Chapter 7
Biopulping

7.1 Introduction

In the manufacture of paper from wood, the wood is first converted to pulp. Pulping involves treating wood to separate the cellulose fibers. Pulping processes are divided into two broad classes: chemical pulping and mechanical pulping. Chemical pulping involves the use of chemicals to solubilize the lignin in the wood cell wall and to release cellulose fibers. Lignin is a natural glue-like material that holds the wood cell wall together. Chemical pulping is a low yield process (about 50%) with significant waste treatment and chemical recycling costs; however, the pulp produced has extremely high strength properties. Mechanical pulping involves the use of mechanical force to separate cellulose fibers. Mechanical processes are high yield (up to 95%) but give paper with lower strength properties, high color reversion, and low brightness. Thus, currently available pulping processes offer a spectrum of pulp properties ranging from high yield, low strength mechanical pulps to low yield, high strength chemical pulp. A mixture of chemical pulp and mechanical pulp is used in many paper production processes to exploit these differences.

It has been suggested that biological systems can be also used to assist in the pulping of the wood. Attempts to improve primary pulp production processes by using isolated ligninolytic enzymes have so far been inhibited by the complex chemistry of the ligninolytic enzyme system, low yields in enzyme production, and the ultrastructure of wood itself. White-rot fungi, however, have great potential for this application. The concept of biopulping is based on the ability of some white-rot fungi to colonize and degrade selectively lignin in wood, thereby leaving cellulose relatively intact. There are certain process conditions and design requirements necessary to gain a biopulping effect (Akhtar et al. 1998). Biopulping can be carried out in bioreactors of different types, including open chip piles, depending on the requirements of the particular microorganism would have for optimal results. High moisture content (around 55–60%) should be kept in wood chips during the biotreatment step to ensure an optimal colonization and penetration of fungal hyphae. The degree of asepsis should be controlled to ensure a successful wood colonization by the

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particular fungal strain used depending on its resistance against contamination and ability to compete with the microbial biota existing in the wood chips.

In mechanical pulping, biotreated wood allows energy savings during refining and provides stronger pulps. In chemical pulping, the wood biotreatment can increase pulp yield, reduce alkali requirement, and increase the cooking capacity during kraft pulping (Bajpai et al. 1999).

7.2 Pulping Processes

The manufacture of pulp for paper and paperboard employs mechanical (including thermomechanical), chemimechanical, and chemical pulping methods.

7.2.1 *Mechanical Pulping*

Mechanical pulping processes are mainly of four types – stone groundwood (SGW) pulping, refiner mechanical pulping (RMP), thermomechanical pulping (TMP), and chemithermomechanical pulping (CTMP) (Leask and Kocurek 1987). The groundwood pulping process was the first process used for the production of paper from wood. This process involves pressing a log against a grindstone to pull off fibers, which are continuously washed away by a water stream. High temperatures in the refining zone caused by friction soften the wood and ease fiberization. The yield is high (about 95%) but because most of the lignin remains, the fibers are stiff and bulky. Paper produced from groundwood pulp has low strength and high color reversion, but the opacity is excellent. Groundwood pulping is an energy-intensive process (Table 7.1). Groundwood pulp has been the quality leader in magazine papers, and it is predicted that this situation will remain (Arppe 2001). In the RMP process, chips are processed through a rotating disk refiner. The refiner plate is made up of three zones first to break the chips, then to produce intermediate size fragments, and finally to produce single fibers. This produces fibers with better bonding properties, and thus better paper strength than SGW pulp. However, opacity is reduced, color reversion is similar, and the energy expenditure is increased compared to SGW pulping (Table 7.1). RMP, as well as TMP and CTMP, is usually performed as a two-stage process. The first stage separates wood into individual fibers. The second stage loosens the structure of the fiber walls to increase fiber flexibility and fibrillation,

Table 7.1 Energy requirement in the production of mechanical pulps

Process	Net-energy requirement (kWh/ton)
Refiner mechanical pulping (RMP)	1,975–2,275
Groundwood pulping (SGW)	1,300–1,675
Thermomechanical pulping (TMP)	2,175–2,900
Chemithermomechanical pulping (CTMP)	1,375–1,775

