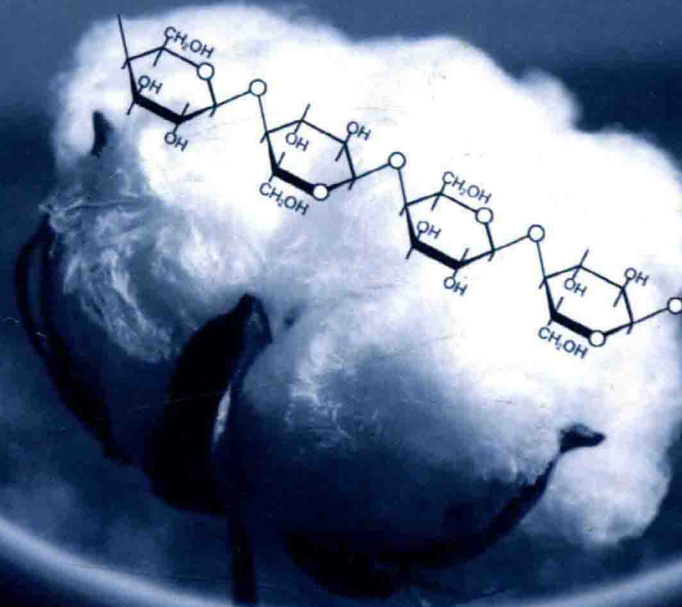


International Fiber Science and Technology

Cotton Fiber Chemistry and Technology



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Cotton Fiber Chemistry and Technology

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Preface

This was published originally as a chapter in the *Handbook of Fiber Chemistry, Third Edition*. Because of particular interest in the new revised and expanded Cotton Fiber chapter, it is also now being published as a separate book. Why does this complex carbohydrate “cotton” get so much attention? Cotton’s many unique properties have made it useful as a textile fiber for over 5000 years. It is the most important natural textile fiber used in spinning to produce apparel, home furnishings and industrial products—about 40% of all textile fiber consumed in the world. Annually, there is over 25 million metric tons of cotton produced in about 80 countries in the world and it is one of the lead crops to be genetically engineered.

Despite over 150 years of laboratory research on cotton and cellulose, there is much exciting new work to learn about. This book’s nationally and internationally recognized contributors have spent their careers gaining in-depth knowledge of cotton fiber chemistry and technology. This includes information on cotton’s origin, biosynthesis, production, structural properties/crystal structure of cellulose, morphology, chemical properties/reaction characteristics, degradation, purification, physical properties, classification and characterization (classing), and utilization which is discussed in this book. Some 650 references cited provide a more in-depth treatment of these subjects.

In particular, we acknowledge professor Menachem Lewin for his many important contributions to cotton chemistry and for inspiring this book. Without his strong support it would not exist. Glenn P. Johnson, ARS, SRRC, USDA was invaluable in converting and updating the previous chapter to this book. Fortunately, this book was mostly finished before hurricane Katrina devastated the city of New Orleans and the USDA Southern Regional Research Center where many of the contributors to this book worked.

In conclusion, we have striven to provide information about the chemistry and technology of cotton fiber. We hope this will assist readers in becoming more informed about the unusual carbohydrate called cotton and why it is such an important textile fiber.

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1 General Description of Cotton

Cotton (Figure 1.1) is the most important natural textile fiber, as well as cellulosic textile fiber, in the world, used to produce apparel, home furnishings, and industrial products. Worldwide about 40% of the fiber consumed in 2004 was cotton [1]. (See also Table 9.1 World Production of Textile Fibers on page 130.) Cotton is grown mostly for fiber but it is also a food crop (cottonseed)—the major end uses for cottonseeds are vegetable oil for human consumption; whole seed, meal, and hulls for animal feed; and linters for batting and chemical cellulose.

Its origin, development, morphology, chemistry, purification, and utilization have been discussed by many authors [2–12]. The chemistry, structure, and reaction characteristics of cellulose, the carbohydrate polymer that forms the fiber, are thoroughly treated in a number of excellent works [8,9,12–19]. This book is intended to provide an overview of the current state of knowledge of the cotton fiber. Much of the information reported here is taken from the references cited at the end of the book, which should be consulted for a more in-depth treatment.

