

# Processing of Biorenewable Resources into Natural Fibers

## 10.1 Introduction

Plant fibers are long, hollow cells that provide structural support and/or conduct water and nutrients through the plant. The cell walls of fibers consist primarily of lignocellulose. Whereas the previous chapter considered how to depolymerize this material into simple molecular building blocks, this chapter is devoted to the processes that liberate fibers for the manufacture of biocomposites, paper, and other cellulose-based products.

The disintegration of plant material to recover fibers is known as pulping, a process that can be accomplished mechanically or chemically. Mechanical pulping, which physically separates the lignocellulosic fibers from one another, has yields of 91–98%. Mechanical pulp, which produces smooth printing surfaces of good opacity, has traditionally been employed in production of newsprint. Mechanical pulp usually needs to be supplemented with chemical pulp, about 5%, to provide the prerequisite strength required to survive modern high-speed printing presses.

Chemical pulping dissolves lignin, which serves as an adhesive in cell walls, thus liberating cellulosic fibers. The advantage of chemical pulping is the production of cellulosic fibers, which are an order of magnitude stronger than the lignocellulosic fibers produced by mechanical pulping. However, it also dissolves hemicellulose, with the result that chemical pulping yields are only 35–60%. Chemical pulping is used for the production of paper for packing, writing, hygienic products, and for cellulose derivatives. Chemical pulping accounts for 70% of the total worldwide production of pulp.

In principle, both woody and herbaceous plant materials can be used for the production of pulp. Indeed, agricultural residues were a major source of pulp in the United States and Europe until the 1920s when issues of quality and supply began to favor woody biomass. Today, more than 90% of pulp and paper is produced from woody biomass.

Although the lengths of fibers from herbaceous materials are comparable to those in hardwoods, they are typically shorter than the fibers obtained from softwoods; thus, paper made from herbaceous plant fibers has relatively low tear strength, an undesirable characteristic for many applications. Herbaceous materials also contain about 30 wt% of pith or parenchyma cells and about 5 wt% of dense epidermis material, neither of which is fibrous in nature. When left in the pulp, they have deleterious effects on paper quality.

Another factor, possibly even more important to the demise of herbaceous biomass pulping, was increased labor costs associated with securing supplies of agricultural residues. These materials have very low bulk density, resulting in tremendous volumes to handle, and they rapidly degrade when exposed to the weather, requiring special provisions for long-term storage.

Depithing processes, described in a subsequent section, can substantially overcome many of the fiber quality issues while modern methods of collecting, storing, and handling herbaceous biomass, previously described in Chapter 5, should help overcome supply problems. Certainly, a substantial volume of agricultural residues goes unused in the world today.

The following sections describe various aspects of fiber processing including mechanical pulping, chemical pulping, and depithing operations.

## 10.2 Mechanical Pulping

Germany introduced groundwood pulping in 1840 as a source of fibers to replace increasingly scarce rags for the production of paper. In this process, wood is mechanically ground by large stones. The pulp is then screened to remove knots and other large pieces of wood followed by washing and bleaching in preparation for papermaking. Thermomechanical pulping was developed in the 1930s. In this process, wood chips are ground under pressure, producing heat that weakens the lignin in the wood chips, making the separation of fibers easier. Thermomechanical processing yields relatively cheap fibers suitable for newsprint. Refiner mechanical pulping was developed in the 1960s. Wood chips are passed repeatedly through a series of rotating discs to remove fibers.

Although mechanical pulping provides high yields of fiber, it is energy intensive and does not remove lignin, which degrades paper strength and is responsible for darkening of newsprint with time.