improving fiber bonding and thus paper strength. The TMP process is a modification of the RMP process involving a steam pretreatment at 110–150°C to soften the wood followed by refining. In the first stage, the refiners are at elevated temperature and pressure to promote fiber liberation; in the second stage, the refiners are at ambient temperature to treat the fibers for papermaking. The higher temperature during refining in the first step, 110–130°C, softens the fibers and allows their recovery with minimal cutting and fines generation. The refining is performed just under the glass transition temperature of lignin, approximately 140°C, so that separation of fibers occurs at the S-1 cell wall layer. This improves fibrillation and access to hydroxyl groups for hydrogen bonding. The high strength of this pulp relative to the other mechanical pulps has made it the most important mechanical pulping process. Energy requirements are 2,175–2,900 kWh/ton (Table 7.1). Over two-thirds of this is used in the primary pressurized refining step, and less than one-third is used in the secondary atmospheric pressure refining step. The pulp yield is >93%. Solubilization of wood components results in relatively high BOD in mill effluents. The CTMP process is a further refinement of TMP which involves pretreatment of wood chips with sodium sulfite (about 2% on dry wood) at pH 9–10 or sodium hydroxide (with hydrogen peroxide in the alkaline peroxide method), then steaming at 130–170°C and finally refining. Liquor penetration is often achieved by a system that compresses the wood chips into a liquid-tight plug that is fed into the impregnator vessel where the chips expand and absorb the liquor. Chemical pretreatments of wood chips are used to enhance the strength properties of mechanical pulps. The addition of CTMP to pulp blends may reduce or eliminate the requirement for kraft pulp. Capital expenditures for a CTMP plant are one-fifth those of a kraft mill of comparable size (Karl 1990). The energy expenditures are decreased (Table 7.1) but the yield is also decreased to 85–91% by removing wood substance. The CTMP process generates more pollutants than other mechanical pulping processes and thus increases waste treatment costs.

Currently, mechanical pulps account for 20% of all virgin fiber material. It is foreseen that mechanical paper will consolidate its position as one major fiber supply for high-end graphic papers. The growing demand on pulp quality in the future can be achieved only by the parallel use of softwood and hardwood as a raw material. The largest threat to the future of mechanical pulp is its high specific energy consumption. In this respect, TMP processes are most affected due to their considerably higher energy demand than groundwood processes.

7.2.2 Semichemical Pulping

Semichemical pulping processes are characterized by a mild chemical treatment preceded by a mechanical refining step. Semichemical pulps, which apply to the category of chemical pulps, are obtained predominantly from hardwoods in yields of between 65 and 85% (average ca. 75%). The most important semichemical process is the neutral sulfite semichemical process (NSSC), in which chips undergo partial chemical pulping using a buffered sodium sulfite solution, and are then treated in disk refiners to complete the fiber separation. The sulfonation of mainly middle lamella lignin causes a partial dissolution so that the fibers are weakened for the subsequent mechanical defibration. NSSC pulp is used for unbleached products where good strength and stiffness are particularly important; examples include corrugating medium, grease-proof papers, and bond papers.

7.2.3 Chemical Pulping

Chemical pulps are made by cooking (digesting) the raw materials, using the kraft (sulfate) and sulfite processes.

7.2.3.1 Kraft Process

Kraft process produces a variety of pulps used mainly for packaging and high-strength papers and board. Wood chips are cooked with caustic soda to produce brownstock, which is then washed with water to remove cooking (black) liquor for the recovery of chemicals and energy. The Kraft process dominates the industry because of the advantages in chemical recovery and pulp strength. It represents 91% of chemical pulping and 75% of all pulp produced. A number of pulp grades are commonly produced, and the yield depends on the grade of product. Unbleached pulp grades, characterized by a dark brown color, are generally used for packaging products and are cooked to a higher yield and retain more of the original lignin. Bleached pulp grades are made into white papers. Nearly half of the Kraft production is in bleached grades, which have the lowest yields. The superiority of kraft pulping has further extended since the introduction of modified cooking technology in the early 1980s.

7.2.3.2 Sulfite Process

This process uses different chemicals to attack and remove lignin. Compared to Kraft pulps, sulfite pulps are brighter and bleach more easily, but are weaker. Sulfite pulps are produced in several grades but bleached grades dominate production. Yields are generally in the range of 40–50%, but tend toward the lower end of this range in bleached grades. Compared to the Kraft process, this operation has the disadvantage of being more sensitive to species characteristics. The sulfite process is usually intolerant of resinous softwoods, tannin-containing hardwoods, and any furnish-containing bark. Sulfite process produces bright pulp which is easy to bleach to full brightness and produces higher yield of bleached pulp which is easier to refine for papermaking applications. The sulfite process is characterized by its high flexibility compared to the kraft process, which is a very uniform method, which can be carried out only with highly alkaline cooking liquor. In principle, the entire pH range can be used for sulfite pulping by changing the dosage and composition of the chemicals. Thus, the use of sulfite pulping permits the production of many different types and qualities of pulps for a broad range of applications. The sulfite process can be distinguished according to the pH adjusted into different types of pulping. The main sulfite pulping processes are Acid (bi)sulfite, Bisulfite (Magnefite), Neutral sulfite (NSSC), and Alkaline sulfite.

