sheet of about 1 cm thickness. The dough sheet is rolled thinner by seven to 10 successive passes through reduction rolls. As a result, a sheet of developed dough with a uniform thickness is formed. Under the conditions of noodle making, the sheeting operations develop dough in much the same way as mixers. However, because the noodle dough is always sheeted in the same direction, the gluten fibrils are aligned in the direction of sheeting. That alignment gives the noodles more strength in their long rather than their short direction.

Two important factors in noodle-dough sheeting are the sheeting speed and the sheeting ratio. The sheeting speed is the speed of the rolls, or how fast the dough passes through the rolls. The sheeting ratio is the thickness of the dough after sheeting divided by the thickness of the dough before sheeting. Both of these variables must be controlled to obtain a good noodle.

Noodle Cutting

After reaching the desired thickness, the dough sheet is passed through a pair of cutting rolls (Fig. 14.6). A pair of slotted rolls is aligned so that a noodle with a square cross section is produced.

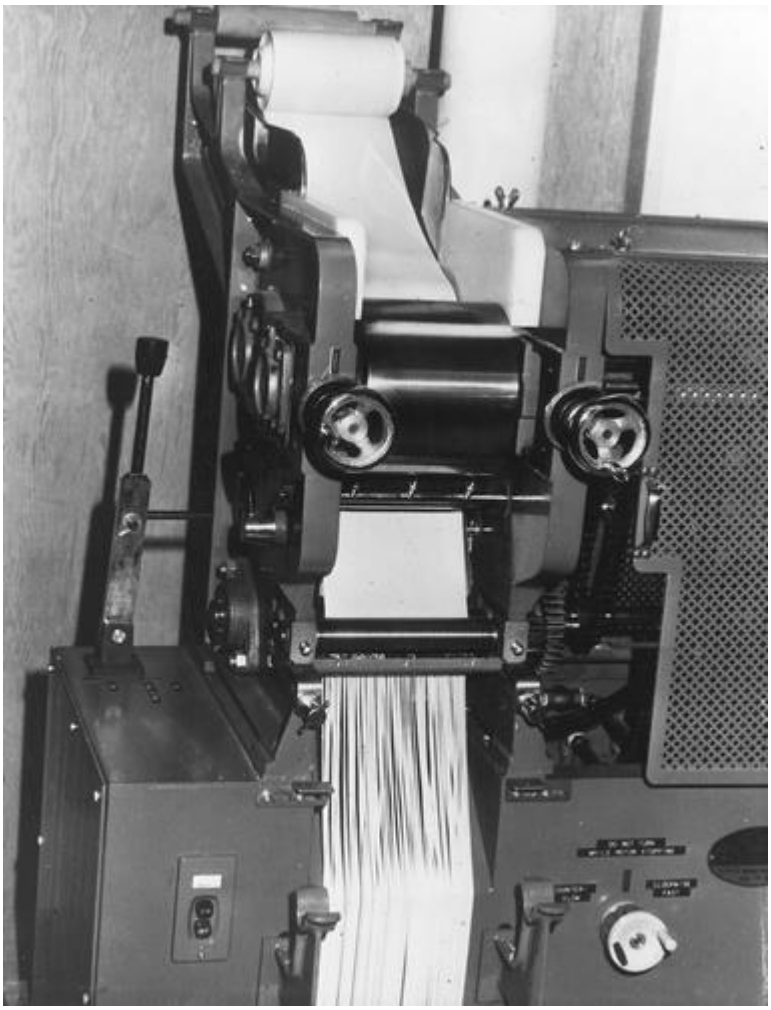


Fig. 14.6. Noodle machine sheeting and cutting noodles. (Courtesy of K. Rho)

Fresh Noodles

Fresh noodles, which are not cooked before sale, contain typically 35% moisture. They deteriorate rapidly unless stored under refrigeration. After 50–60 hr at refrigeration temperatures, the noodles darken and become moldy. For good consumer acceptance, they must be white or light yellow. The darkening with storage is thought to be caused by polyphenol oxidase (EC 1.10.3.1). Fresh noodles are usually produced with a thin cross section, which allows them to cook rapidly. They are made from relatively strong flour, so they can be handled in the wet form. This gives the cooked noodles a chewy texture.

Wet Noodles

Wet noodles are cooked in boiling water before they are sold. Once cooked, they have a moisture content of about 52%. Their shelf life is typically 40 h at room temperature. The boiling denatures the polyphenol oxidase; therefore, the noodles do not turn brown during storage. Chinese wet noodles are made with a relatively weak all-purpose flour and *kansui.*

Dry Noodles

Dry noodles are formed at a moisture content of about 35% and then dried to 8–10% moisture content. The freshly cut noodles (2–3 m long) are put over wooden dowels. The goal is to dry the noodles as soon as possible and to produce them with a uniform white color and strong shape. Because noodles contain added salt, moisture loss is not as fast as for pasta, and, therefore, checking is not as serious a problem with noodles. However, noodle drying is still done in three-stage regimes that are similar to some used for pasta.

Dry noodles can be easily handled and have a long shelf life. For dry noodles, color and opaqueness are the major quality factors. Dull, gray, or brown noodles are considered inferior. In addition, the noodles should have a uniform shape and cleanly cut sides. Because of the importance of color, low-ash flour (see Chapter 8) is generally used.

Instant Fried Noodles

Instant fried noodles are cut, waved (i.e., formed into characteristic shapes), precooked with steam, formed into individual servings, and fried in oil at, typically, 140–150°C for 0.5–2 min. Frying rapidly reduces the moisture content of noodles to 5–8% and fixes their structure. A porous noodle structure is formed that rehydrates quickly when water is added. That, of course, is an important property of instant noodles. Instant fried noodles are called "ramen" or "ramyeon" and are usually packaged with seasonings. They have a distinctive taste, different from that of the other noodles, probably because they typically absorb about 20% fat during frying. For good consumer acceptance, instant fried noodles should be white and free of rancidity. This requires the noodles to be fried in good-quality oil for short times and at relatively low temperatures (see above). When ramen noodles are cooked by the consumer in boiling water, no fat should separate into the cooking water. After cooking, the noodles should have a relatively strong texture and bite and a firm, nonsticky surface. Because fried noodles are relatively dry, they have good storage properties, particularly if packaged to exclude oxygen and light.

Steamed and Dried Noodles

Steamed and dried noodles are precooked with low-pressure steam, shaped, and then dried to about 10% moisture content to give another type of instant product. Steaming is preferred to cooking in boiling water because no solids are lost in the cooking water and the noodles retain their shape. During steaming, noodles that touch stick together. Therefore, with proper waving and shaping, individual servings can be produced that are continuous but with an open network. Drying is generally in the sun or with a convection oven. Steamed and dried noodles have a shelf life of about one year. They require a longer cooking time than dry noodles of a similar size. The taste and texture are also different from those of the fried or dry noodles.

CHAPTER 15: Breakfast Cereals

After fasting overnight, one breaks the fast in the morning with, of course, breakfast. Although certainly anything can be and is eaten at breakfast, morning is traditionally a time when many cereal products are consumed. The products, in addition to rolls and breads, can be divided into two types. The first type, which is as old as civilization, requires cooking. The second type is the first of the convenience foods, the ready-to-eat cereals. They were developed only a little over 100 years ago by a number of vegetarians wanting to improve and add variety to their diets.

Cereals that are cooked before being served can be made from a number of cereal sources. In what follows, several aspects of wheat-, oat-, maize-, and rice-based products are discussed.

FARINA

As outlined elsewhere (Chapter 8), farina is a fraction of middlings from hard wheat (North American terminology; see Chapter 1). Farina can be obtained in typical yields of 30% from hard wheat. The U.S. Standards of Identity specify that 100% of the product must pass a No. 20 sieve (833 μm) and that not more than 10% must pass a No. 45 sieve (350 μm). In its classical form, farina must be boiled in water for several minutes because, for the product to taste cooked, the particles must be wet throughout and the starch gelatinized. For the production of "instant" farina, i.e., farina with a short boiling time, use is made of proteolytic enzymes. Their action allows water to penetrate the particles faster. As in the cooking of all cereal products, the product must be hydrated with water of high enough temperature to gelatinize the starch. Farina is usually enriched with vitamins and minerals, commonly added as a dry mix. The products are often flavored with malt or cocoa.

OATS

Most oats that are consumed directly as food are served as breakfast cereal. Of the type that must be cooked, the most popular by far is rolled oats. The process for making them is shown in Fig. 15.1. The cleaned oats are treated with dry steam at 100°C. This has two important effects. First, it inactivates enzymes, in particular, the lipase system. This is important because oats have high lipid contents and would otherwise be very susceptible to rancidity. Second, the treatment reduces the moisture content to about 6%. Drying the hulls makes them more brittle and therefore easier to remove.