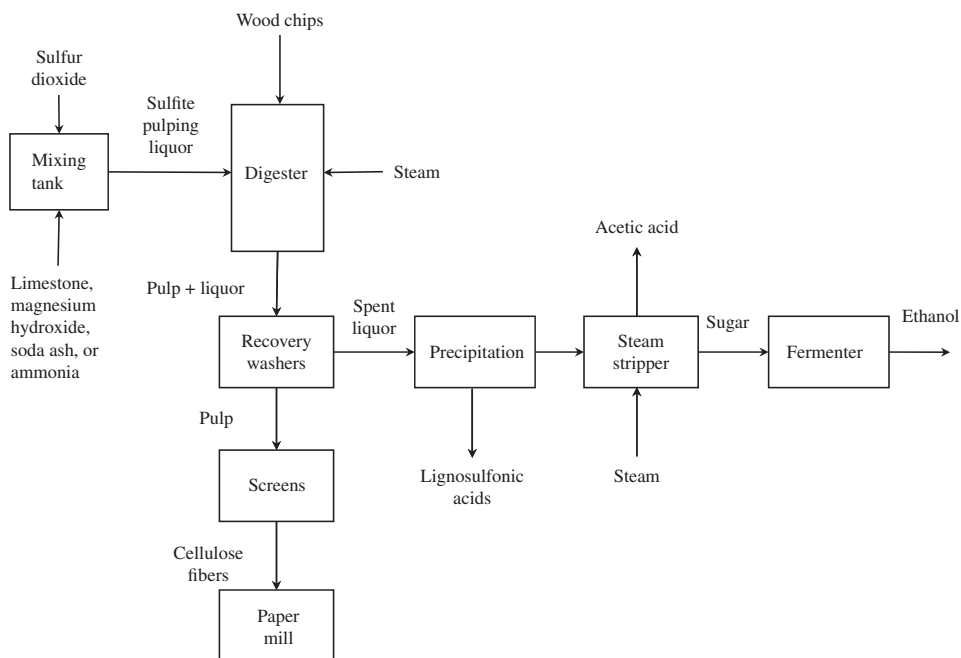
## 10.3 Chemical Pulping

The two principal chemical pulping processes are the sulfite process and the sulfate process, also known as the kraft process. Until recently, the sulfite process was

preferred because it produced a much lighter, easier to bleach pulp. However, the environmental impact of the sulfite process is greater than the kraft process, which has well-established methods for recovering processing chemicals and utilizing lignin that would otherwise be discharged to the environment. Since the 1950s, the kraft process has gradually replaced the sulfite process and today accounts for over 80% of chemical pulp. Nevertheless, the sulfite process presents some useful lessons in co-product utilization that will be described here.

### 10.3.1 Sulfite Pulping

The sulfite process is illustrated in the flow chart of Figure 10.1. The sulfite pulping liquor is an acid solution of bisulfite of calcium, magnesium, sodium, or ammonia, which is added to wood chips in a digester operated at 160°C. In about 2 hours, the lignin is sulfonated and the salts of the sulfonic acid are dissolved. Hemicellulose is hydrolyzed to pentoses and hexoses, depending on the chemical composition of the hemicellulose. The backbone of hemicellulose from hardwoods and herbaceous materials is primarily xylan, which yields xylose upon hydrolysis. The hemicellulose from softwoods is predominately mannan, which yields mannose, an epimer of glucose, upon hydrolysis. In addition, the liquor from pulping hardwood contains almost twice as much acetic acid as the liquor



**FIG. 10.1** Flow chart of sulfite pulping.

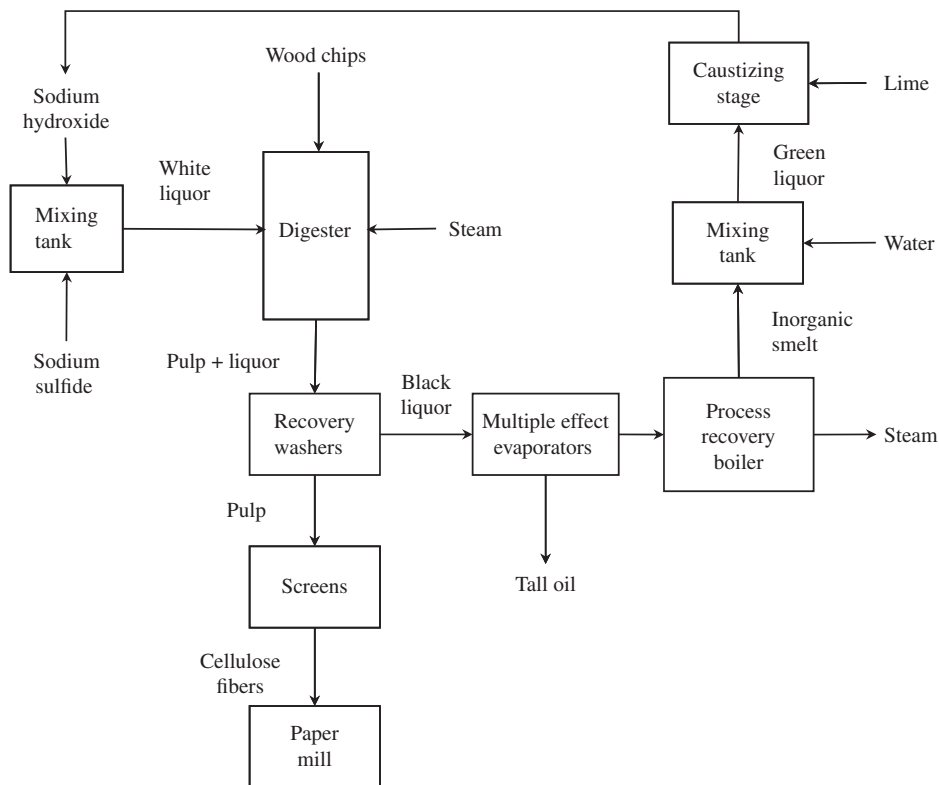
from pulping softwood due to higher acetyl content of hardwood hemicellulose. The sulfite process has not been generally employed for herbaceous fibers because of inferior yields and fiber strengths compared to the kraft process.