7.3 Biomechanical Pulping

White-rot fungi have great potential for biotechnological applications. They not only produce the whole set of enzymes necessary for lignin degradation, but can also act as a transport system for these enzymes by bringing them into the depth of the wood chips and create the physiological conditions necessary for the enzymatic reactions. Fresh wood chips stored for pulp production are rapidly colonized by a variety of microorganisms, including many species of fungi. These organisms compete vigorously while easily assimilable foodstuffs last and then their population decreases. They are replaced by fungi that can degrade and gain nourishment from the cell wall structure polymers: cellulose, hemicelluloses, and lignin. Left unchecked, these last colonizers, mostly white-rot fungi, eventually decompose the wood to carbon dioxide and water. Some white-rot fungi selectively degrade the lignin component, which is what chemical pulping process accomplishes. It is these fungi which are useful for biopulping.

Fungal delignification of wood for biopulping was first seriously considered by industrial researchers of West Virginia Pulp and Paper Company (now Westvaco Corporation) in 1950s (Lawson and Still 1957). The researchers wondered whether wood chips could be inoculated with a lignin-degrading fungus during transport and storage, and thereby become partially pulped. They published a survey of 72 lignin-degrading fungi, summarizing knowledge about fungal degradation of lignin. In the 1970s, Eriksson's group at the Swedish Forest Products Laboratory (STFI) launched a more intensive investigation. A fungus isolated in Sweden, *Phanerochaete chrysosporium* was characterized by a high optimum temperature for growth, rapid growth, and selective lignin degradation in incipient stages of birch wood decay. This fungus was proposed to be a useful "wood defibrator" in the pulping process. A U.S. patent was obtained by STFI for the process (Eriksson et al. 1976). Considerable efforts at STFI were directed toward developing cellulase-less mutants of selected white-rot fungi to improve the selectivity of lignin degradation and thus the specificity of biopulping (Johnsrud and Eriksson 1985). In one study, using spruce and pine wood, up to 23% energy savings and an increase in tensile index were noticed. On a large scale, success was achieved on bagasse (Johnsrud et al. 1987) while the results using wood chips were less encouraging. An energy requirement of 4,800 kWh/ton for producing chemimechanical pulp (CMP) of 70°SR according to the Cuba-9 process (6% NaOH treatment at 90°C for 10–20 min) was

Table 7.2 Energy requirement for chemimechanical pulp (CMP) and biochemimechanical pulp (BCMP) from bagasse

	Energy input (kWh/ton)	
Refining equipment	CMP	BCMP
Defibrator and PFI mill	4,800	1,700
Disk refiner	3,100	2,100

Based on Johnsrud et al. (1987)

decreased to 1,700 kWh/ton by pretreating the bagasse with fungi as shown in Table 7.2. The strength properties of biochemimechanical pulp (BCMP) were better than those of CMP but there was a small drop in the yield of BCMP due to fungal degradation of bagasse. STFI's work has been summarized in a number of publications on biomechanical pulping and related aspects (Eriksson et al. 1976, 1980; Johnsrud and Eriksson 1985; Johnsrud et al. 1987; Ander and Eriksson 1975; Eriksson and Vallander 1980, 1982; Eriksson 1985; Setliff et al. 1990).

Preliminary research on biopulping was conducted at Forest Products Laboratory (FPL-USDA) at Madison, Wisconsin in 1970s (Kirk 1993). Kirk et al. (1994) at FPL showed that aspen wood chips treated with *Rigidoporus ulmaris* consumed less energy during pulping and produced stronger paper (FPL internal report 1972). Bar-lev et al. (1982) showed that treatment of a coarse mechanical pulp with *P. chrysosporium* decreased the energy requirement (25–30%) for further fiberization and improved the paper strength properties. Akamatsu et al. (1984) found that treatment of wood chips with white-rot fungi decreased the mechanical pulping energy and increased paper strength.

A comprehensive evaluation of biomechanical pulping was launched in 1987 at the FPL at Madison, Wisconsin after the establishment of Biopulping Consortium I, which involved the FPL, the Universities of Wisconsin and Minnesota and 20 pulp and paper and related companies. The overall goal was to establish the technical feasibility of using fungal treatment with mechanical pulping to save energy and/or improve paper strength. It was assumed that fungal pretreatment would have less environmental impact than would chemical pretreatments, which turned out to be the case. The consortium research was conducted by seven closely coordinated research teams: fungal, pulp and paper, enzyme, molecular genetics, economics, engineering and scale-up, and information. The scientists of the consortium investigated all fields of research relating, to biopulping (Kirk et al. 1994; Lawson and Still 1957; Otjen et al. 1987; Blanchette et al. 1988, 1992a, b; Myers et al. 1988; Sachs et al. 1989, 1990, 1991; Leatham and Myers 1990; Akhtar et al. 1992a, b, 1993, 1998; Leatham et al. 1990a, b; Wegner et al. 1991). The first report of Biopulping consortium I, a 5-year research and information program, was published in 1993 (Kirk 1993). Biopulping Consortium II was established in 1992 and extended until June 1996, mainly for the scale-up of the process and other important aspects. Several white-rot fungi were screened for their biopulping performance using aspen wood chips (Myers et al. 1988; Leatham and Myers 1990; Leatham et al. 1990a, b; Akhtar et al. 1996). Based on energy savings and improvements in paper strength properties, six fungi – *P. chrysosporium*, *Hypodontia setulosa*, *Phlebia brevispora*, *Phlebia subserialis*, *Phlebia tremellosa*, and *Ceriporiopsis subvermispora* – were selected. The energy-saving potentials of these fungi on biomechanical pulping of loblolly pine are given in Table 7.3.