Cotton fibers are seed hairs from plants of the order Malvales, family Malvaceae, tribe Gossypieae, and genus *Gossypium* [2–5,10,11]. Botanically, there are four principal domesticated species of cotton of commercial importance: *hirsutum*, *barbadense*, *aboreum*, and *herbaceum*. Thirty-three species are currently recognized; however, all but these four are wild shrubs of no commercial value. Each one of the commercially important species contains many different varieties developed through breeding programs to produce cottons with continually improving properties (e.g., faster maturing, increased yields, and improved insect and disease resistance) and fibers with greater length, strength, and uniformity.

Gossypium hirsutum, a tetraploid, has been developed in the United States from cotton native to Mexico and Central America and includes all of the many commercial varieties of American Upland cotton. Upland cottons now provide over 90% of the current world production of raw cotton fiber. The lengths, or staple lengths, of the Upland cotton fiber vary from about $\frac{7}{8}$ to $1\frac{1}{2}$ in. (22–36 mm), and the micronaire value (an indicator of fiber fineness and maturity but not necessarily a reliable measure of either; see Chapter 8) ranges from 3.8 to 5.0. If grown in the United States, *G. hirsutum* lint fibers are 26–30 mm (1 to 1–3/16 in.) long [20]. Fiber from *G. hirsutum* is widely used in apparel, home furnishings, and industrial products.

Gossypium barbadense, a tetraploid, is of early South American origin and provides the longest staple lengths. The fiber is long and fine with a staple length usually greater than $1\frac{3}{8}$ in. (35 mm) and a micronaire value of below 4.0. If grown in the United States, *G. barbadense* lint fibers are usually 33–36 mm ($1\frac{5}{6}$ to $1\frac{1}{2}$ in.) long [20]. Commonly known as extra-long-staple (ELS), it supplies about 8% of the current world production of cotton fiber. This group includes the commercial varieties of Egyptian, American–Egyptian, and Sea Island cottons. Egypt and Sudan are the primary producers of ELS cottons in the world today. Pima, which is also ELS cotton, is a complex cross of Egyptian and American Upland strains and is grown in the western United States (mainly California with some in Arizona, southwestern Texas, and New Mexico), as well as in South America. Pima has many of the characteristics of the

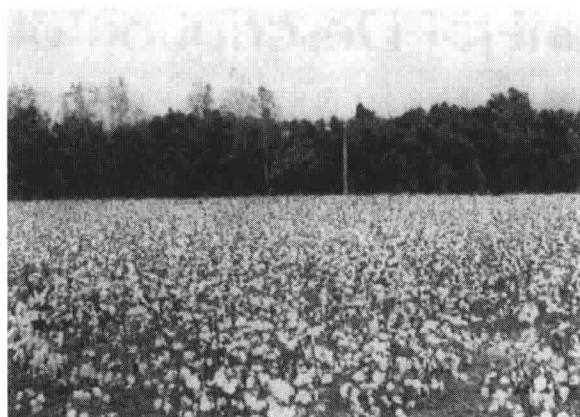


FIGURE 1.1 Mature cotton in the field ready for harvesting. (Courtesy of the National Cotton Council of America, Memphis, TN.)

better Egyptian cottons. This fiber from *G. barbadense* is used for the production of high-quality apparel, luxury fabrics, specialty yarns for lace and knitted goods, and sewing thread.

The other commercial species—*Gossypium aboreum* and *Gossypium herbaceum*, both diploids—are known collectively as “Desi” cottons, and are the Asiatic or Old World short staple cottons. These rough cottons are the shortest staple cottons cultivated (ranging from $\frac{3}{8}$ to $\frac{3}{4}$ in. (9.5–19 mm)) and are coarse (micronaire value greater than 6.0) compared with the American Upland varieties. Both are of minor commercial importance worldwide but are still grown commercially in Pakistan and India. *G. aboreum* is also grown commercially in Burma, Bangladesh, Thailand, and Vietnam [3,10].