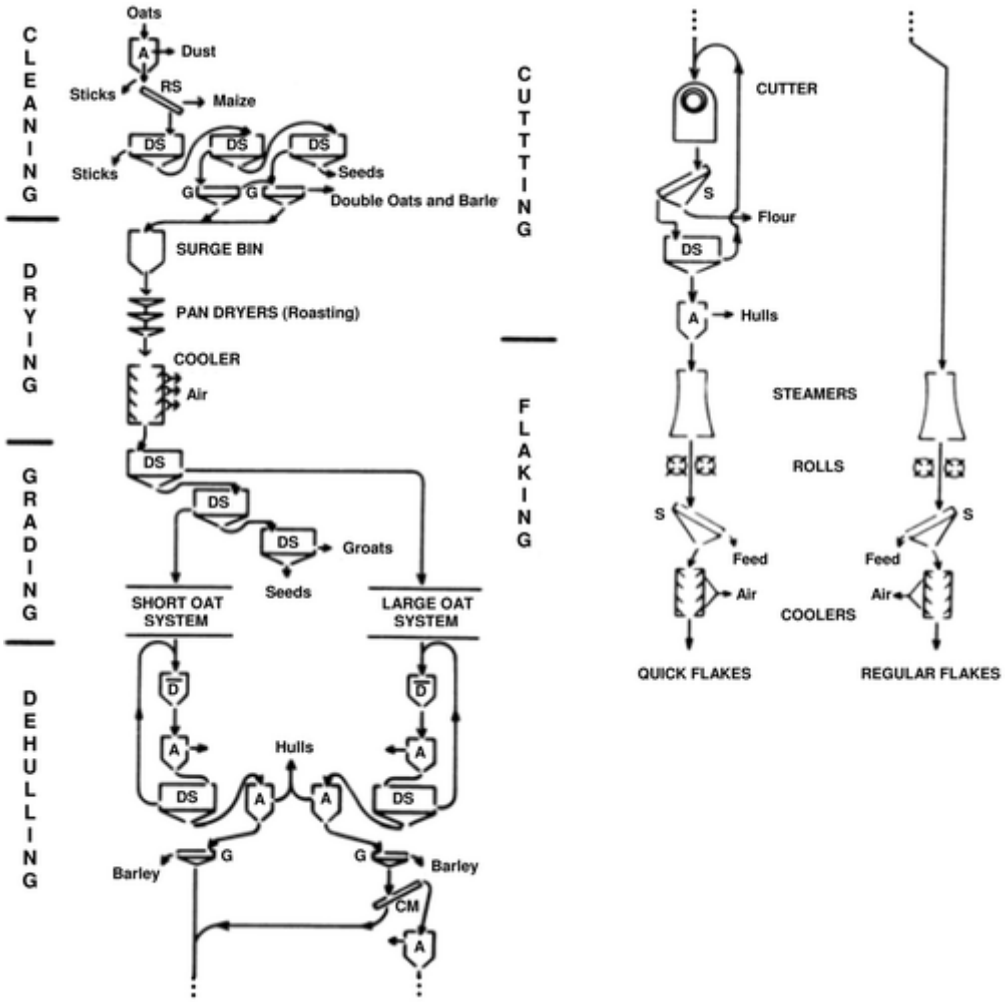


Fig. 15.1. Scheme for producing rolled oats. A = aspirator, RS = receiving sieves, DS = disk separators, G = width graders, D = dehuller, CM = cell machine (gravity table), S = sieve. (Adapted from Youngs et al 1982)

The dehulling is then done with equipment similar to that described for rice dehulling in Chapter 10. Following dehulling, the hulls need to be separated from the dehulled groats and from the whole oats that were not dehulled in the process. In general, removing the hulls by aspiration is not difficult because they are very light. It is much more difficult to make a clean separation of groats from whole oats. Generally, a gravity table (Fig. 8.2) is used to make the separation. Nonetheless, this is a very critical step because the presence of even a small percentage of whole oats in the groats is unacceptable; hulls in the final rolled oats product make it unpalatable.

The groats are then rolled, or flattened, with large, very heavy rolls to give the rolled product. Flaked whole groats take 10–15 min to cook. The cooking time, i.e., the time required for the hot water to penetrate to the center of the flake, is determined by the thickness of the rolled oats. Of course, the cooking time is controlled by the thickest point and, therefore, a uniform piece is desirable. To obtain rolled oats that cook more quickly, one must produce a thinner flake. This is accomplished by cutting the groats into two or three pieces before flaking. The smaller pieces give a thinner flake that cooks faster (3–5 min). However, such cooked products do not retain their quality if held under hot conditions and rather quickly turn into a gruel. Instant-cooking oatmeal is produced by making even thinner flakes.

MAIZE AND RICE

Maize is also used to produce a breakfast cereal that requires cooking. The product, called "grits" or occasionally "hominy grits," is very popular in the southern part of the United States. It is generally made from white maize. The grits are produced by dry milling of maize and are essentially small pieces of endosperm. As with farina, the particle size is important. A similar breakfast cereal is also made from rice.

Ready-to-Eat Cereals

For many years, the most popular ready-to-eat cereal was corn flakes. Today, much variety exists in ready-to-eat cereals. Their popularity, to a great extent, can be ascribed to their convenience as well as to their stability. In the following sections, corn flakes, wheat flakes, shredded biscuits, cereal granules, and puffed cereals and their production methods are briefly discussed, as is the application of extrusion cooking for the production of ready-to-eat cereals.

CORN FLAKES

Corn flakes are produced from No. 4 or No. 5 maize grits. Such large half-kernel pieces are obtained by dry milling of maize to remove the germ and bran. The large grits retain their identity throughout the corn flake manufacturing process, and each thus produces a single flake. During the milling, part of the maize endosperm is, of course, broken into smaller grits. However, these are not used in corn flake manufacture.

The maize grits are pressure cooked with a solution containing sugar, malt (nonenzymatic), and salt. Typical cooking conditions are 2 h at 0.125 MPa (i.e., 18.13 psi or 1.25 bar) of steam pressure, but different lots of grits may vary considerably in cooking time. The end point of cooking can be determined by visual inspection. Uniform translucency is desirable because it indicates that the water has penetrated to the center of the piece. The particles then contain about 50% moisture. After cooking, the lumps are broken up, and the cooked grits are partially dried to about 20% moisture content. This is done in a tower dryer. In such a dryer, which may be several floors high, the wet product falls countercurrent to a stream of hot air (typically 65°C). This process dries the outside of the particles so that they are no longer sticky. However, the moisture distribution is not uniform because the piece is dry on the outside and moist in the interior. Therefore, it is given a temper time of, typically, 24 h to allow the moisture to equilibrate.

After being tempered, the grit is ready for flaking and toasting. The flaking rolls are large, smooth rolls weighing as much as a ton each (Fig. 15.2). After coming from the flaking rolls, the flakes are toasted for about 50 s at 300°C. The toasting not only dehydrates the flakes to less than 3% moisture but also browns and blisters the product. After cooling, the flakes may be sprayed with a solution of vitamins and minerals.

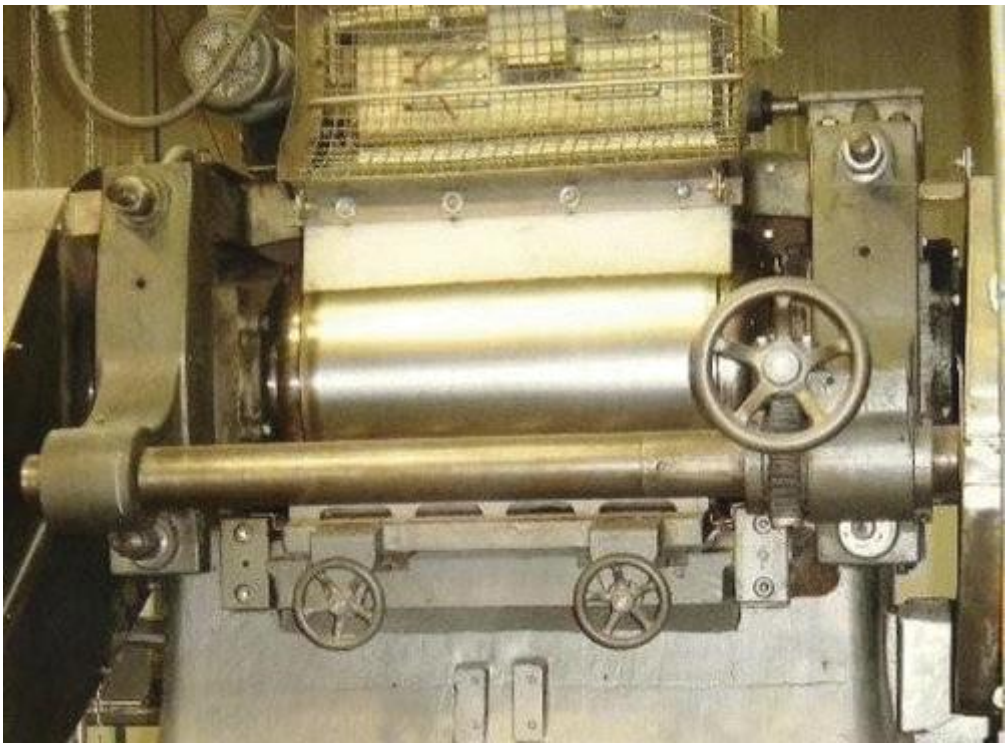


Fig. 15.2. A photograph of a set of flaking rolls. (Courtesy D. Ortiz, Kellogg Company, Battle Creek, MI)

