Cotton Linters: An Alternative Cellulosic Raw Material

Axel Sczostak

Summary: Cellulose in fibrous or in chemically modified form plays a relevant part in products for industrial applications and in products which are used in human daily life. Besides wood, cotton is an important natural source for cellulose. Linters are a by-product of the oil mills. The position of the linters in the technology of cotton is explained. In linters bleaching plant, the raw linters are purified mechanically and chemically. The principle of this process is shown. The resulting bleached linters (cotton linters pulp, CLP/cotton linters cellulose, CLC) have an alpha-cellulose content of about 99%. Due to their purity and to their properties, the cotton linters pulp is the cellulosic basis for a large number of special and niche products in the paper and chemical industry.

Keywords: cellulose; cotton; fibres; linters; market; processing

Introduction

The purpose of this review is to give you an overview of

- cotton and cotton linters
- the technology of cotton and cotton linters
- cotton linters fibres and their morphology
- cotton linters fibres and their attributes
- the basics of the linters bleaching process
- purified cotton linters celluloses and their applications.

The focus will be on the fibres, their characteristics, and their potentials in chemical conversions and in papermaking.

Cotton and Cotton Linters

The cotton plant - botanically *Gossypium* - is a genus of the Mallow family (*Malvaceae*) which makes it a relative of such well-known garden plant like hibiscus.[1,2]

MILOUBAN M.C.P. Ltd., European Office, Am Markt 9, 25348 Glückstadt, Germany
Fax: +49 (0) 4124 60 97 95;
E-mail: sczostak@milouban.com

From the fertilized cotton flowers seed capsules develop, each including 30-40 oil-containing seeds. Each cotton seed is capable of producing about 5000[2] up to 20000[3] single seed hairs, the cotton fibres. Each fibre represents a single cell emerging from the seed coat, it is an outgrowth of the epidermis cell.[1,3]

When the ripe capsule bursts open, the fibres ooze from it. They had passed a three-stage development period consisting of elongation, thickening, and maturation. The open capsules are typically named bolls (see Figure 1).[1,3]

The cotton seed in cross-section as shown in Figure 2 visualizes the basic difference between lint and linters: The lint or staple cotton is the long-fibre population which develops first. Once this population is established, the short and thick-walled fibres of the fuzz develop. This fuzz is known as linters.

The cotton plant is an annual shrub which is grown in the subtropical and tropical regions North and South of the equator. Most of the cotton is cultivated in the Northern hemisphere. The cotton farmers can choose between many varieties of cotton seeds which are bred to be productive under various conditions when grown in different environments. All these

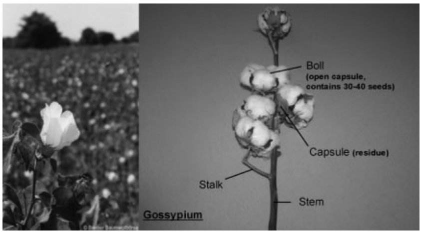


Figure 1.
The cotton plant.

varieties are predominantly based on four cotton species, which are of commercial relevance:

- *G. hirsutum* (native to Mexico and Central America)
- *G. barbadense* (historically originating from Peru)
- *G. arboretum* (native to India/Pakistan)
- *G. herbaceum* (historically originating probably from Southern Africa).

The cotton species which is cultivated most commonly is *G. hirsutum*. For example, *G. hirsutum* accounts for more than 95% of the U.S. cotton production.[3] In the U.S., the cotton varieties which are based on *G. hirsutum* are known as American Upland Cotton.

G. barbadense is the species among the four which is the most sensitive to day length (photoperiodic), so its cultivation is limited to a few countries like

- the U.S. where it is known as American Pima (5% of the domestic cotton production).
- Israel (70% of the domestic cotton production
- Egypt (100% of the domestic cotton production).