Varietal development programs were once confined to classical methods of breeding that rely on crossing parents within species. Currently, in addition to the conventional breeding methods, research is underway on hybrids to produce new varieties, and modern biotechnology (recombinant DNA technology) to produce biotech or transgenic cottons [21,22], which enhance production flexibility. Biotech cottons deliver high-tech options to farmers and consumers without compromising environmental quality. Since the introduction of *Bacillus thuringiensis* (Bt) biotech cotton in 1996, cotton has been one of the lead crops to be genetically engineered, and biotech cotton has been one of the most rapidly adopted technologies ever. The current varieties of commercial importance address crop management or agronomic traits that assist with pest management (insect resistant) or weed control (herbicide tolerance). Nine countries, representing over 59% of world cotton area, allow biotech cotton to be grown: Argentina, Australia, China (Mainland), Colombia, India, Indonesia, Mexico, South Africa, and United States. Other countries (e.g., Pakistan, Brazil, Burkina Faso, Egypt, and the Philippines) are considering approving the cultivation of biotech cotton. In 2003–2004, about 21% of the world’s cotton acreage and about 30% of the cotton produced in the world was biotech cotton; in 2004–2005, about 35% of world’s cotton production was biotech cotton; and within five years, world biotech cotton production could be close to 50%.

The initial biotech efforts have been centered on insect resistance and herbicide tolerance. Insect resistance has been conferred through the incorporation of genes from Bt that produce Bt δ -endotoxin, a naturally occurring insect poison for bollworms and budworms. The reduction in the use of insecticides minimizes the adverse effects on nontarget species and beneficial insects. Herbicide tolerance enables reduced use of herbicides and encourages use of safer, less persistent materials to control a wide spectrum of weeds that reduce yield and lint quality of cotton. Transgenic herbicide tolerance moves cottonweed management away from

protective, presumptive treatments toward responsive, as-needed treatments. While insect resistance and herbicide tolerance are the only traits currently available in biotech cottons, a broad range of other traits are under development using modern biotechnology. These may impact the agronomic performance, stress tolerance, fiber quality, and yield potential directly. However, in 2005 few of these traits are close to commercialization. As soon as new developments in bioengineered cotton for insect resistance, herbicide tolerance, stress tolerance, yield potential, improved fiber quality, etc., are available, they will be incorporated into conventional cotton varieties.

The cottons of commerce are almost all white (creamy yellow to bright white). In recent years, there has been a renewed interest in naturally pigmented and colored cottons, which have existed for over 5000 years [23,24]. These cotton varieties are spontaneous mutants of plants that normally produce white fiber. The availability of inexpensive dyes and the need for higher-output cotton production worldwide caused the naturally colored cottons to almost disappear about 50 years ago. Yields were low and the fiber was essentially too short and weak to be machine spun. Breeding research over the last 15 years reportedly has led to improvement in yields, fiber quality, fiber length and strength, and color intensity and variation [25]. Naturally colored cottons are a very small niche market. The cottons available today are usually shorter, weaker, and finer than regular Upland cottons, but they can be spun successfully into ring and rotor yarns for many applications [26]. They can be blended with normal white cottons or blended among themselves. For a limited number of colors, the use of dyes and other chemicals can be completely omitted in textile finishing, possibly generating some savings, which can compensate for the higher raw material price. The color of the manufactured goods can intensify with washing (up to 5 to 10 washings), and colors vary somewhat from batch to batch [26]. Naturally colored cottons are presently grown in China, Peru, and Israel. The amount available in 2005 is very small, perhaps 10,000 U.S. bale equivalents (about 2270 metric tons). Shades of brown and greens are the main colors that are available. Other colors (mauve, mocha, red) are available in Peru in a very limited supply and some others are under research. The color for brown and red-brown cottons appears to be in vacuolar tannin material bodies in the lumen (Figure 1.2a). The different colors of brown and red-brown are mostly due to catechin–tannins and protein–tannin polymers [27]. The green color in cottons (Figure 1.2b) is due to a lipid biopolymer (suberin) sandwiched between the lamellae of cellulose microfibrils in the secondary wall [27–29]. The brown fibers (and white lint) do not contain suberin. Green cotton fibers are characterized by high wax content (14–17% of the dry weight) whereas white and brown fibers contain about 0.4–1.0% wax [27].