WHEAT FLAKES

To make wheat flakes, the whole kernel is used and each kernel makes one flake. As a first step, water uptake by the kernels needs to be facilitated and, therefore, the wheat bran must be damaged. Indeed, when intact, the bran coat acts as a container for the endosperm and limits the degree of swelling and thereby the level of water taken up. To damage the bran, the wheat is tempered, often with atmospheric-pressure steam to raise the moisture content, typically to 21%. The steamed wheat is then subjected to bumping; i.e., it is passed between rolls set at a gap just slightly smaller than the thickness of the wheat. This causes the kernel to be temporarily distorted. This distortion ruptures the bran, which is not as flexible as the other parts of the kernel, and facilitates water uptake in the later phases of the production.

The kernels are then cooked in a pressure cooker with sugar, salt, and malt flavor added, for typically 90 min at 0.140 MPa (i.e., 20.3 psi or 1.40 bar). After cooking, the kernels are soft, translucent, and contain about 50% moisture. They are then dried to about 21% moisture content, tempered, heated rapidly (usually by infrared lamps) to about 88°C, and sent to flaking rolls similar to those used for corn flakes. The heating step immediately preceding the flaking operation is necessary because it plasticizes the kernel and prevents it from tearing during flaking, thus giving irregularly shaped pieces (Fig. 15.3) that are fragile and fall apart during shipping. After leaving the rolls, the wheat flakes typically contain 15% moisture. To obtain the desired crispness, they are oven toasted and dried to a moisture content of less than 3%.

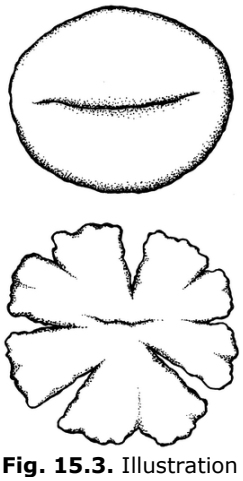


Fig. 15.3. Illustration of a flattened kernel, with plasticizing **(top)** without plastizing **(bottom).**(Courtesy K. Zeleznak)

SHREDDED BISCUITS

Shredded biscuits are one of the oldest of the ready-to-eat cereals. They are made from whole wheat with no addition of flavoring agents. The whole wheat is boiled in water at atmospheric pressure for 1 h, which increases the moisture content to about 50%. The cooked kernels are tempered to homogenize the moisture distribution and then sent to shredding rolls. The shredding rolls are typically 20 cm in diameter and the length of a biscuit. They produce a set of wet strands of dough (ground whole-wheat paste). Eighteen to 20 pairs of rolls layer the dough strands lightly on top of each other, as illustrated in Figure 15.4. The layered strands of dough are separated into biscuits by passing them below blunt knives.

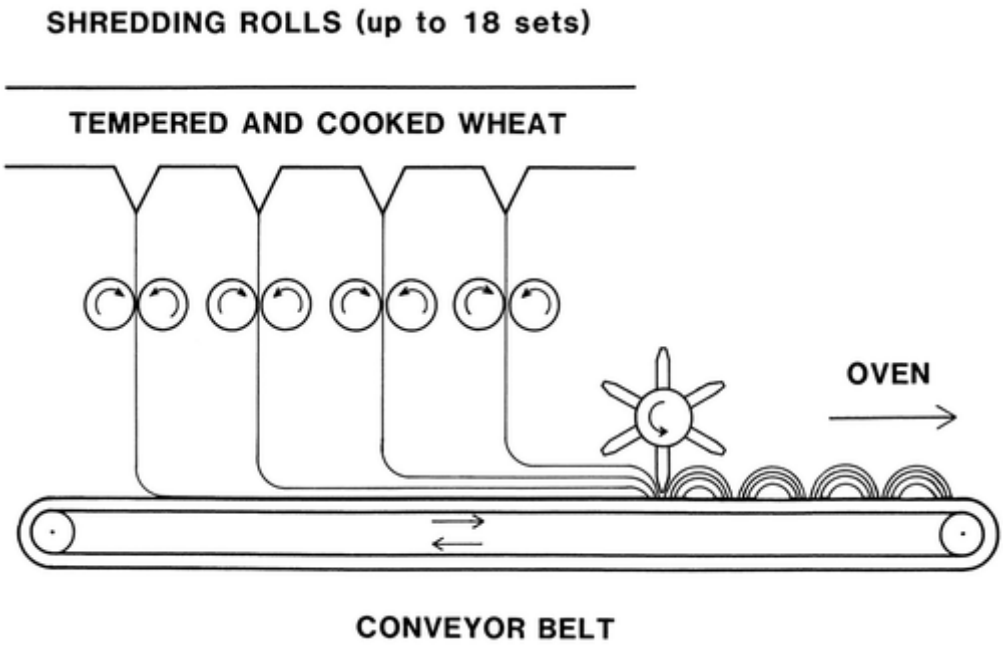


Fig. 15.4. Schematic representation of the process for making shredded biscuits. Cooked and tempered wheat kernels are sent to shredding rolls that produce wet strands of dough that are layered on top of each other. They are then sent below knives dividing them into individual biscuits. (Courtesy K. Zeleznak)

The fragile biscuits are then baked at a relatively high temperature for 10–15 min. This toasts the outside but leaves the interior still wet. The temperature for 10–15 min. This toasts the outside but leaves the interior still wet. The temperature is then typically lowered to 120°C for the remainder of the bake. The final product moisture content is about 11%. Because the biscuits are made from whole wheat, rancid odors develop during storage. Even small levels of these odors make the product unacceptable. Therefore, the product is packaged in breather-type boxes with no inner or outer gas barriers. This allows the rancid odors to diffuse from the boxes and gives the product a longer shelf life. Another way to increase the shelf life of cereals is to use packaging materials that contain antioxidants such as butylated hydroxylanisole (BHA) and butylated hydroxytoluene (BHT). Such materials are quite effective for increasing shelf life.

CEREAL GRANULES

Cereal granules (as in Grape-Nuts) also are one of the oldest type of ready-to-eat cereal. They are made from stiff (low-moisture) dough prepared from wheat and barley flour, salt, yeast, and water. The dough is typically fermented at 27°C for 5 h, made into loaves, and baked without a proof period. The resulting loaves, which are quite dense, are fragmented by shredding knives. The fine particles are removed and reused in later dough batches. The larger fragments are baked for, typically, an additional 2 h at 120°C and then reground and sized. The final products are thus very dense and hard pieces of toast in very small sizes.

PUFFED CEREALS

For puffing of cereals and greatly decreasing their bulk density, two general methods are used. Both process types depend upon water going to a vapor as the driving force. The key to the degree of puffing is a sudden change in either temperature or pressure.

The first process is the sudden application of heat at atmospheric pressure to a prewetted cereal. In this technique, water is vaporized before it has time to diffuse to the surface of the piece. The internal vaporization then expands, or puffs, the product. Oven-puffed rice is an example of a product made based on this principle.

In the process, milled rice is cooked at typically 0.1 MPa (i.e., 14.5 psi or 1 bar) until it is uniformly translucent, dried to 30% moisture, tempered for 24 h, and dried to 20% moisture. The intact kernels are subjected to radiant heat to plasticize the outside of the kernel. The kernels are bumped to destroy their internal structure and again tempered for 24 h. They then pass through the oven at 300°C for about 30 sec. In this technique, the water vaporizes before it has time to diffuse to the surface of the product, and the product expands to two to five times its original size.