Table 7.3 Energy savings from biomechanical pulping of loblolly pine chips with different white-rot fungi (4-week incubation)

Fungus	Energy savings (%)
Phanerochaete chrysosporium	14
Hyphodontia setulosa	26
Phlebia brevispora	28
Phlebia subserialis	32
Phlebia tremellosa	36
Ceriporiopsis subvermispora	42

Based on Leatham et al. (1990a, b)

Out of about 200 strains, two fungi exhibiting a great deal of intraspecific variation (Akhtar et al. 1992a and Blanchette et al. 1992b) seem to be especially useful for biopulping: *P. chrysosporium* for hardwoods and *C. subvermispora* for hardwoods and softwoods. Various reactor types including rotary drums (Myers et al. 1988), stationary trays (Akhtar et al. 1992a, 1996) and a static bed bioreactor (Akhtar et al. 1992b) were tested on a 2–5 kg scale. The best results were obtained with strains of *C. subvermispora* on aspen and loblolly pine (Akhtar et al. 1992b). On aspen, energy savings of 48% were accompanied by increases in burst and tear indices of 40 and 162% respectively. The effects on loblolly pine amounted to 37% energy savings and 41 and 54% increase in burst and tear indices, respectively. The optical properties deteriorated with both types of wood. After 4 weeks of treatment, a weight loss of 6% for aspen and 5% for loblolly pine was measured. *C. subvermispora* proved to be superior to other selective white rotters (Leatham et al. 1990a, b). However, *P. chrysosporium* has the advantage of competitiveness at temperature between 35 and 40°C. When different strains of *C. subvermispora* were tried on pine, the energy savings ranged from 21 to 37% (Kirk 1993). Adding nutrient nitrogen to the chips as a defined source (L-glutamate or ammonium tartrate) increased energy savings and improved strength properties but led to a high weight loss. Addition of a chemically undefined N source to aspen chips gave large biopulping benefits with low weight loss, using both *P. chrysosporium* and *C. subvermispora*. Wood batch was found to have little influence on the outcome of biopulping and chip storage method (fresh, air dried or frozen) and inoculum age and form (spore, mycelial suspension or colonized chips) were without significant influence.

Another American group has also reported that aspen chips treated with *C. subvermispora* for 17 days required 20% less energy for pulping, while the refining energy of Norway spruce was reduced by 13% (Setliff et al. 1990). Strength properties were increased with aspen and spruce, but no increase was found with eucalyptus.

In Japan, biopulping research has been conducted mainly in industrial laboratories. Kobe steel and Oji paper seem to be the major industrial players. Kobe steel has obtained a broad US patent on the use of white-rot fungi particularly NK-1148, for the treatment of primary mechanical pulp to save energy (Kobe Steel 1988). Applications for four Japanese patents were filed: (1) an inoculum method (Kojima 1988), (2) two improved biopulping strains (Kobe Steel 1988), (3) a silo type bioreactor (Akamatsu et al. 1988), and (4) treatment of chips during transport in ships with a white-rot fungus to enhance pulping (Heden et al. 1988). Nishida (1989) and Nishida et al. (1988) have developed a screening method for selective lignin degradation which was used to identify the strains used in two of the above patents.

Biomechanical pulping of nonwood fibers-straw, kenaf, and jute was also successful (Martinez et al. 1994; Sabharwal et al. 1994, 1995). The energy consumption in refining was substantially lower and the strength properties were higher for the fungal-treated bast strands (Sabharwal et al. 1994, 1995). The opacity and drainage properties were also superior for biomechanical bast pulps, but the brightness level was lower. Scanning electron microscopy of fungus-treated bast strands after refining showed that fibers appeared to separate more readily from adjacent fibers than in noninoculated treatments. Italian researchers studied treatment of nonwoody raw materials with a mixture of various type of enzymes for saving energy and reducing chemical consumption while maintaining good properties of CTM pulp (Giovannozzi-Sermanni et al. 1997). The level of energy savings was found to depend on the type of raw material, ranging from 21% for rice straw up to 40% for kenaf bast. Enzyme treatment significantly improved tear index regardless of the cellulose source whereas the tensile index decreased in wheat straw and kenaf bast samples. Burst index was slightly improved in all the biotreated samples, except kenaf. Pulp yields of the biotreated samples were, without exception, significantly higher than those of the corresponding control samples. This was apparently due to the lower chemical charge needed for biotreated samples.