Cotton grown without the use of any synthetically compounded chemicals (i.e., pesticides, fertilizers, defoliant, etc.) is considered as “organic” cotton [30–34]. It is produced under a system of production and processing that seeks to maintain soil fertility and the ecological environment of the crop. To be sold as organic it must be certified. Certified organic cotton was introduced in 1989–1990 and over 20 countries have tried to produce organic cotton. Since 2001, Turkey has been the largest producer of organic cotton. There are small projects in Mali, Kyrgyzstan, and some other developing countries [35]. In 2001, about 14 countries in the world produced about 27,000 U.S. bale equivalents (5700 metric tons) of organic cotton, with Turkey, the United States, and India accounting for about 75% of production [36]. In 2003, in the United States, 4628 U.S. bale equivalents of organic cotton were produced; in 2004, 4674 acres were planted and about 5000 U.S. bale equivalents were produced [37]. In 2005, the world’s production of organic cotton was about 100,000 U.S. bale equivalents (about 25,000 metric tons), which is less than 0.12% of world’s total cotton production [38].

Unlike synthetic fibers, which are spun from synthetic or regenerated polymers in factories, cotton fiber is a natural agricultural product. The United States and some other countries use the newest and latest tested technology to produce the cotton crop [8,9]. Cotton

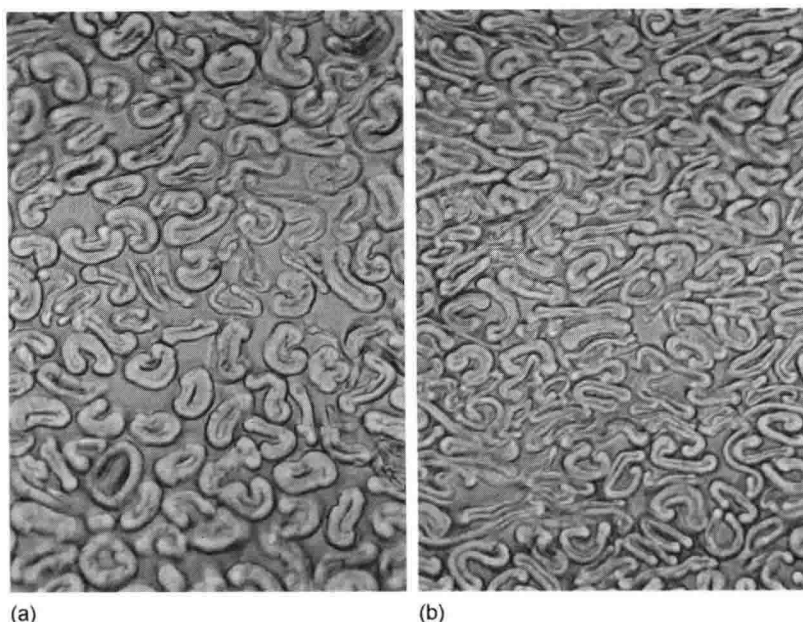


FIGURE 1.2 Fiber bundle cross-sections obtained with transmitted light microscopy (a) for natural brown cotton where the presence of material bodies are visible within the lumens of some fibers and (b) for natural green cotton where the fibers are quite immature and are characterized by the presence of suberin in the fiber walls and not material bodies in the lumen.