The pulp of cellulosic fibers is filtered from the spent liquor and then further processed to paper or cellulose derivatives. The spent liquor contains carbohydrates and lignin as well as pulping chemicals that should be treated as byproducts rather than waste streams discharged to the environment. The sulfonic acids of lignin, which are highly condensed, high molecular weight compounds, can be precipitated from the spent liquor and sold as a binder in the preparation of fertilizers, animal feed, and fuel pellets, as a glue substitute and drilling mud additive, and as a phenol substitute in the preparation of phenol–formaldehyde resins. Oxidation of lignosulfonic acids by air in strongly alkaline solution yields vanillin, a common flavoring agent and the raw material for the production of L-dopa, a pharmaceutical used for the treatment of Parkinson's disease.

Until recently, it was common to ferment the hexoses in spent liquor from softwood pulping to ethanol. Although phenol from lignin fragments inhibits fermentation, yeast was adapted to tolerate their presence in spent pulping liquor. Scandinavian pulping mills, in particular, generated ethanol for use as a 25% blend with gasoline although the practice was phased out in 1958. Fermentation of spent liquor from hardwood pulping was not widely practiced for two reasons: the high acetic acid concentrations are toxic to most microorganisms and xylose, the predominant sugar, is not readily fermented by common yeast. Steam stripping can reduce acetic acid to less than 0.5 g/L, an acceptable level for fermentation. In recent years, good progress has been made in identifying and developing pentose-fermenting microorganisms. Alternatively, the xylose could be dehydrated to furfural, as described in Chapter 6.

### 10.3.2 Kraft Pulping

Kraft pulping was developed in Germany near the end of the nineteenth century in an effort to improve upon an early pulping process known as the soda process or alkaline pulping, which used sodium hydroxide (NaOH) to pulp wood. The soda process could not compete with the sulfite process due to the relatively high cost of NaOH. The key innovation in kraft pulping was the replacement of sodium carbonate as make-up chemical with inexpensive sodium sulfate ( $\text{Na}_2\text{SO}_4$ ). Upon heating,  $\text{Na}_2\text{SO}_4$  is converted to sodium sulfide, which reacts with water to form NaOH and sodium hydrosulfide (NaSH). The process produced a strong pulp, which was the source of its name, kraft being the German word for “strong.” It is also known as the sulfate process for the compound used as make-up chemical. The kraft process was quickly adopted in the United States, where it allowed commercial pulping of southern pines, which do not fare well in the sulfite process due to their high resin content.



**FIG. 10.2** Flow chart of kraft pulping.

The kraft process is illustrated in the flow chart of Figure 10.2. Biomass is first steamed before being continuously added to a digester. Pulping is performed with a hot mixture of NaOH and sodium sulfide ( $\text{Na}_2\text{S}$ ) known as “white liquor.” Roughly half of the biomass is degraded and dissolved to form a mixture of lignin, polysaccharides, and a small fraction of extractives. A substantial amount of the hemicellulose fraction of the wood is converted to hydroxy carboxylic acids. The lignin is degraded to a complex mixture of compounds. The soluble fraction is known as “kraft lignin” but has little resemblance to the native lignin in the wood.

The pulp of cellulosic fibers is washed to remove the spent liquor, which is known as “black liquor,” and screened to remove knots. Additional processing of the pulp may include oxygen delignification to further remove lignin binding together with fibers and bleaching to brighten the fibers.

The black liquor is concentrated to 65–80% solids content with multiple-effect evaporators. Extractives present in the raw biomass and liberated during pulping can be removed during this stage. This so-called “tall oil” is comprised of soaps

formed from the saponification of fatty acid glycerides and the esters of resin acids, especially from the pulping of softwoods. Acidification of these soaps yields “crude tall oil,” which contains 35% resin acids, 30% fatty acids, and 35% unsaponifiable terpenes and terpenoids, the latter resembling terpene hydrocarbons but with various oxygenated functional groups attached.