The second process is the sudden transfer of a piece containing superheated water to a lower pressure, thus allowing the water to suddenly vaporize. Pressure-puffed, often also referred to as "gun-puffed," products can be made from dough mixed and steam-cooked to about 40% moisture content. The dough is forced through an extruder to give it a specific shape and is dried to 12–15% moisture content. The pellets are then loaded into guns or popping vessels. These guns are typically 75 cm long and 15 cm in diameter. They are sealed, rotated, and heated to 425°C. As a result, the pressure may increase to 1.5 MPa (i.e., 218 psi or 15 bar). The trip valve is then opened, and the material explodes out. Many variations are possible, using different flavors, shapes, types of doughs, etc.

Wheat and rice kernels can also be gun-puffed. Milled rice and pearled wheat are generally used; the bran that is blown off during the process would be unsightly in the product. The degree of expansion obtained with gun puffing is 15–20 times and thus much greater than with oven puffing.

Puffed products must be kept at less than 3% moisture to maintain crispness. The more the product is expanded, the more critical and harder the levels are to maintain. Thus, gun-puffed products require special packaging.

EXTRUSION COOKING

Extrusion cooking is another method of expanding cereal products. The major advantage of the process is that it handles cereal flours at relatively low moisture contents, i.e., typically 12–20%. In most other systems, more water is added and must subsequently be removed, which is very expensive. In this continuous process, both temperature and pressure are used to expand the product. In general, cereal flour or grit that has been moistened with steam or water is fed into the extruder.Figure 15.5 shows a barrel of a double-screw cooker-extruder. It is essentially a nonefficient screw pump in which the screw's channel depth decreases at the end close to the die. As the material is transported through the barrel, heat is generated by friction. In addition, the barrel may be heated by steam or electricity. The process temperature, which may approach 175°C, and pressure, which may approach 3.5 MPa (i.e., 508 psi or 35 bar), are chosen such that the cereal product "melts" to form a plastic mass in the extruder barrel. Under these conditions, the dough is quite flexible and adapts to any die configuration. Upon exiting the die, the dough expands as the pressure is released. Moisture is flashed off, and, of course, this cools the product. The final product typically contains 8–15% moisture. Therefore, most of the products must be dried after extrusion.

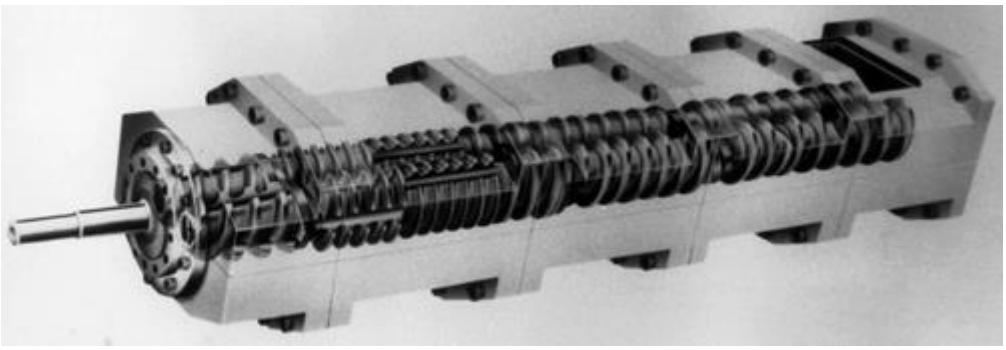


Fig. 15.5. Barrel of a twin-screw extruder. (Courtesy Wenger Manufacturing Inc, Sabetha, KS)

Not only process variables but also the type of cereal flour, its composition and, more particularly, the level of fat affect the extrudate and its degree of expansion. Monoacylglycerol addition increases the smoothness and uniformity of the products obtained. At the same time, it also reduces expansion.

COATINGS

Many cereal products are sugar-coated before they are sold. The sugar coating protects the product from moisture and thus increases its shelf life. The coating process is quite simple. A cement-mixer type of apparatus keeps the cereal agitated while the molten sugar syrup is slowly dripped onto the mass. Coconut oil is often added to decrease foaming and to keep the particles separate. The syrup hardens quite rapidly upon cooling. The glaze accounts for 25–50% of the product weight, mainly because of its much higher density than that of the cereal product.

CHAPTER 16: Snack Foods

The subject of this last chapter before the final one, which deals with animal feeds, is snack foods. These products are defined as foods generally eaten just as they are removed from the package. They include cookies and crackers (Chapter 13) and even bread (Chapter 12) and breakfast cereals (Chapter 15). In the present chapter, several maize- and wheat-derived products and the production processes for them are described. Maize-based products include popcorn, corn nuts, and corn curls, as well as the masa-derived products corn chips, tortillas, and taco shells. Wheat-based products include pretzels, bagels, and wheat-germ-based synthetic nuts.

Maize-Based Products

Maize-based snack products can be produced from whole kernels, such as in the production of popcorn and corn nuts; from maize flour, such as in the production of corn curls; or from masa.

POPCORN

Among the cereal grains, only popcorn and certain lines of sorghum and pearl millet pop. All grains expand in volume to lesser extents, but only these three give the explosive pop with the accompanying large increase in volume. In India, certain varieties of sorghum and pearl millet are popped and eaten like popcorn. The major difference, in addition to the flavor and size, is that, in India, the grains are popped in hot sand rather than in oil.

The quality of popcorn is linked to the popped volume, the shape of the popped kernels, their tenderness, and, of course, their flavor. During popping, the volume of the raw material increases up to about 30 times. The popped volume is of particular importance because the raw material is bought by weight but generally sold by volume. The tenderness of popcorn has also been positively correlated with the popping volume.

Popcorn is readily made by heating oil and unpopped kernels. Similarly to what happens to puffed cereals (Chapter 15), the expansion is due to vaporization of the moisture in the kernel. The fact that popcorn expands to a large extent, while most other cereals do not, is due to its pericarp, which acts as a pressure vessel and allows the water in the kernel to be superheated. At a typical tenmperature of 177°C, the pressure becomes so high that the pericarp ruptures, allowing the endosperm to expand. When the pericarp is damaged (Table 16.1), the expansion of the popcorn is greatly reduced.

TABLE 16.1
Effect of Popcorn Pericarp Treatments on Popping Volume[a]

Treatment	Popped Volume (cm^3/10 g of grain)
Control, intact kernels	270
Pericarp cut just through	120
Pericarp cut just through in two places	90
Opaque endosperm cut into	70
Kernel cut in half	40
Pericarp removed by hand	20
Unpopped kernel	11

[a] Source: Hoseney et al (1983); used by permission.

Figure 16.1A shows a longitudinal cross-section of an unpopped popcorn kernel. The kernel is made up of pericarp (Fig. 16.1D), endosperm, and germ. As outlined in Chapter 1, in maize, the endosperm is composed of a translucent and an opaque portion (Fig. 16.1B and C). The degree of expansion in popcorn is related to the proportion of translucent endosperm. This endosperm is tightly packed and contains no air spaces, whereas the opaque endosperm has many such spaces. During popping, the pericarp (Fig. 16.2) appears to undergo no change other than the obvious fracture. It is often blown free or partially free of endosperm tissue. The

aleurone and subaleurone cells as well as the germ undergo minimal change during popping. At the outer edge of the kernel, the moisture loss is excessive.

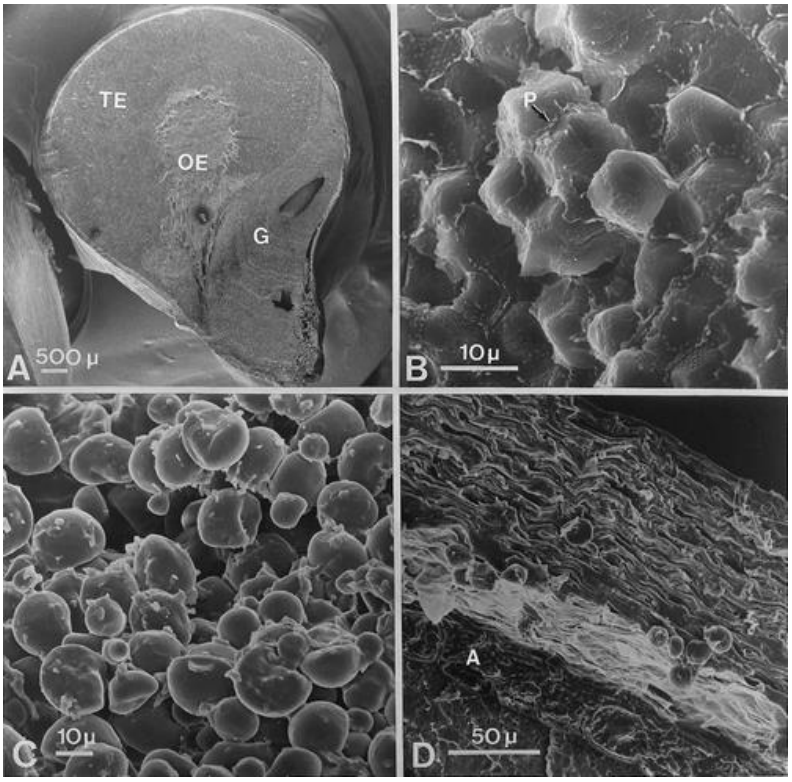


Fig. 16.1. Scanning electron micrographs of an unpopped popcorn kernel. **A,** longitudinal section showing translucent endosperm (TE), opaque endosperm (OE), and the germ (G); **B,** translucent endosperm showing starch and protein bodies (P); **C,** opaque endosperm; **D,** outer edge of the kernel, showing the aleurone (A) and the pericarp. (Reprinted, with permission, from Hoseney et al 1983)