The famous Sea Island Cotton from the U.S. which is said to have the best cotton fibre quality world-wide also belongs to the *G. barbadense* species. The other two species, *G. arboretum* and *G. herbaceum*, are cultivated mainly in Asia (not in the U.S.) and embrace cottons of shorter fibre length. In this context it is interesting to realize that the species *G. barbadense* develops seed which is free of any fuzz. This so-called naked seed bears staple cotton fibres only but no linters fibres. The other species mentioned above do have the linters fuzz.[1,3]

The world-wide production projected for 2008/09 is about 24–25 millions metric tons of staple cotton.[4] The global distribution of cotton is shown in Figure 3.[2]

The only purpose for growing cotton was and still is to gain the staple cotton fibre, the lint, for supplying the global textile industry. This is the reason why there is a lot of statistical data available regarding staple cotton but almost none regarding cotton linters. We will see later in more detail that cotton linters are a by-product and simultaneously a cellulose specialty which appears at a later stage of the whole cotton technology chain.

Figure 4 visualizes the route of the staple fibres and of the cottonseed within the cotton technology chain:

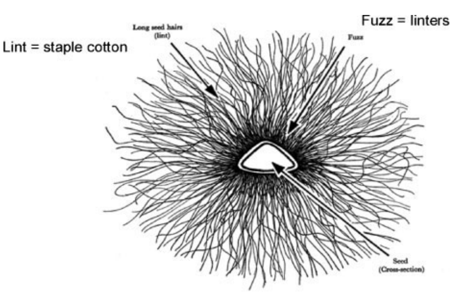


Figure 2.
Cross-section of a cotton seed.[1]

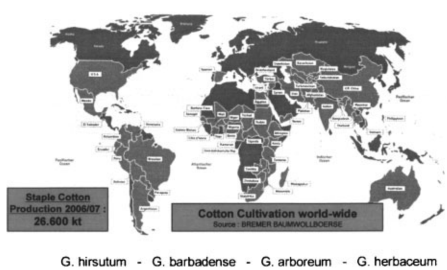


Figure 3.
Global cotton cultivation.

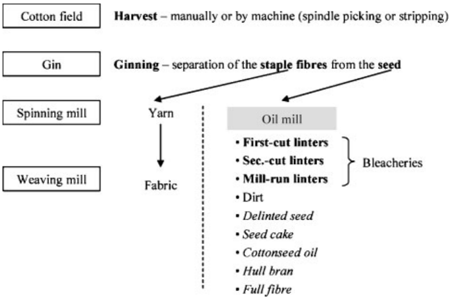


Figure 4.
Cotton linters and the technology of cotton.

- The cotton is harvested manually or by machine (spindle picking or stripping). The resulting product is the cotton balls.
- The cotton balls are delivered to the gins. Their task is to separate the staple fibres from the cottonseed by roller ginning (used with extra-long staple cotton) or by saw ginning (typically used).
- While the separated staple fibres are further processed in the spinning and the weaving mills, the cottonseed with the linters fuzz is delivered to the oil mills.
- The fundamental objective of the oil mills is to produce cottonseed oil[5], a valuable vegetable oil, and to simultaneously market for economic reasons all those by-products which are produced during cottonseed processing[6]: (1) Cotton linters (first-cut, second-cut, millrun), (2) seed hulls, and (3) seed cake (meat).

The oil mill process (Figure 5) consists of several stages in order to get an optimum

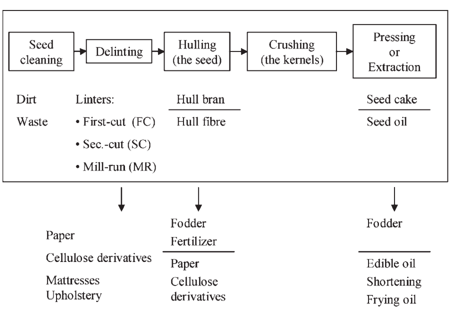


Figure 5.
The oil mill process.

yield of cottonseed oil. In the oil mill, the cottonseed is processed through a machine which uses rotating saws to remove the linters fibres before the oil is pressed and extracted from the crushed seed. This machine is called ‘‘linter’’, hence the name linters for the fibres. The linters fibres are generated typically in two successive stages (first and second-cut).[1]

The oil mill products aim at different markets:

- Cotton linters are regarded world-wide as a valuable cellulose raw material for paper manufacture, for the conversion to cellulose derivatives and for regenerated fibres. The global cotton linters trade mainly distinguishes between first-cut, second-cut, and millrun linters.
- Hull bran, i.e. ground seed hulls, are used as livestock feed and as fertilizer.
- Hull fibres are of subordinate relevance. It is a fibre material of very short fibre length.
- Seed cake (meat) is marketed as feed for beef and diary cattle.
- Cottonseed oil, the actual target product, is sold as a versatile vegetable oil that however requires a refinement later for removing the toxic pigment gossypol[3] before it is used in food manufacturing (cooking and salad oil, potato chip frying, household shortening).