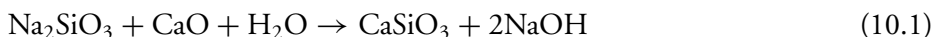
The black liquor also contains degraded polysaccharides and lignin. The polymeric lignin fraction can be precipitated by acidification although kraft lignin has only limited applications compared to the lignosulfonates obtained from sulfite pulping. Acid-precipitated kraft lignin had been used as an adhesive in panel boards. More generally, it has been employed as boiler fuel because of its high heating value compared to raw wood. The degraded polysaccharides are typically used as boiler fuel, too, although their relatively low heating value suggests that higher value applications should be explored.

The black liquor, containing degraded polysaccharides and lignin, is burned in a process recovery boiler, which generates steam and recovers pulping chemicals. Combustion of black liquor produces an inorganic smelt of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and  $\text{Na}_2\text{S}$  with a small amount of sodium sulfate ( $\text{Na}_2\text{SO}_4$ ). The smelt is dissolved in water to form “green liquor,” which is reacted in the causticizing stage with lime ( $\text{CaO}$ ) to convert  $\text{Na}_2\text{CO}_3$  into  $\text{NaOH}$  and regenerate the original white liquor. Due to incomplete reaction in the recovery cycle, the white liquor also contains  $\text{Na}_2\text{CO}_3$  and sodium salts of oxidized sulfur-containing anions. The use of the process recovery boiler is integral to economic operation of a kraft pulping mill.

Herbaceous materials obtained from agricultural residues, including wheat and rice straw and bagasse from processed sugarcane, have relatively low lignin content, often only one-half that of woody material. Thus, chemicals more easily penetrate plant cell walls, and pulping of herbaceous materials may be accomplished in only one-fourth to one-third the time required for woody materials. In fact, pulping is so rapid that there is no advantage in using sodium sulfide as part of the white liquor prepared for the kraft pulping process. Instead, the simpler soda process, using only sodium hydroxide, is often used to pulp herbaceous biomass.

Complicating the pulping of agricultural residues are the large quantities of ash, particularly silica, compared to woody materials. This silica appears in the black liquor of kraft or soda processes, where it creates severe problems in recovery operations, especially in the formation of silica scale on heat transfer surfaces of evaporators and boilers.

Desilication of the black liquor can be accomplished with either lime treatment or by pH adjustment. Lime precipitates silica as calcium silicates by the reaction:



The calcium silicate precipitates from the solution and is removed by filtration. Because this reaction also precipitates out sodium carbonate and sodium sulfate,

pH adjustment by passing carbon dioxide in the form of flue gas through the black liquor is considered the best approach to desilication. This approach precipitates silicon dioxide, which is removed by band filters. Alkali consumption is economized by vacuum stripping the carbon dioxide from the desilicated liquor, which decomposes the bicarbonates formed.