One of the major costs foreseen during the scale-up of biopulping was for inoculum production. Akhtar et al. (1996, 1997a, b) discovered that the amount of inoculum could be lowered to 5 kg/ton wood chips (dry weight basis) or less by adding an inexpensive and commercially available nutrient source, corn steep liquor (CSL), to the mycelial suspension. Subsequent studies have also identified a better strain of *C. subvermispora* that gave up to 38% energy savings and improved tear index by 51% compared to the control in the presence of CSL (Akhtar et al. 1996). After the practical and economical feasibility of biopulping was proved on the laboratory scale, accurate kinetic data were needed to determine the potential for the biopulping process on a large scale. Techniques for monitoring dry weight loss and growth rate as functions of time using carbon dioxide production data have been developed (Wall et al. 1993). Other aspects of biomechanical pulping like prediction of energy saving and brightness stability were also studied (Akhtar 1994; Akhtar et al. 1995a, b; Sykes 1993). Based on the practical and economical feasibility study of biopulping, a chip pile-based system has been proposed (Fig. 7.1) (Akhtar et al. 1997a).

Biopulping Consortium conducted successful 5 and 100 ton trials in outdoor chip piles at the FPL-USDA, Madison, WI. The results obtained were similar to those obtained in the laboratory scale bioreactors. The fungal treatment saved 32% electrical energy (Akhtar et al. 1997a). Equipment and techniques for the pilot scale treatments and scale-up to mill scale were discussed by Scott et al. (1997). Contaminating microorganisms on the chip surfaces are controlled by brief exposure of the chips to steam, before addition of the fungal inoculum fortified with CSL. Metabolic heat from the growth of the fungus on the wood chips is removed by forced ventilation. The fungus *P. subserialis* showed operational advantages over *C. subvermispora*, because less mycelial growth outside the chips and lower compressibility of the treated chips resulted in lower resistance to air flow (Scott et al. 1997). Economic analysis of a mill-scale design suggested net savings of about

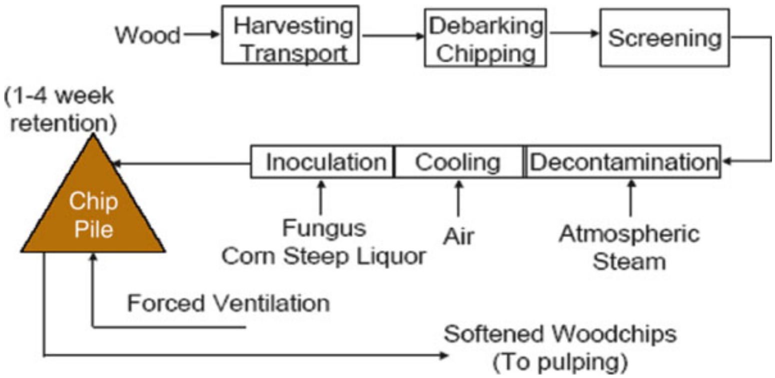

Fig. 7.1 Biopulping process can be fitted into an existing mill's wood handling system

$10/ton and a 25% annual return on investment (Scott et al. 1997). The Biopulping consortium has obtained several patents on the process (Blanchette et al. 1991; Akhtar et al. 1995a, b; Akhtar 1997).

Brazilian researchers biotreated *Eucalyptus grandis* wood chips with *C. subvermispora* in a 50-ton chip pile and evaluated for TMP and CTMP processing on a mill scale (Guerra et al. 2004, 2005, 2006). Biotreatment on the 50-ton chip pile was performed after a series of scale-up procedures starting with precolonized wood chips prepared in 20 L bioreactors. The first step included 760 kg of decontaminated wood chips and 40 kg of the start-up precolonized wood chips. Second scale-up used the 800 kg colonized wood chips to prepare an 8-ton pile. A final scale-up was conducted using the wood chips precultured in the 8-ton pile as inoculum seed to build a 50-ton pile. After 60 days of biodegradation, the wood chips from the last pile were refined on a mill-scale by using a two-stage thermomechanical process (Guerra et al. 2006). In this trial, the wood weight loss was 9% based on basic wood density values of untreated and biotreated samples: 413 and 376 kg/m^3, respectively. The average energy consumption for producing TMP pulps with 450–470 CSF was 913 and 745 kWh/ton for control and biotreated wood chips, respectively (18% of energy saving in the pulping process). In the case of CTMP pulps with similar CSF, energy consumption was 1,038 and 756 kWh/ton for control and biotreated wood chips, respectively (27% of energy saving in the pulping process). Tensile indexes of biomechanical pulps were higher in comparison to reference pulps (Table 7.4). However, chip pile contamination with opportunist fungi has been observed when the process was initiated by wood chip inoculation with blended mycelium and CSL as a co-substrate (Ferraz et al. 2008).