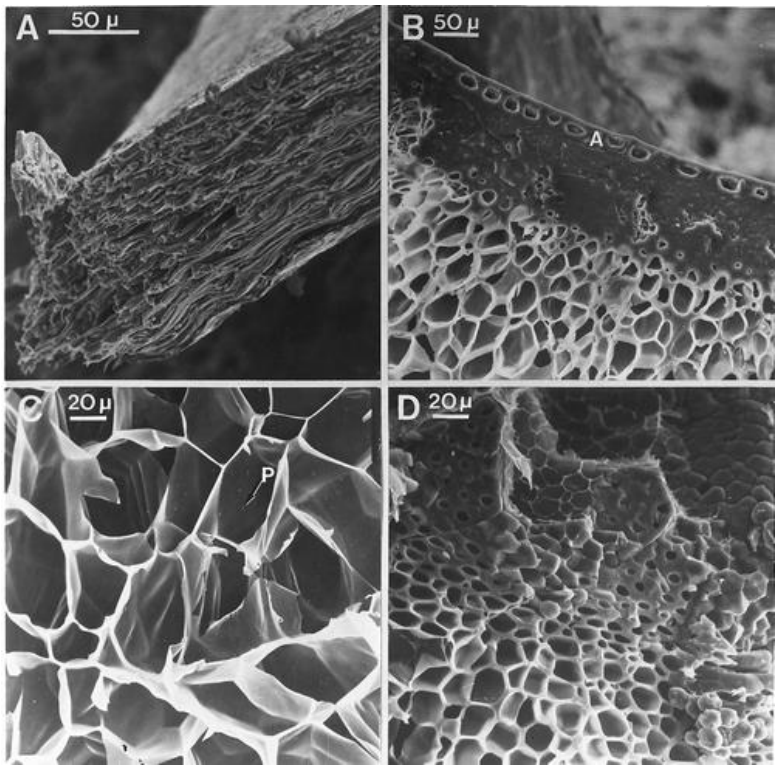


Fig. 16.2. Scanning electron micrographs of popped popcorn. **A,** pericarp "hull" blown free as a result of popping; **B,** the outer edge of the endosperm, showing the aleurone (A); **C,** inner portion of the endosperm,

showing the protein bodies (P) still intact; **D,** the endosperm in a partly popped kernel, showing starch granules ranging from intact to expanded forms. (Reprinted, with permission, from Hoseney et al 1983)

Deeper in the endosperm, the expanded structure becomes more evident. Figure 16.3illustrates that, during popping, the opaque and translucent endosperms behave differently. The starch granules in the opaque endosperm appear to stay intact and do not expand during popping. The moisture vaporizes into the void surrounding the granules, creating large voids. In the translucent endosperm, the moisture vaporizes into the hila of the starch granules (Fig. 16.3D) and greatly expands the granules. However, the protein bodies are still visible and apparently are unaffected by the popping process.

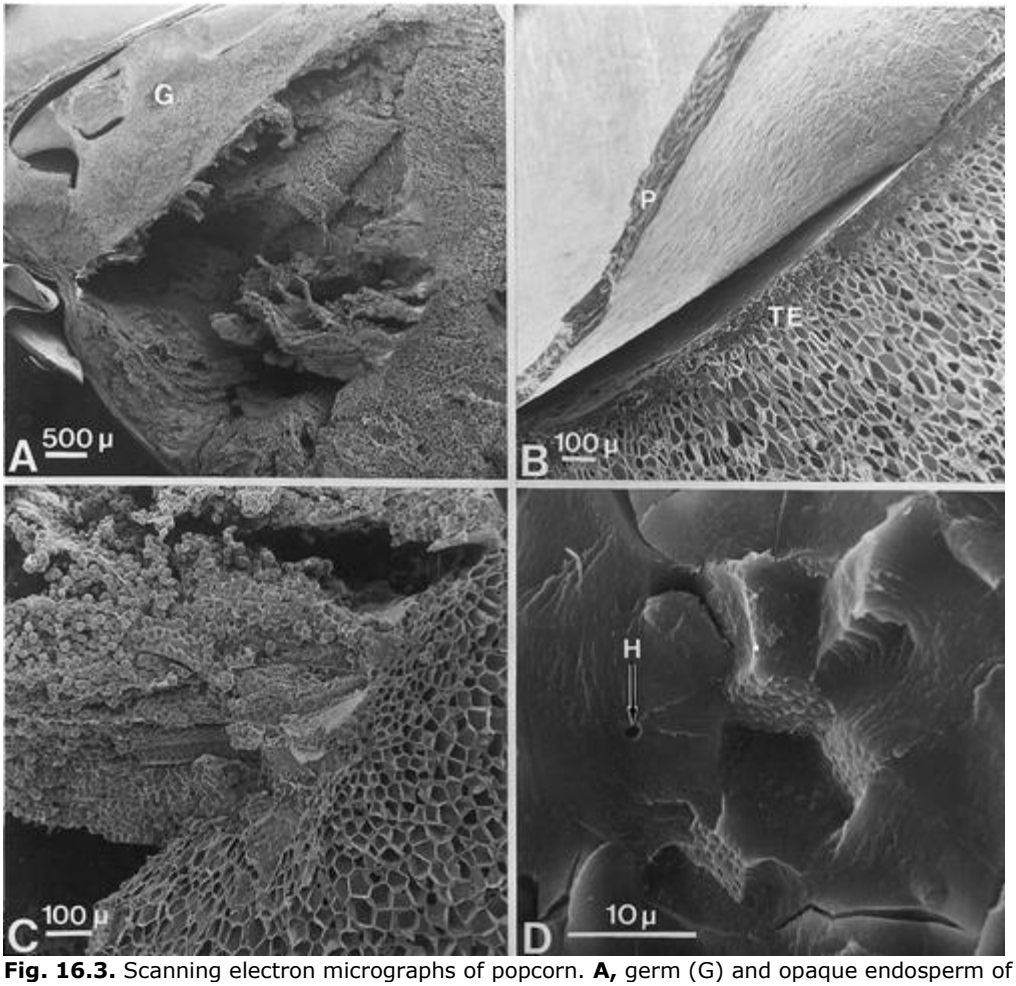


Fig. 16.3. Scanning electron micrographs of popcorn. **A,** germ (G) and opaque endosperm of a popped kernel; **B,** pericarp (P) separating from the translucent endosperm (TE) of a popped kernel;**C,** interface between the opaque and translucent endosperm in a popped kernel; **D,** hilum (H) at the center of a broken starch granule from an unpopped kernel. (Reprinted, with permission, from Hoseney et al 1983)

CORN NUTS AND CORN CURLS

Corn nuts, another snack, are made from a specific maize type that has very large, opaque, white kernels. These are tempered and then fried in fat and salted. They have a very nice taste but are rather hard.

Corn curls are another maize-based snack. They are made from maize flour by extrusion cooking (see Chapter 15). The volume increases typically by a factor of 12 in the process. Corn curls are often flavored by being sprayed with oil and then coated with cheese or other flavoring agents. In newer types of snacks, also produced with the cooker-extruder, the products are not expanded after cooking but are cooled and cut into small shapes. These products are then expanded by frying or hot-air popping. They are liked for their fresh taste.