production is scattered among hundreds of thousands of small, independent farms (about 20,000–25,000 in the United States), whereas the synthetic fiber industry is concentrated in a few corporations that have production plants worldwide. Cotton is grown in about 80 countries in the world; in 2004–2005, 59 countries cultivate at least 5000 ha (12,350 acres (1 ha = 2.47 acres)) [39]. In many developing countries, cotton farms range in size from less than 1 to about 10 ha. In 2004, developing countries accounted for about 75% of the world's production, and China, the United States, India, Pakistan, Uzbekistan, Turkey, and Brazil account for over 81% of the world's cotton production [40]. Cotton production in the United States is usually about 18–20 million U.S. bale equivalents (8.6–9.6 billion pounds (3.9–4.4 million metric tons)) annually and worldwide production is about 90–105 million bales (45.0–52.5 billion pounds (20.4–23.8 million metric tons)) annually. Raw cotton is exported from about 57 countries and cotton textiles from about 65 countries.

Cotton production, harvesting, and ginning are described in more detail in other sources [2–5,8,9,41,42]. The cotton plant is a tree or a shrub that grows naturally as a perennial, but for commercial purposes it is grown as an annual crop. Botanically, cotton bolls are fruits. Cotton is a warm-weather plant, cultivated in both hemispheres, mostly in North and South America, Asia, Africa, and India (in tropical latitudes). Mostly it is cultivated in the Northern Hemisphere. It is primarily grown between 37°N and 32°S but can be grown as far north as 43°N latitude in Central Asia and 45°N in mainland China. Planting time for cotton varies with locality, i.e., from February to June in the Northern Hemisphere [2–5,8–11]. The time of planting in the Northern Hemisphere is the time of harvest in the Southern Hemisphere. Seedlings emerge from the soil within a week or two after planting, 5–6 weeks later flower buds or squares form, and white (Upland cotton) or creamy yellow (Pima cotton) to dark-yellow blossoms appear in another 3–4 weeks. The time interval from bloom to open boll is about 40–80 days. The open boll lets air in to dry the white, clean, fiber, and fluff it for the harvest (Figure 1.3).

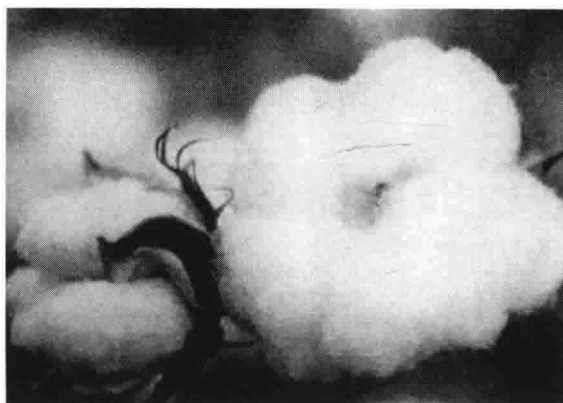


FIGURE 1.3 Open cotton boll. (Courtesy of the National Cotton Council of America, Memphis, TN.)

Each cotton fiber is a single, elongated, complete cell that develops in the surface layer of cells of the cottonseed. The mature cotton fiber is actually a dead, hollow, dried cell wall [4,5,43]. In the dried out fiber, the tubular structure is collapsed and twisted, giving cotton fiber convolutions, which differentiate cotton fibers from all other forms of seed hairs and are partially responsible for many of the unique characteristics of cotton. The biosynthesis and morphology of the cotton fiber are discussed in more detail later (see Chapter 2).

The relatively long fiber lengths (about 1 in. (25.4 mm) or longer) on the cottonseed relate to the fiber that is used by the textile industry. This raw cotton fiber, which can be spun into textile yarns, is called lint. However, another type of fiber, *linters* or *fuzz fibers*, which are very short, is also produced on the seed along with the lint [44]. The distribution of the lint and fuzz fibers over the seed surface is neither uniform nor random. The base of the seed mostly produces lint fibers, whereas cells near the tip of the seed mostly produce fuzz fibers.