Brazilian researchers further investigated biopulping of *E. grandis* wood chips with *P. chrysosporium* RP-78 under nonaseptic conditions in laboratory and mill wood-yard (Masarin and Ferraz 2008; Masarin et al. 2009). The ability of *P. chrysosporium* to compete with indigenous fungi present in fresh wood chips was notorious under controlled laboratory experiments. A subsequent step involved an industrial test performed with 10 ton of fresh wood chips inoculated and maintained

Table 7.4 Tensile indexes of biomechanical pulps

Properties	Laboratory-prepared 2-stage TMP/RMP (blank)	Laboratory-prepared 2-stage BioTMP/RMP	Mill-prepared 2-stage TMP/RMP (blank)	Mill-prepared 2-stage BioTMP/RMP	Mill-prepared 2-stage CTMP	Mill-prepared 2-stage BioCTMP
Tensile index (Nm/g)	5.2	11.3	12 ± 2	11 ± 2	16 ± 3	16 ± 2
CSF (mL)	402	390	472 ± 31	455 ± 26	485 ± 16	409 ± 23

Based on Ferraz et al. (2008)

Table 7.5 Properties of mill-refined pulps prepared from *Eucalyptus* wood chips treated with *Phanerochaete chrysosporium*

Samples	Consistency, first disk refiner (%, w/v)	Shive content of the pulps (%, w/w)	Refining degree (degree SR)	Specific volume (cm^3/g)	Average fiber length (mm)	Tensile index (Nm/g)	Delamination strength (kPa)
Control	29.4	0.12	22	2.9	557	25 ± 1	217 ± 19
Fungal-treated	22.5	0.04	22	2.5	562	33.6 ± 0.5	295 ± 30

Based on Masarin et al. (2009)

at 37 ± 3°C for 39 days in a biopulping pilot plant. Biotreated wood chips were pulped in a CTMP mill. Net energy consumption during refining was 745 and 610 kWh/ton of processed pulp for control and biotreated wood chips, respectively. Accordingly, 18.5% net energy saving could be achieved. Biopulps contained lower shive content and had improved strength properties compared to control pulps. Tensile index improved from 25 ± 1 to 33.6 ± 0.5 Nm/g and delamination strength from 217 ± 19 to 295 ± 30 kPa (Table 7.5).

Mechanical pulping processes release organic materials (sugars, low molecular weight lignins, extractives) from wood, and these materials appear in the effluent stream (Eriksson 1985). Mill effluents could contain as many as 100 potentially toxic constituents. Moreover, even low levels of several benign compounds could interact synergistically to produce a toxic effluent (Johnson and Butler 1991). CTMP processes produce effluents of high color and BOD which may be difficult to treat; environmental considerations have kept this process from being used in many locations. Canadian CTMP mills have been reported to generate effluents having pollution loads of 35–65 kg BOD/ton pulp and 70–200 kg COD/ton pulp, depending on the pulping conditions and process as well as wood species used (Environment Canada Report 1988). Lo et al. (1991) based on the characterization of effluents from 17 different sources in a Canadian CTMP pulp and paper mill, showed that the concentrations and loadings of BOD, COD, resin and fatty acids (RFA), and other polluting constituents in the effluent from CTMP washing were very much higher than those in other effluents. The approximate pollutant amounts sent to the receiving water from the primary clarifier are BOD 63.3 kg, COD 90 kg, and RFA 0.43 kg/ton pulp. RFA constituents of wood are extracted during mechanical pulping/refining, and are major contributors to effluent toxicity (Leach and Thakore 1976).

Table 7.6 Characteristics of bleached CTMP wastewater

Parameter	Value
pH	6.5
Acetic acid (mg/L)	1,360
COD-total (mg/L)	9,300
COD-soluble (mg/L)	5,030
TSS (g/kg)	2.45
VSS (g/kg)	1.98
Resin acids (mg/L)	36–40

Based on Kennedy et al. (1992)

Table 7.7 Composition of resin acids in bleached CTMP wastewater

Resin acid	Percentage
Pimaric	7
Sandarocopimaric	6
Isopimaric	12
Levopimaric	21
Dehydroabietic	22
Abietic	26
Neoabietic	6
Total	*100*

Based on Kennedy et al. (1992)

CTMP wastewater characteristics are given in Table 7.6 and the composition of resin acids is represented in Table 7.7 (Kennedy et al. 1992). It has also been observed that the CTMP wastewater can be toxic to anaerobic bacteria (anaerobic treatment is sometimes given to CTMP effluents to reduce their pollution load) because of the presence of resin acids (Welander 1988; Hall and Cornacchio 1988). However, Kennedy et al. (1992) reported that resin acids were toxic to anaerobic bacteria but were not responsible for all the toxicity in bleached CTMP effluent. Furthermore, resin acid shocks were found to be inhibitory to the batch anaerobic system. However, short-term shocks of resin acids up to concentrations of 400 mg/L (38 mg resin acid/g VSS.d) had little effect on UASB (Upflow anaerobic sludge blanket) reactor efficiency. Long-term continuous exposure to abietic acid up to a concentration of 600 mg/L (60 mg resin acid/g VSS.d) did not significantly affect UASB reactor performance. In other words, anaerobic bacterial biomass can be acclimatized, to some extent, to the resin acid containing wastewater from CTMP plants.