The terminology ‘‘first-cut’’, ‘‘second-cut’’, and ‘‘millrun’’ refers to the oil mill process and to the number of delinting operations used. After the first delinting stage, the fibre product is called first-cut linters. The raw linters obtained after a second delinting stage has been passed are called second-cut linters. The millrun linters result if the oil mill only runs one single delinting stage. A longitudinal section of the seed visualizes the progress in delinting when using a two-stage delinting process (Figure 6).[1]

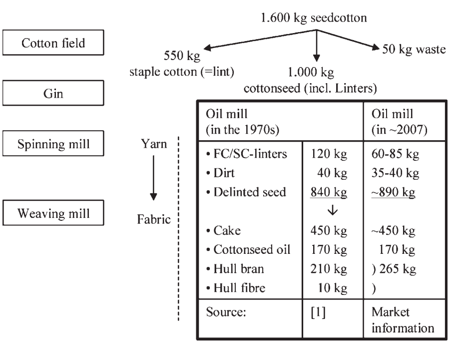
There is an interesting aspect when looking at the product balance of a ‘‘typical’’ oil mill (Figure 7). In the 1970s, the oil mills gained 120 kg of (raw) linters

Figure 6.
Cotton seed in longitudinal section during the oil mill process: Before delinting, after 1st cut, after 2nd cut (from left to right).[1]

fibres from 1000 kg of cottonseed (= 12%).[1] Today, it is roughly only half of it (6-8.5%). It is said that this phenomenon is the consequence of the permanent breeding of new varieties in order

- to increase the cotton yield per hectare
- to get cotton fibres which have all reached the same grade of maturity when harvested
- to improve the fibre properties of cotton
- to apply genetic engineering (since 1996 in the U.S.) for creating either a tolerance towards herbicides ("Roundup Ready Cotton") or a resistance towards insects like the bollworm ("BXN Cotton").[3]

After having had a look to the technology of cotton and cotton linters, it is useful to have a look to the morphology of a cotton linters fibre as it is shown in



	Oil mill (in the 1970s)	Oil mill (in ~2007)
• FC/SC-linters	120 kg	60-85 kg
• Dirt	40 kg	35-40 kg
• Delinted seed	840 kg	~890 kg
• Cake	450 kg	~450 kg
• Cottonseed oil	170 kg	170 kg
• Hull bran	210 kg	) 265 kg
• Hull fibre	10 kg	)
Source:	[1]	Market information

Figure 7.
Typical product balance of an oil mill.

Figure 8.[3,7] The primary wall, the thin wall of the seedcoat epidermis cell, develops during the elongation period. Once the fibre length is established and the fibre stops growing, the 2nd stage of fibre formation takes place: Cellulose is deposited in successive layers on the inner surface of the primary wall. It is the thickening stage where the secondary walls (S1, S2, S3) are formed. During the maturation period, the boll opens. The fibre dries and collapses. The lumen which was filled with protoplast at the beginning becomes a central void space.[1,3]

In Table 1, the attributes of cotton linters are compared with those ones of staple cotton fibres.[1]

Cotton linters are short, thick-walled, quite curly and basically cylindrical whereas staple cotton fibres are long, thin-walled, relatively straight and shaped like a flat twisted ribbon.

The curl of a fibre is defined as the ratio of the true length (L) to the projected length (Lp) and is expressed in %: $(L/Lp-1) \times 100\%$.

Linters fibres have a higher reactivity than staple fibres due to their better accessibility for chemical reagents. In addition, the curly shape provides a three-dimensional character especially for the second-cut linters fibres which produces bulky and porous structures.

Staple fibres have a two-dimensional character being the precondition for high strength.