MASA

Maize has been used directly as a human food for centuries in South and Central America. The traditional production method that is still practiced in many areas of Latin America and the industrial method of making masa are not very different. Maize is heated with water containing calcium hydroxide (typically 0.5–1.0%) or with wood ashes (Fig. 16.4). The calcium hydroxide is added for two reasons. First, it gives a flavor that is identified with maize products. Second, the alkaline character of the calcium hydroxide weakens the outer layer of the maize pericarp. The temperature is brought to at least 82°C for about 1 h but is generally held below boiling. Because the maize kernel is quite hard and dense, such a long period of time is needed for the water to diffuse to the center of the kernel. The amount of cooking required varies from raw material to raw material and is apparently related to the rate of water penetration. It is important that the whole kernel be hydrated to the same extent. Therefore, determination of the end of cooking is an important aspect of the process. Although the temperature under excess water conditions would be sufficiently high to gelatinize the starch, the water level and the concentration of soluble salts and sugar in the kernel are too low to allow significant starch gelatinization.

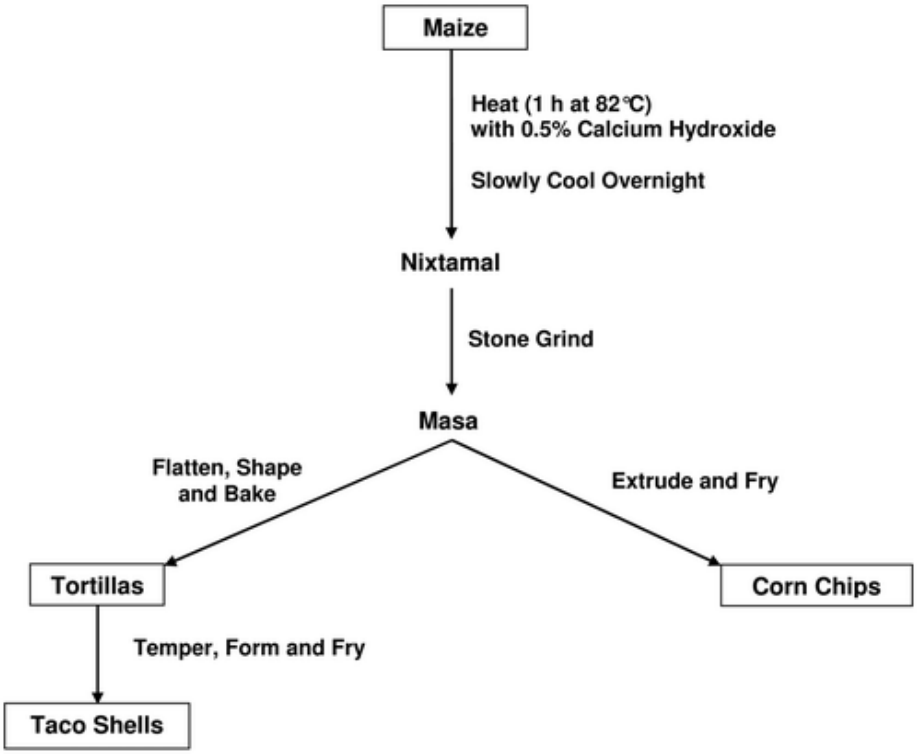


Fig. 16.4. Typical process scheme for producing masa, tortillas, taco shells, and corn chips.

The product obtained following cooling overnight to room temperature is referred to as "nixtamal," i.e., heat-treated, alkaline water-steeped maize, which is then cooled. Although in some products, the pericarp is retained, in most instances, the nixtamal is rubbed or washed to remove pericarp (see Chapter 1), and the excess calcium hydroxide and the excess water are removed. It is then ground either by hand or machine. Stone mills are generally thought to produce the correct particle size distribution. Small levels of water may be added during grinding to obtain the desired moisture content.

The resulting wet-ground product is "masa." It typically contains 55% moisture and forms cohesive dough, presumably because of its particle size distribution and moisture. Scattered references in the technical and patent literature refer to the development of maize or sorghum proteins into cohesive doughs, but none of the reports is very convincing. While masa dough is certainly cohesive, it lacks the elastic properties of wheat flour dough. The cohesiveness can probably be explained in the same way as that of "mud pies," in which the inert particles are held together by the surface tension properties of water. When the voids between the particles are just filled with water, the system is most cohesive. Evidence for this view is that masa dough is sensitive to both the level of water in the system and the masa particle size distribution. The secret to producing cohesive nonwheat dough is indeed to produce the correct distribution of a fine particle size and add the optimum level of water.

Finally, it is useful to mention that the typical flat chapatti and roti flat breads of India, which are made from cohesive sorghum and millet flour doughs, respectively, also fall under the definition of snack foods in this book.

MASA PRODUCTS

Masa can be extruded into hot fat to produce a corn chip (Fig. 16.4).

Tortillas are formed by pressing masa, either by hand or mechanically, into a round, flat pancake shape and baking. Tortillas are thus flat breads. The baking is generally at relatively high temperature. During baking, the product often puffs and then collapses. The tortilla generally is turned two or three times during baking.

Some corn chips and taco shells are prepared by frying tempered tortillas in fat. In the tempering process, the tortilla is kept under conditions that allow the moisture in its interior to equilibrate.

Tortillas can also be made from viscoelastic wheat flour dough. Such tortillas evidently have a structure that differs from that of their masa-based counterparts. Wheat tortillas have become very popular in different parts of the world, including North America.

Wheat-Based Products

The wheat-based products covered here include pretzels, bagels and, as a curiosity, wheat-germ-based synthetic nuts.

PRETZELS

Pretzels are a baked food with a unique shape and hard outer surface. The formula (Table 16.2) for pretzels is somewhat unusual in that it generally contains both yeast and a chemical leavening agent, although occasionally one finds a formula that contains only chemical leaveners. The water level is about two-thirds that of bread dough and gives dry, tough dough. The flour used varies widely, depending on the manufacturing location and the processing equipment available.

TABLE 16.2
Typical Formula for Pretzels

Ingredient	Parts[a]
Flour	100
Shortening	1.25
Malt syrup (nondiastatic)	1.25
Yeast	0.25
Ammonium bicarbonate	0.04
Water (variable)	~42

[a] Based on flour.

Figure 16.5 outlines the pretzel-making process. Dough is mixed and typically fermented for 30 min. This fermentation time is quite short, considering the low level of both yeast and water. The fermented dough is then rolled into a rope and goes through a twisting machine that forms it into the traditional shape. The formed dough piece is passed through rolls to set the knots. The preformed pretzels are then typically given a relaxation period or proof of 10 min. The proofed pieces are transferred to a wire mesh band and passed through a bath of 1.0% sodium hydroxide, typically at 93°C for about 25 s. This treatment gelatinizes the starch on the outer surface of the piece. After the lye bath, the residual sodium hydroxide on the product reacts with the carbon dioxide in the air to form sodium bicarbonate. Immediately after the bath, the pieces are salted with a coarse-flake salt (typically 2.0% of the final product weight). After salting, they are baked, first at high temperature to produce a dark brown color on the product, then at lower temperature to allow drying of the dense knot areas. The drying process is a critical unit operation, because, if heated too fast, the product will check and fall apart during shipping.

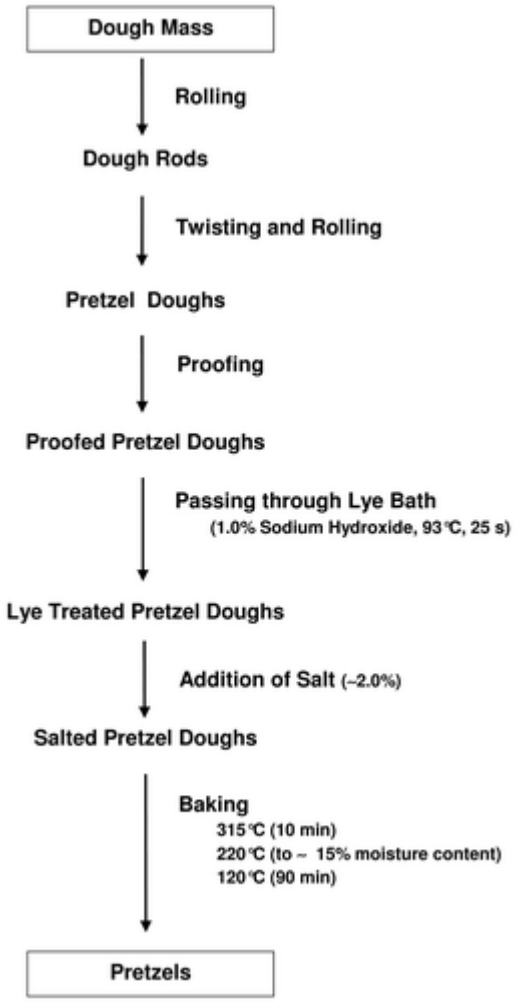


Fig. 16.5. Outline of a typical process for production of pretzels.