The environmental impact of a new pulping process is a critical factor in assessing its viability. Ideally, a new process should be more environmentally compatible than existing processes. One question about biopulping is whether its effluents are more detrimental to the environment than are effluents from traditional mechanical pulping and refining. Specifically, do fungal metabolites or fungal degradation products of wood introduce additional toxicity to the effluent or significantly increase the BOD and COD load?

The microtox method of toxicity test has been used satisfactorily as a rapid screening method in the evaluation of acute toxicity of pulp mill effluents (Firth and

Table 7.8 BOD, COD, and toxicity of nonsterile aspen chips after treatment with *C. subvermispora*

Pulp[a]	BOD (g/kg pulp)	COD (g/kg pulp)	EPA toxicity[b] (100/EC_{50})
Raw chips	18	40	33
Control			
No nutrients	10	30	5
Nutrients added	12	33	9
Fungus treated			
No nutrients	10	33	6
Nutrients enriched	11	35	4

Based on Sykes (1994)

[a] All pulps incubated for 4 weeks at 27°C, except raw chips

[b] EC_{50} is a measure of toxicity

Backman 1990). Microtox assay uses luminescent bacteria to measure acute toxicity. Samples of wastewater from the first refiner passes of aspen chips pretreated with either *P. chrysosporium* or *C. subvermispora* were analyzed for BOD, COD, and microtox toxicity (Kirk 1993; Sykes 1994). Effluents from pulping fungus-treated chips were substantially less toxic than effluents from pulping raw chips (Table 7.8) (Sykes 1994). BOD values for effluents from fungus-treated pulps were slightly higher than for RMP of raw chips. The COD values for effluents from fungus-treated pulps were considerably higher than for RMP of raw chips probably because of the release of lignin degradation products (Sykes 1994). Addition of nutrients to the aspen chips also affected the BOD and COD loads of effluents. BOD decreased after 4-week incubation with nutrient-enriched *P. chrysosporium*, while BOD remained unchanged following incubation with nutrient-enriched *C. subvermispora*. COD remained unchanged after 4-week incubation with nutrient-enriched *P. chrysosporium*, while COD increased in effluents from chips pretreated for 4 weeks with nutrient-enriched *C. subvermispora*. As different white-rot fungi used for pulp treatment have differing nutrient requirements, an important factor in optimizing the biopulping process is to establish the minimum amount of nutrient required to assure fungal growth. The BOD and COD data indicate that *C. subvermispora* does not require much added nutrients. It has been concluded that the aspen biopulp effluents were less toxic, and probably contained considerably lower BOD and COD levels, than aspen TMP or CTMP at comparable yields (Sykes 1994) although no data on CTMP were available for comparison. It is likely that the environmental impact of CTMP effluent will be more than that of RMP or TMP effluents because of more extractives in the CTMP effluent. As the resin content of the wood chips decreases on fungal treatment (Fischer et al. 1994), it is expected that the amount of these extractives will be less in the effluent after mechanical pulping/refining of these chips, resulting in reduced toxicity (Table 7.9).

Published values for BOD load, based on the EPA survey for establishing effluent guidelines, are 20 kg/ton of o.d. pulp for TMP and 95 kg/ton of o.d. pulp for CTMP (Springer 1986). A commercial CTMP mill reported a BOD load of 45 kg/air dry ton, or approximately 52 kg/ton of o.d. pulp, for aspen CTMP (Jakko Poyry Inc 1985). *C. subvermispora* biopulping effluents contained approximately 24 kg/ton pulp and *P. chrysosporium* biopulping effluents contained 20 kg/ton pulp, at

Table 7.9 Effect of fungal treatment on resin content (% of dry wood) of loblolly pine and spruce chips

Time (weeks)	Loblolly pine		Spruce		
	Control	*C. subvermispora*	Control	*C. subvermispora*	*P. chrysosporium*
0	2.55	2.55	1.2	1.2	1.2
1	2.62	2.04	–	–	–
2	2.64	1.93	1.2	0.8	0.9
3	2.55	1.75	–	–	–
4	2.63	1.75			

Based on Fischer et al. (1994)

comparable yield (Sykes 1994) less than half the commercial CTMP values. *P. chrysosporium* has been used to remove color in the MyCoR (mycelial color removal) system (Eaton et al. 1982; Joyce and Pellinen 1995) and it was later discovered that this also decreased effluent toxicity. The decrease of toxicity observed for the fungus-treated biopulps is consistent with biotreatment of mill effluents by MyCoR system.