The photomicrographs shown in Figure 9[8] visualize the difference in the cross-section of a second-cut cotton linters fibre and a cotton staple fibre: The cross-section of the linters fibre is more roundish, the cell wall is thicker.

Cotton linters fibres comprise a certain amount of staple fibres because - after ginning - the fuzz remaining on the seed consists of cotton linters fibres and a varying quantity of staple fibres. A method for visually estimating the staple fibre content in linters is to comb out cotton linters samples and to generate linters bands where the overlengths can be

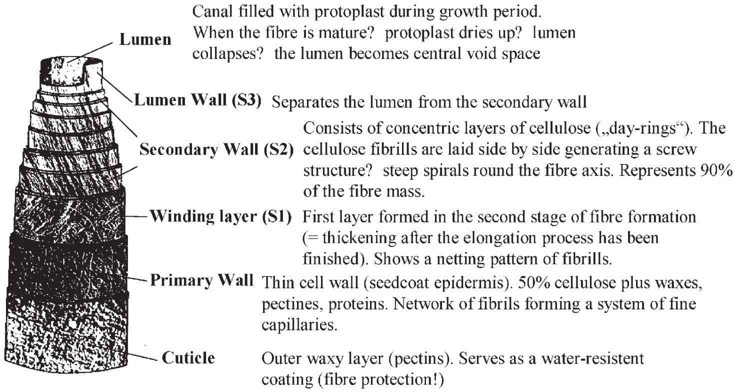


Figure 8.
Morphology of a cotton linters fibre.[7]

recognized. This so-called fibrosampler classing is shown in Figure 10.

At this point it has to be noted that the most important difference in the paper-making properties between first-cut and second-cut linters is derived from their staple fibre content. Combers, a waste product of the spinning mills, are 100% staple fibres.

When saying that linters fibres are typically less clean than staple fibres, then it refers to those contaminations which have been technically caused, like seed hulls in particular (Table 2). All the other constituents like pectins, proteins, fats, waxes, and minerals are natural components of the cotton fibre, irrespective of whether it is lint or linters. Typically, cotton linters have a cellulose content of 80% on bone-dry basis.[1,3,7]

One of the objectives of the linters bleaching process is to remove all these natural and non-natural contaminations - or at least to significantly reduce them - in order to get a cotton linters cellulose at the end which is as pure as possible. The flow chart shown in Figure 11 shows the principle of such a linters bleaching process.

Table 1.
Attributes of cotton linters fibres compared to cotton staple fibres.[1]

Attribute	Cotton linters	Staple cotton (Lint)
Fibre lenght	Short (2-6 mm)	Long (20-45 mm)
Wall thickness	Thick (6-12 µm)	Thin (2.5-6 µm)
Lumen shape	Roundish	Flat, kidney-like, relatively large
Fibre diameter	Thick (17-27 µm)	Thin (12-22 µm)
Fibre shape	Basically cylindrical, quite curly, tapers to a point	Flat, twisted ribbon with a little curl
Cross-section		
Relative chemical reactivity	SC FC/MR ← decreasing ←	staple cotton

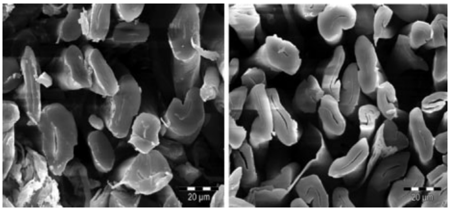


Figure 9.
Cross-section of second-cut cotton linters fibres (left) and of cotton staple fibres (right, Scanning electron microscope CamScan, samples vaporized with gold, accelerating voltage 20 kV (FIBRE, Bremen)).[8]

The cotton linters bleaching process is a collection of mechanical and chemical purification steps:

- The cleaning - after bale opening - is to remove physical impurities like field trash (via dry cleaning) and sand, stones, and seed hulls (via wet cleaning). As a side effect of wet-cleaning, you even reduce a certain amount of natural contaminations like pectins, proteins and fats.
- The alkaline digesting in caustic soda is a primary chemical purification stage: Firstly, it is to saponify the fats and waxes and to dissolve the resulting degradation products and the pectins and proteins in the alkaline medium. Secondly, it is to give the proper degree of polymerization (DP). The DP is roughly adjusted by the selected conditions of temperature and caustic soda concentration, depending on the DP/viscosity you are striving for in the finished product. To promote mixing and uniformity, the linters are cooked in tumbling digesters or in continuous horizontal tube digesters. During digesting, the cuticle of the fibres is totally removed, the primary wall loses those parts which are soluble in caustic soda, and the secondary walls with their screw structure and the 95% of cellulose content are chemically attacked.
- Typically, the bleaching section consists of three stages where the last one is an optional one. Frequently used bleaching sequences are