The long lint fibers are removed at the cotton gin, but the short linter fibers are still attached to the seed after ginning for *G. hirsutum* (Upland cotton); *G. barbadense* seed does not contain linters. The linter fibers are removed at the cottonseed oil mill by the delinting process prior to the oil extraction process, producing fibers of different lengths. In general, ginned cottonseed is composed of about 8% linters. Linters can be distinguished from lint by several characteristics:

1. Length (commercial lint averages 1 in. (25.4 mm) and first-cut linters average about 0.5 in. (12–15 mm))
2. Pigmentation (linters are often light brown or highly colored)
3. Strength of adherence to seed (linters are more tightly held to the seed)
4. Chemical and physical properties

Linters are also much coarser than lint fibers; linters have a coarse, stiff form without the flexibility or convolutions of lint fibers; and the tips of linter fibers are somewhat tapered but not to the same extent as those of lint fibers. Linter fibers have hardly any lumen. The diameter of the linter fiber is usually about twice the diameter of the lint fiber. In lint fibers, the growth of the primary cell wall starts on the day of flowering and within 20 days they exhibit a 3000-fold increase in length, whereas fuzz fibers (linters) initiate elongation about 4 days after flowering. The secondary cell wall, formation of which begins about 20 days after flowering, is different in lint and in fuzz fibers; for example, the secondary cell wall at the base of the fiber is much thicker in linters than in lint. Although not suitable for textile processing, the linters are used in other applications, for example, second-cut linters (the shortest linter

fiber) are used as a chemical feedstock for manufacturing plastics and rayons, whereas first-cut linters (the longer fiber) can be used for batting and padding in bedding, upholstered furniture, automotive applications, and paper (most currencies are made of cotton paper).

Harvesting time for cotton varies with locality (Table 1.1).

TABLE 1.1
Typical Weight and Densities of Cotton Bales in Various Countries and Harvest Date

Country	Harvest	Bale Weight				Density	
		Avg.		Range		kg/m ³	lb/ft ³
		kg	lb	kg	lb		
North and Central America							
U.S.	July–Jan.	225	495	217–230	477–506	427.1	26.7
Mexico	June–Jan.	227	499	180–240	396–528	380.1	23.8
Guatemala	Nov.–Mar.	227	499	220–236	484–519	251.4	15.7
South America							
Brazil	Aug.–Jan. or Feb.–May	140	308	110–180	242–396	243.1	15.2
Argentina	Feb.–June	220	484	195–250	429–550	346–429	21.6–26.8
Paraguay	Feb.–June	198	436	160–225	352–495	420.9	26.3
Columbia	July–Sept. or Dec.–Mar.	225	495	220–240	484–528	516.2	32.3
Peru	Feb.–Oct.	240	528				
Venezuela	Feb.–May						
Europe							
Greece	Sept.–Nov.	234	516				
Spain	Sept.–Nov.	225	495	200–250	440–550	396.8	24.8
Asia–Oceania							
Uzbekistan	Sept.–Nov.	200	440	190–220	418–484	490.2	30.6
China Bale I	Sept.–Nov.	85	187	80–90	176–198	442.7	27.7
Bale II	Sept.–Nov.	200	440	190–210	418–462	439.8	27.5
India	July–Jan. or Dec.–May	170	375	165–175	363–385	379.8	23.7
Pakistan	Sept.–Feb.	170	375	160–185	352–407	547.5	34.2
Turkey	Sept.–Dec.	217	478	190–245	418–539	342.3	21.4
Australia	Apr.–June	227	499	150–240	330–528	449.6	28.1
						327.6	20.4
Iran	Oct.–Dec.	200	440	170–240	375–528	226.8	14.1
Syria	Sept.–Nov.	205	451	192–212	422–466	425–434	26.6–27.1
Africa							
Egypt	Sept.–Oct.	327	720	290–345	638–759	541.6	33.8
Sudan	Jan.–Apr. or Sept.–May	188	414	185–191	407–420	361–397	22.6–24.8
South Africa	Apr.–May	206	453	170–240	375–528	437.4	27.3
Ivory Coast	Oct.–Jan.	215	474				
Tanzania	May–July	183	403				
Nigeria	Dec.–Feb.	185	407				

Source: Bale weights—From Munro, J.M., *Cotton*, 2nd ed., Longman Scientific and Technical, Essex, England and John Wiley & Sons, New York, 1987, p. 333; Bale survey—From International Cotton Advisory Committee, Oct. 1995; and Harvest date—From Volkart Brothers Holding, Ltd., Switzerland, 1991.