Figure 16.6 shows the outline of an industrial pretzel line. Following lamination, the pretzels are cut, sprinkled with lye rather than being dipped through a bath, baked, and cooled.

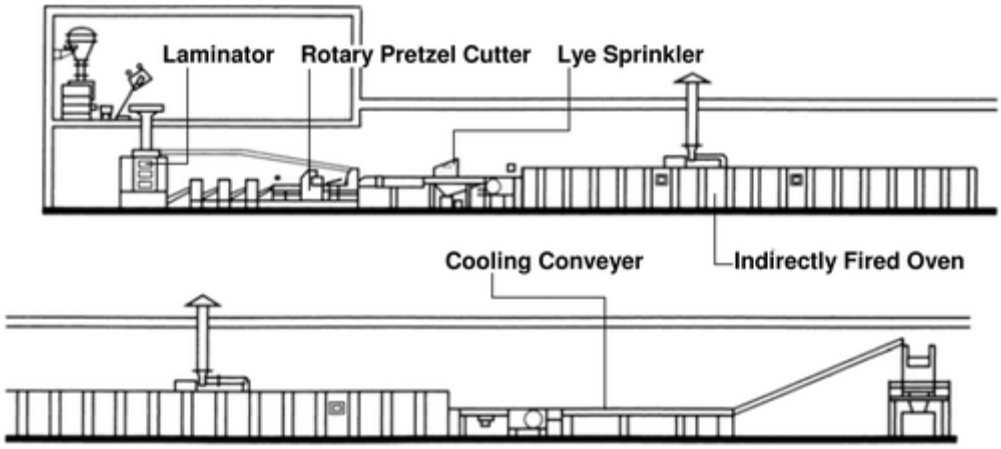


Fig. 16.6. Schematic representation of a line for production of pretzels. (Courtesy Werner and Pfleiderer, Stuttgart, Germany)

In Western countries, large soft pretzels, which are quite different from those described above, are also popular. They are based on similar formulations but are not taken through a lye bath. Some are bathed with sodium carbonate and others just baked in a hot oven.

BAGELS

Bagels originated in Vienna. Legend tells that after horsemen drove away an attacking force (the Ottoman Turks) from the city, the bakers wanted to produce a new bread type in honor of the riders. They attempted to form the bread into the shape of a stirrup (i.e., the part of the saddle that the rider's foot goes into). To have it retain that shape after baking, they made strong dough by using high-protein flour with a relatively low water absorption and boiled the dough before it was baked. This gave it the necessary strength to retain its shape and made it a unique baked product.

The traditional process for bagel production starts with the production of dough that contains low levels of yeast, sugar, and salt. The flour used usually has either high protein content or added wheat gluten. The dough is formed into the desired shape and held at 1°C, typically for 18 h. The retardation step is necessary to obtain the hard, shiny surface characteristic of traditional bagels. The retarded dough is allowed to warm at room temperature for 15 min and is then placed into boiling water for 2 min. It is turned and boiled for an additional 2 min. After draining for about 30 s, it is baked.

Many modified systems for bagel production have been developed, with short or no retardation times and often with steaming rather than boiling in water.

SYNTHETIC NUTS

An interesting product developed as a food for astronauts is a synthetic nut made with wheat germ (see Chapter 8) as a major ingredient. For such products, an oil-in-water emulsion is produced, with a film-forming protein from wheat germ in the aqueous phase. The emulsion is then carefully dried to set the protein into a solid. The products can be produced with the texture of nuts. Because the oil is protected inside the nut and away from air, the products have a long shelf life.

CHAPTER 17: Feeds

In many ways, the distinction between human food and animal feed is arbitrary. Many of the raw materials that we use for food are also used for feed. Modern grinding, mixing, and pelleting technologies allow formulating feeds with optimal feed efficiencies, i.e., ratios of animal weight gain over feed consumed to realize the gain. The present chapter covers some basic aspects of feed manufacturing and also describes some alternatives for grinding cereal materials. Finally, some remarks on specialty feeds are given.

Basics of Feed Manufacturing

Feed manufacturing involves grinding and pelleting of feed raw materials that are formulated to meet the specific needs of the target animal type.

GRINDING

Anything used to break or remove the hull or outer protective layers of cereal grains generally improves feed efficiency. The hulls that are removed may be useful as fiber in the diets of some monogastric animals. However, although digestible by ruminant animals, the nonendosperm parts of the cereal slow the rate at which the remainder of the grain is digested. Passing the grain through a roller mill with the rollers set closely enough together to break the grain is effective in breaking the outer layers and increasing the endosperm's exposure to digestion. In dry rolling, the passage thorough the roller is done at the native grain moisture content. Addition of moisture before the grinding reduces dust formation. The moisture addition is as water or as steam. The steam treatment is usually short, 1–8 min, and appears to have little, if any, additional effect on the digestibility of the grain over that achieved by dry rolling. However, it improves palatability.

Grinding the grain more finely, i.e., not only breaking the pericarp but also greatly increasing the surface area of the feed material, greatly increases its exposure to digestive enzymes. Fine feed grinding is most efficiently executed with a hammer mill (Fig. 17.1). In such a mill, the grinding action, which is low-cost and efficient, is essentially by impact. The hammers are affixed to a rotating shaft, and the material to be ground is retained in the grinding area by a screen. The screen has holes that allow material of sufficiently small size to pass through. The larger material is retained on the screen and ground again. By varying the size of the screen, one can roughly control the particle size of the ground material. Apart from this, the feed load rate also affects the grinding efficiency. The particle size distribution with a hammer mill is usually quite wide.

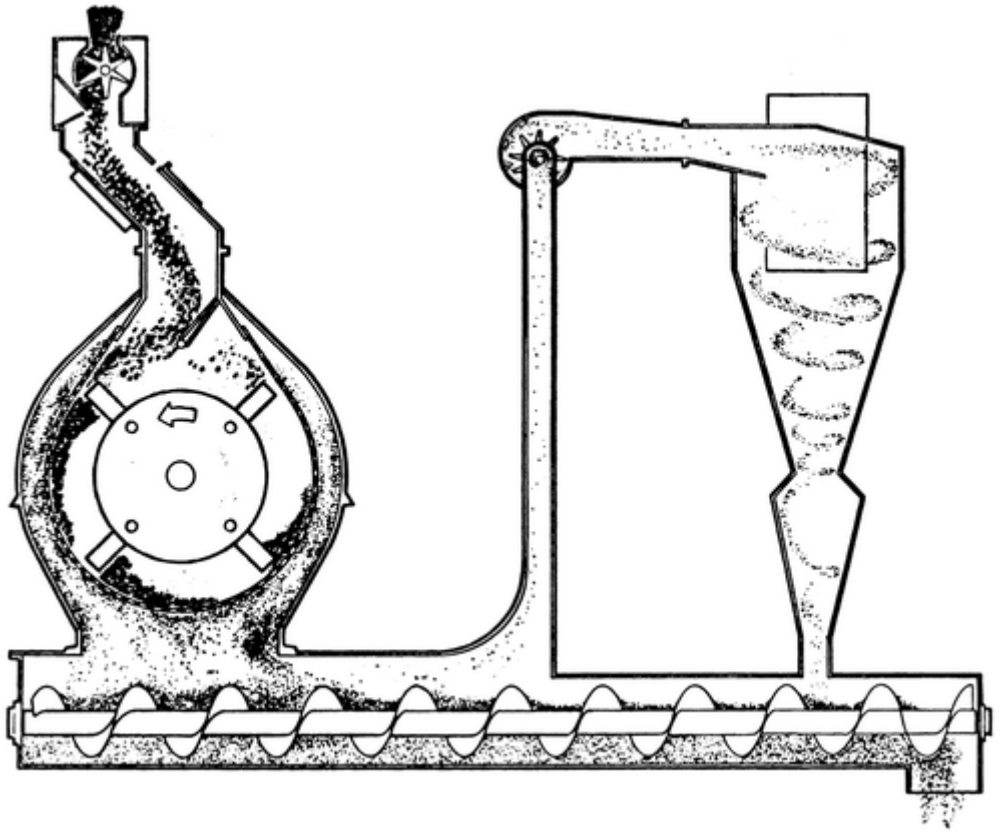


Fig. 17.1. Cut-away view showing air and material flow as they move through an air-assisted hammer milling system. (Reprinted, with permission, from Olson 1983)

Disadvantages of fine grinding are that it produces a very dusty product. The fine material can easily be blown out of feed bunks and is also subject to other forms of waste. The fine, dusty material also makes the feed less palatable to certain animals.