→ C – H
→ C – H – D
→ C – P – D

where C represents elemental chlorine, H sodium hypochlorite, P hydrogen peroxide, and D chlorine dioxide. In the hypochlorite stage, the viscosity of the finished product is adjusted if necessary. It is also possible to avoid any bleaching for producing unbleached cotton linters

Rough description of cotton linters fibre class	Staple fibre content (estimated)
1. Very short SC	5%
2. Short SC	10%
3. Long SC	15%
4. MR	20%
5. Long MR/Short FC	25%
6. FC	30%
7. Long/extra long FC	More than 30%

Combers (for comparing purposes): 100% →

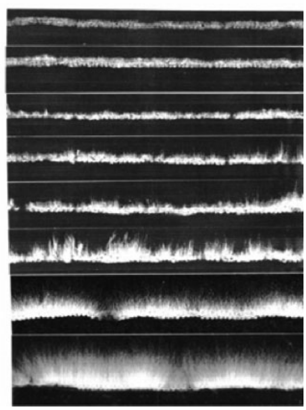


Figure 10.
Cotton linters and their staple fibre content (Fibrosampler classing).

Table 2.
Constituents and contaminations of cotton linters.

Contamination	Typical level (%)	Origin	Place of removal in the linters bleaching process
Hemicelluloses	2	Capsules and seed hulls: Seed hulls: 20–27% xylan, 28–30% lignin	Mainly in (dry/wet) cleaning and in alkaline cooking
Pectins	1	Cell wall	Alkaline cooking
Proteins	2	Cell wall	Alkaline cooking
Lignin	(0)	Seed hulls and stalks	Wet cleaning and alkaline cooking
Fats	2	Seed	Alkaline cooking
Waxes		Cuticle	Alkaline cooking
Minerals	2	Fibre	De-ashing
Sand and foreign matter	1	Technically caused (oil mill, transport)	Wet cleaning
Seed hulls	10	Technically caused (oil mill)	Wet cleaning and alkaline cooking
Stalks and capsules	0.2	Technically caused (oil mill)	Final wet cleaning

celluloses. This is for cellulose grades where high purity is of subordinate relevance.

- The design of the final section for finishing and drying depends on whether the cotton linters cellulose is to be marketed in flock form (flash-dried) or in sheeted form. Rolls and sheets require a wet grinding stage where the cellulose fibres are shortened and fibrillated (beating, refining).
- At the end of the process, the purity of the cotton linters cellulose is typically min. 99% when bleached and min. 98% when unbleached.

Purified cotton linters cellulose (CLC) can be characterized in general as follows: It is

→ very pure and has a high alpha-cellulose content
→ free of lignin
→ low in ash
→ low in carbonyl, carboxyl, and aldehyde groups
→ potentially of high DP
→ of relatively high crystallinity
→ swell in water moderately
→ a natural product (‘‘cotton’’).

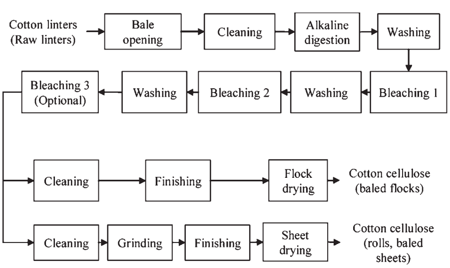


Figure 11.
Principle of a cotton linters bleaching process.

On the conversion to cellulose derivatives, these characteristics have the following effects: They provide

- high yields (in general)
- good filterability and good spinnability of dissolved CLC as a multi-factor result (for regenerated celluloses like cuprammonium silk and viscose)
- resistance of the derivatives to light, heat, ageing (for acetates)
- stability (with cellulose esters like nitrates and acetates)
- clear, transparent, colourless solutions (with esters and ethers)
- highest viscosity if needed (for ethers and nitrates)
- a moderate reaction rate resulting in quite uniform reaction products (for esters and ethers).