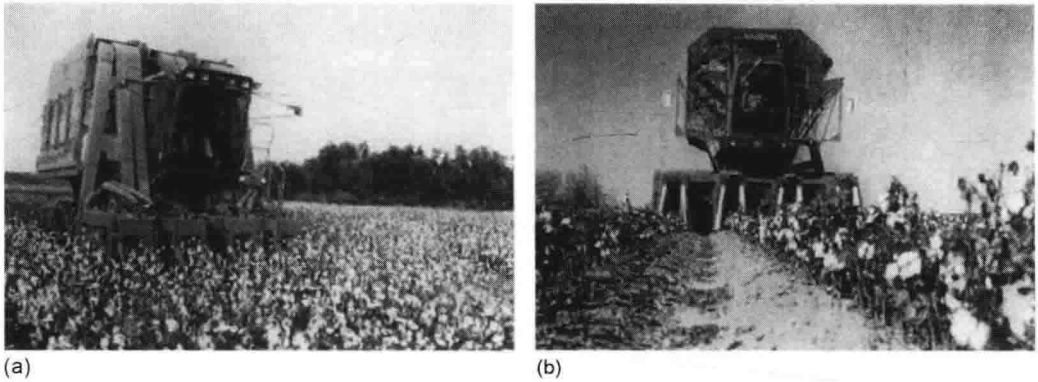


FIGURE 1.4 (a) Mechanical harvesting by means of a cotton picker. (b) Mechanical harvesting by means of a cotton stripper. (Courtesy of the National Cotton Council of America, Memphis, TN.)

The operations of harvesting [11] and ginning the fiber [41], as well as cultural practices during the growing season, are very important to the quality of the cotton fiber [5,11]. Harvesting is one of the final and most important steps in the production of a cotton crop [5,9,11,12], as the crop must be harvested before the inclement weather can damage the quality and reduce the yield. Because of economic factors, virtually the entire crop (>99%) in the United States and Australia is harvested mechanically (Figure 1.4). In rest of the world (~75%) hand harvesting of cotton, one boll at a time, is still quite prevalent, particularly in the less developed countries and in countries where the labor is cheaper [45].

Mechanically harvested cotton, either with cotton picker machines (cotton burr remains attached to the stalk) or with stripper machines (cotton burr is removed along with the seed cotton), can contain more trash and other irregularities than hand-harvested cotton. However, according to “Cotton contamination surveys” by the International Textile Manufacturers Federation (ITMF), the most contaminated cottons originate from some of the countries where cotton is hand-picked, whereas some of the cleanest can be sourced in the USA where cotton is machine harvested [34]. Most of the mechanically harvested cotton is harvested with cotton pickers (~75% in the United States and all in Australia).

After harvesting, the seed cotton (consisting of cotton fiber attached to cottonseed and plant foreign matter), a raw perishable commodity, is transported to the ginning plant in trailers or modules, or is stored in the field in modules. In the United States, module storage is used for almost the entire crop. Field storage in modules maximizes efficiency at the gin.

Ginning is the separation of the fibers from seed and plant foreign matter [41,42]. Cotton essentially has no commercial value or use until the fiber is separated from the cottonseed and the foreign matter at the gin. Ginning operations, which are considered a part of the harvest, are normally considered to include conditioning (to adjust moisture content), seed–fiber separation, cleaning (to remove plant trash), and packaging (Figure 1.5). Upland cottons are ginned on saw gins (Figure 1.6), whereas roller gins are used for ELS cottons.

Raw cotton in its marketed form consists of masses of fibers in densely packed bales (>22 lb/ft³ (352 kg/m³), Figure 1.7) [42].

The bales into which cotton is packed are of varying dimensions, volumes, densities, and weights (see Table 1.1) and are mainly covered with woven polypropylene, polyethylene film, burlap, or cotton fabrics (Figure 1.8).