PELLETING

Pelleting the feed into a more dense material largely overcomes the above-cited disadvantages. This is conveniently done with a pellet mill (Fig. 17.2). The feed material along with water, usually in the form of steam, is fed into the pellet mill. The material is forced into the pellet die with great force. After coming through the die, the pellets are broken off. They are hard but much less so than the original feed material. They can be made in various sizes and shapes, from large cubes designed to be fed on the ground to range cattle to small pellets for song birds. It is not totally clear what forces hold the pellets together. Apparently, when the granules in the feed pieces are forced closely enough together, short-range forces are sufficient to hold them together. In addition, different materials in the feed make the pellets stronger or weaker. Pellets are hard and glassy on the surface but mealy in the center. Scanning electron microscopy studies of the pellets show a porous inside with a dense outer layer (Fig. 17.3). Differential scanning calorimetry studies have shown that, at the surface of the pellet, but not in its center, most of the starch is gelatinized. This might be expected considering the shear and heat it undergoes in the pellet die.

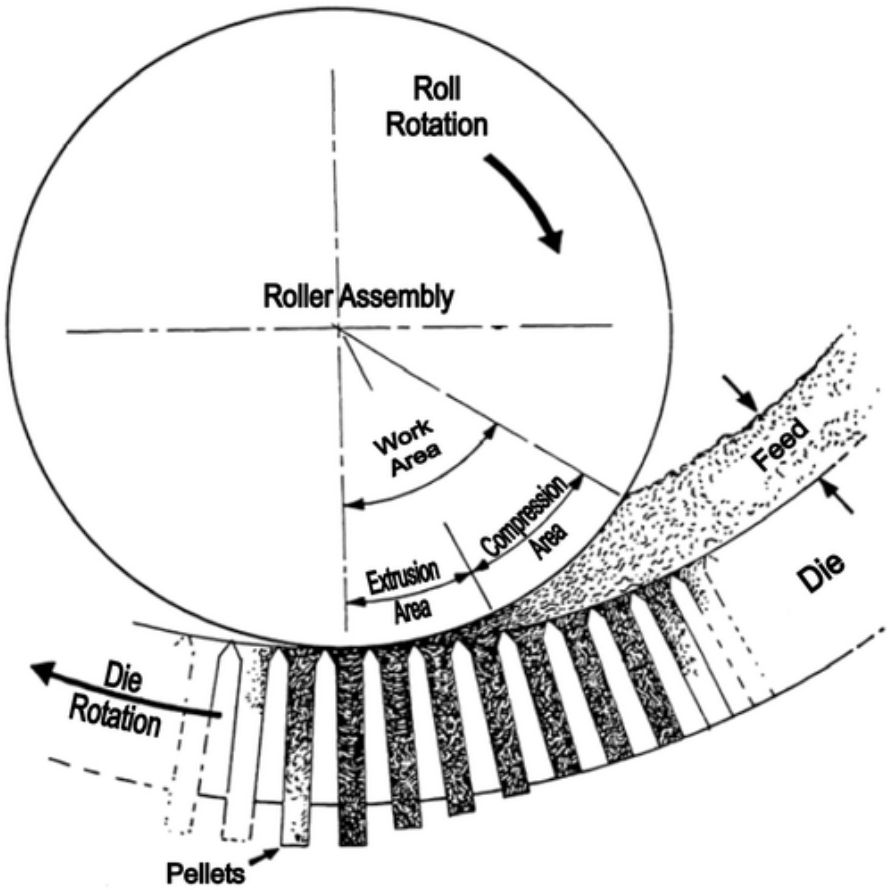


Fig. 17.2. Drawing showing the operation of a pellet mill. (Reprinted, with permission, from Leaver 1988)

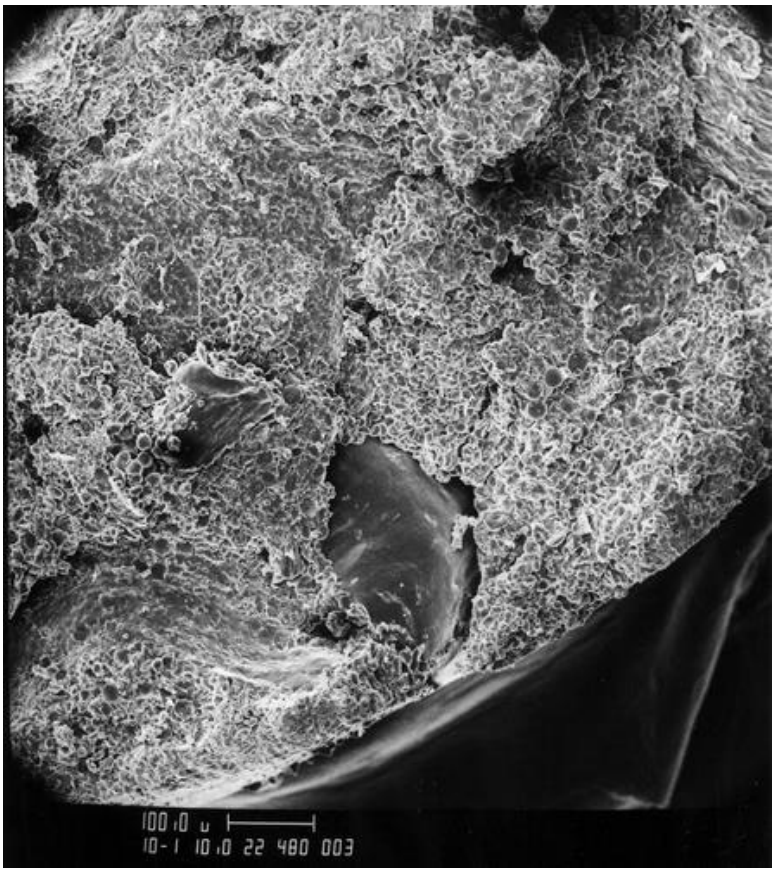


Fig. 17.3. Scanning electron micrograph of a cross-section of a feed pellet. (Courtesy C. Stark)

Alternatives to Grinding

Several dry or wet processes can be used as alternatives to grinding. In what follows, micronizing, popping, and roasting are briefly described, as are steam flaking and extrusion cooking.

DRY HEAT PROCESSING

Micronizing, popping, and roasting are three processes used to heat dry grain for animal feeding.

Micronizing is the heating of grain with infrared heaters. The moisture content is typically reduced to about 7%, and the grain is slightly expanded. Micronized maize generally has a bulk density of about 400 kg per metric ton, while the bulk density of untreated maize is typically 720 kg per metric ton. Micronizing improves both the rate of gain and the feed efficiency of the grain.

Popping of grain is achieved by rapid, intense heating. The degree of expansion depends on the heating rate and the type of grain being heated. Most feed grain does not pop in the sense that popcorn pops (see Chapter 16), but it still expands under a similar treatment. At the same time, the starch gelatinizes. This makes the grains much more available to digestive enzymes and/or organisms. Popped grain is a good material to start cattle on feed. However, its greatly reduced bulk density can be a problem, which manifests itself in two major ways. First, the feed is often blown from the feed bunks, causing waste. Second, the animal cannot consume sufficient feed, resulting in reduced gains. Most users of popped cereals roll the popped grain in an effort to increase its bulk density. Moisture is also often added, often in the form of molasses.

Roasted grain is similar to popped grain except that the grain is heated at a much slower rate. This allows water to be lost and thereby causes much less expansion. Depending upon the rate of heating, the starch is gelatinized, and a small amount of puffing occurs. This leads to improved rates of gain and improved feed efficiencies.

WET HEAT PROCESSING

The most popular wet processing of feed is steam flaking. Steam flaking differs from steam rolling in the amount of time used to steam the grain. In steam flaking, the grain is steamed for longer times than in steam rolling, such that part of the starch gelatinizes and becomes more available to digestive enzymes. As a result, steam flaking improves rates of weight gain and feed efficiency.

Extrusion cooking (see Chapter 15) is another type of wet processing. The grain is heated with water to a temperature and pressure that cause the grain to become a plastic material. It is then extruded to the atmosphere, where it expands. As the material expands, the water is flashed off. The resulting material is glassy in texture but honeycombed with voids that reduce the bulk density. The glassy nature of the extrudate make it adsorb water slowly. The combination of low bulk density and slow absorption make this type of feed useful for fish and other aquatic dwellers.

Fish and Crustacean Feeds

Fish feeds meet a number of specific criteria. One often wants them to float on water, which allows monitoring the feed uptake. This is important because unconsumed feed not only presents an economic loss but also quickly leads to water quality problems. Fish feeds need to be high in protein and relatively low in energy compared to other animal feeds, as fish do not need energy to maintain their body temperature. Crustaceans tend to be slow eaters, and the length of time the feed pieces stay together is of great importance.