For paper manufacturing and for the use as fibrous material, the CLC characteristics have the following effects: They provide

- resistance to light, heat, and ageing (for fine and archive papers)
- neutrality (for analytical and medical papers)

- high electrical resistance (for insulating papers and transformer boards)
- high strength as a multi-factor result (for security and banknote papers)
- high volume and high absorbency as a multi-factor result (for filtration papers)
- resistance to chemical, thermal, mechanical degradation (for battery separator papers, vulcanized papers)
- the potential for more beating
- a marketing argument ("cotton" with cotton-content papers and non-wovens).[9–11]

Laboratory tests for characterizing CLC when tailored for chemical conversions are typically carried out on viscosity (in cuam or in cuen), whiteness, solubility in caustic soda, and on ash. Additional testing is done according to specific requirements.

For papermaking, strength properties like tensile, tear, or double fold are determined. These properties are generated - among others - by wet refining. The photomicrographs shown in Figure 12[8] visualize the effect of refining on first-cut (FC) cotton linters. After refining, the fibres are fibrillated which is a precondition for sheet formation. The extent of fibrillation depends on the chosen refining conditions.

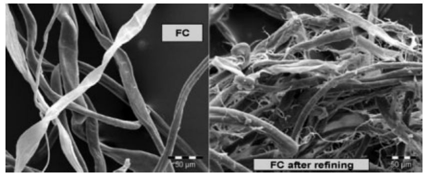


Figure 12.
Bleached first-cut cotton linters - before and after refining (Scanning electron microscope CamScan, samples vaporized with gold, accelerating voltage 20 kV (FIBRE, Bremen)).[8]

Table 3.
Cotton linters celluloses and a selection of their applications.

For chemical conversions	For use as fibres
1. Cellulose regeneration (Cellulose I->II)	**1. Reinforcement fibres**
Cuparammonium silk ("cupro", CU)	Plastic masses ("Bakelite")
Textile fibres	
Hollow fibres	
	2. Filter aids
	Fibre suspensions
Viscose (VIS)	
Sausage skins	**3. Technical papers**
Technical fibres	Filter papers for analytical purposes
Sponges	Diagnostic papers
	Automotive filter papers
2. Esterification	Insulating papers
Acetates	Battery separator papers
Plastics (di-ac)	Transformer boards
Injection moulding compounds (tri-ac)	Vulcanized papers
Electrical insulating foils (tri-ac)	Calendar roll papers
Photographic and X-ray films (tri-ac)	Blotting papers
Liquid crystal displays/LCD (tri-ac)	
Nitrates (CN)	**4. Fine papers**
Lacquers	Writing papers
Printing inks	Drawing and artist papers
Smokeless powder	Graphic papers
Explosives/dynamite	Map papers
	Security papers
3. Etherification	Banknote papers
Ethers (CE)	
Thickeners in food	
Additive to paint formulations	
Aid in pharmaceuticals	
Aid in oil drilling	

There is a wide range of applications for cotton linters celluloses in the chemical industry, in the paper industry, and in industries where the CLC is simply used as fibrous material. The overview shown in Table 3 is just a selection of all the CLC applications of today.

Conclusion

Cotton linters cellulose (CLC) is an alternative cellulosic material indeed, in particular for applications in the chemical and the paper industry where special requirements have to be met. CLC is the principal source for high-viscosity cellulose ethers and nitrates, for purest cellulose acetates being used in LCD manufacturing, for purest cellulose nitrates being used in clear and colourless lacquers, for regenerated celluloses used for hollow fibre membranes, for specialty papers like high-strength papers and high-porosity papers, and for fibrous materials in insulating and reinforcement applications. One of the determining factors for papermaking properties of a CLC-based paper is the staple fibre content in FC and SC linters because of the difference in fibre morphology. CLC may be tailored to specific requirements regarding product properties (strength, formation, porosity) and processing behaviour (reactivity, refining resistance). Cotton linters cellulose is based on a natural product and may be directly linked with the positive image of cotton.

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