In the United States, bales weigh on an average 490 lb (222 kg). A single pound of cotton may contain 100 million or more individual fibers (about 50 to 55 billion fibers in a 480-lb bale).

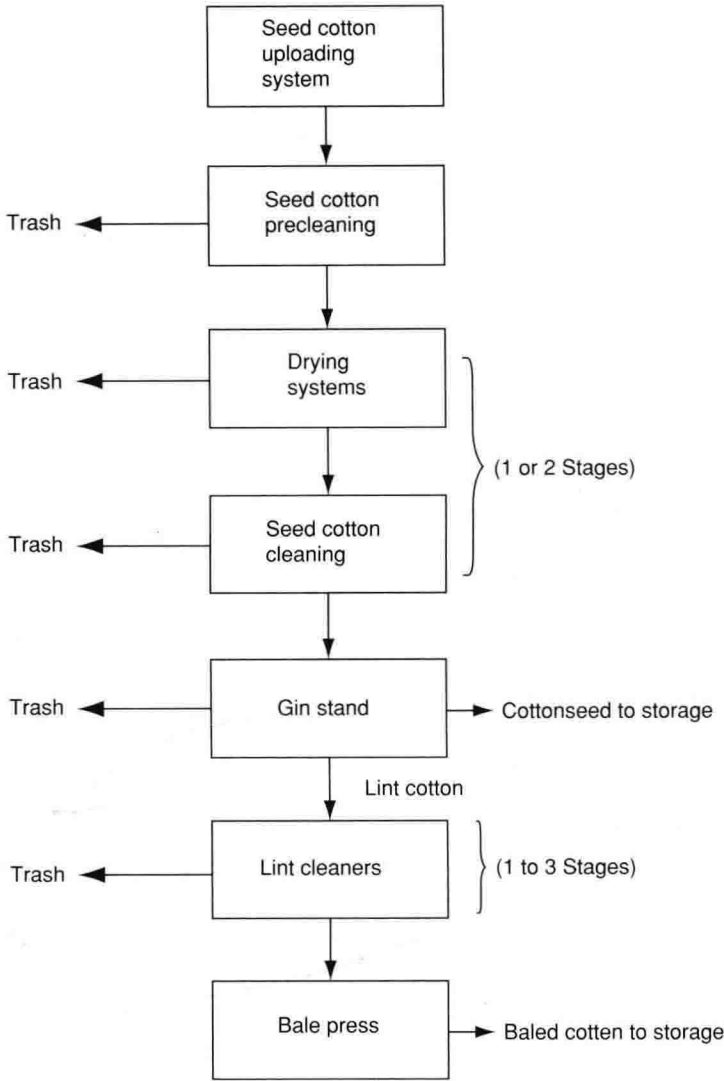


FIGURE 1.5 Simplified flow chart of ginning systems. (Courtesy of the National Cotton Council of America, Memphis, TN.)

In the rest of the world, bales usually weigh 375–515 lb (170–233 kg), depending on the country where they are produced (Table 1.1) [19,41]. The *International Organization for Standardization* (ISO) specifies (ISO 8115 [46]) that bale dimensions and densities should be: length 1400 mm (55 in.), width 530 mm (21 in.), height 700–900 mm (27.5–35.4 in.), and density of 360–450 kg/m³ (22.5–28.1 lb/ft³). Typical bale dimensions for the U.S. universal density (UD) bales are 1400 mm (55 in.) length × 533 mm (21 in.) width × 736 mm (29 in.) height, resulting in a bale density of approximately 448 kg/m³ (28 lb/ft³).

At the gin, baled cotton is sampled so that grade and other quality parameters can be determined and the cotton is classed at the U.S. Department of Agriculture (USDA) classing offices. Classification is a way of measuring the fiber quality and physical attributes of this natural product that affect the manufacturing efficiency and quality of the finished product (see Chapter 8). Cotton bales are usually stored in warehouses prior to going to the textile mill [42].