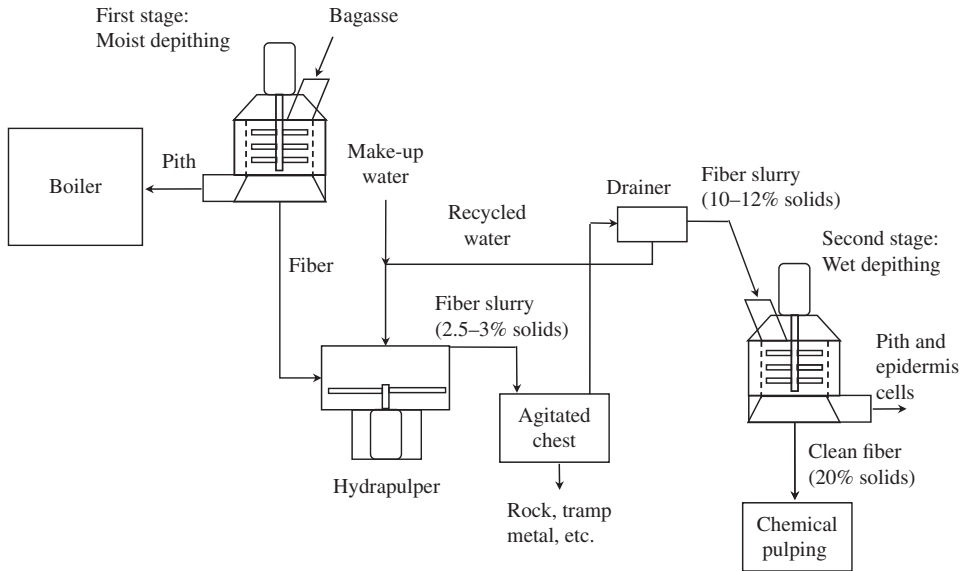
## 10.4 Depithing

The stalks of some herbaceous plants, such as sugarcane and corn, contain 25–35% on a dry weight basis of parenchyma cells (pith), which do not have the characteristics of fiber. Pith, containing a high portion of hemicellulose, is readily penetrated and reacted by pulping chemicals; thus, pith consumes a large fraction of the chemicals while yielding little useable pulp. Furthermore, the outer surface of these stalks consists of tough, waxy epidermis cells that are resistant to pulping chemicals. Representing about 5% of the dry weight of stalks, epidermis cells leave troublesome residues in the finished pulp, usually appearing as dark specks. Depithing is the process of removing parenchyma cells from herbaceous plant stalks. Many types of depithing operations also remove epidermis cells, producing a pulp suitable for paper products that do not require high tear strengths.

Sugarcane bagasse, the fibrous stalk residue remaining after pressing the cane for sugar, has been widely explored as a source of pulped fibers. The following depithing operations were developed for bagasse although they could equally apply to other herbaceous plant stalks.

Approximately 50% of the dry weight of bagasse stalks consists of high-quality fiber bundles concentrated in the hard, dense rind of the stalk. These fiber bundles are separated relatively easily from the pith tissue in which they are embedded. An additional 15% of the stalks are shorter, less resistant fiber bundles scattered throughout the interior pith portion. These bundles are more easily dissociated into individual fibers than those found in the rind. Separation of these two kinds of fibers during depithing operations is not generally considered economical.

Depithing can be classified into three categories: dry depithing, moist depithing, and wet depithing. Dry depithing separates the pith from bagasse after it has been dried to 10–25% moisture content. Although widely used prior to 1960, the method was inadequate for production of high quality pulp. Other depithing methods are more appropriate for modern storage and processing of bagasse. Moist or humid depithing employs bagasse “as received” from a sugar mill, which usually has moisture content of 50%. This operation is the most economical of the three but does not achieve fibers as clean and uniform as can be obtained by wet depithing. The third type of depithing operation employs a slurry of water and bagasse to improve depithing. Wet depithing also has the advantage of removing epidermis cells as well as pith if stalks are well broken up in the milling process.



**FIG. 10.3** Flow chart of two-stage depithing operation.

However, wet depithing of raw bagasse generates a large amount of wet pith, which is difficult to handle.

Many commercial operations employ a two-stage depithing operation consisting of moist depithing, which economically removes most of the pith, followed by wet depithing, which removes the residual pith as well as epidermal cells from the fiber. An example of such a two-stage operation is illustrated in Figure 10.3. As-received bagasse is fed to a depithing machine consisting of a rotor to which are attached swinging or rigid hammers. The mechanical action rubs or breaks loose the pith from the fiber, which is flung radially outward through screens or perforated plates enclosing the rotor. Fibers, which are too large to pass through the screens, fall downward where they are separately collected. If this process is performed at the sugar mill, the pith removed, representing 30–40% of the weight of bagasse, can be employed as fuel in the mill's boiler. The cost of transporting the resulting fiber to a pulping mill is substantially less than for the raw bagasse.

The second stage of depithing occurs at the pulping mill. Bagasse and water are continuously added to a “hydrapulper,” which thoroughly wets the bagasse and helps break loose dirt and pith. The resulting slurry, which contains 2.5–3% solids, is pumped to agitated chests where rock, tramp metal, and other heavy material settle out. Since wet depithing machines are designed to operate with slurry of 10–12% solids content, the slurry passes through a dewatering device such as rotary drum, vibrating screen, drag drainer conveyor, or a screw-type drainer conveyor.



The drainers remove a considerable amount of dirt and some pith cells from the slurry, which is then pumped to the wet depither. The wet depithing machine, like moist depithing machines, consists of hammers attached to a rotor enclosed within a perforated drum. Pith and epidermal cells are small enough to pass through perforations, while the clean fiber slurry, with solids loading increased to about 20%, flows out the bottom. A screw feeder conveys the fiber slurry to the chemical pulping digester. The wet pith leaving the machine has solids content of only about 1%. Some places in the world use this waste stream to irrigate cane fields. Otherwise, wet pith must be dewatered to at least 15% for landfill or close to 50% for use as boiler fuel.

## Further Reading

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