7.4 Biochemical Pulping

Fungal pretreatment of wood before chemical pulping has received relatively little attention. However, the fungi that are effective in biomechanical pulping have been tested as pretreatments for both kraft and sulfite pulping in a few studies (Messner et al. 1997).

Kraft pulps prepared from chips of aspen or red oak pretreated with *P. chrysosporium* for 10–30 days cooked faster and gave higher yields at a given kappa number (residual lignin content) than pulps from untreated chips (Oriaran et al. 1990, 1991). The improved cooking properties of the fungus-treated chips were attributed to enhanced penetration of cooking liquor and a lower lignin content. The fungus-pretreated pulps were more responsive to beating and gave higher tensile strength than the control pulps (Oriaran et al. 1990). The environmental consequences of the fungal treatments were not addressed in these studies, but the substantial wood weight loss (up to 17%) during the fungal pretreatment would negate the reported yield improvement, and the darkening of the wood by the fungus would probably require application of more bleaching chemicals.

Pretreatment of mixed hardwood chips with the Cartapip® 97 fungus, *Ophiostoma piliferum*, for 21 days improved kraft pulping efficiency; the kappa number decreased by 29% or the active alkali concentration in the pulping liquor decreased by 20% (Wall et al. 1996). Pulp yield was unaffected and viscosity, an indicator of pulp strength, was increased. The improvements were attributed to enhanced liquor penetration resulting from removal of ray parenchyma cells, resin deposits, and pit membranes. The Cartapip pretreatment could be used to reduce the environmental impact of kraft pulp production by decreasing bleach chemical usage or by decreasing cooking chemical usage (Wall et al. 1996).

Table 7.10 Biokraft pulping of eucalyptus with *C. subvermispora* at reduced active alkali charge

	AA charge (%)			
	17	14	14	14
Parameter	Control	Treated	Control	Treated
(a) Pulp properties				
P. No.	13.50	15.86	16.28	15.86
Lignin (%)	1.55	1.57	–	–
Unbleached brightness (% ISO)	27.3	28.3	25.9	28.3
Unbleached pulp yield (%)	45.67	45.53	47.15	45.53
Final brightness (% ISO)	87.0	88.3	87.6	89.1
Bleach chemical consumption (kg/ton)				
Elemental Cl_2	37.5	37.5	46.1	46.1
NaOH	19.1	19.1	18.9	18.9
Hypo	13.5	13.5	12.8	12.8
Chlorine dioxide	6.0	6.0	6.0	6.0

	Unbleached			Bleached	
	Control		Treated	Control	Treated
Parameter	17% AA	14% AA	14% AA	17% AA	14% AA
(b) Strength properties					
Wetness (SR)	16.5	17.0	17.5	35.0	35.0
Beating time (min)	–	–	–	29.0	22.5
Tensile index (Nm/g)	33.68	34.10	40.75	66.25	72.26
Breaking length (m)	3,435	3,478	4,157	6,757	7,364
Burst index (kN/g)	1.38	1.62	1.89	4.30	4.85
Tear index (mNm^2/g)	5.45	5.77	6.81	7.68	7.88
Double fold (No.)	5	8	10	58	80

Fungal treatment for 2 weeks; Inoculum level, 5 g/T wood
From Bajpai et al. (2001, 2003)

Screening of 283 basidiomycetes for ability to improve the efficiency of kraft pulping of pine chips revealed *Coriolus versicolor, Pycnoporus sanguineus,* and *Stereum hirsutum* as the most promising species (Wolfaardt et al. 1996). Pretreatment of the pine chips with *S. hirsutum* for 9 weeks reduced the cooking time required to reach a kappa number of 28, but increased alkali consumption and lowered pulp yield and viscosity. The fungal pretreatment did not seem to give economical or environmental benefits.

Bajpai et al. (2001, 2003) observed that extractive content reduced by 17–39% and the AA requirement reduced by 18%, when eucalyptus chips treated with the fungus *C. subvermispora* for 2 weeks were subjected to Kraft pulping (Table 7.10). Brightness and strength properties of biopulps were better than the control and the pulps were easier to bleach and easier to refine – requiring less energy (by 18–30%).

Çöpür and Tozluoğlu (2007) examined the effects on pulp and paper properties of pretreating Brutia pine wood chips with *C. subvermispora* and adding AQ and sodium borohydrate to the white liquor. Results showed that, compared with the control kraft method, pulp rejects were lower for biokraft pulp and a significant reduction was observed when the biokraft process was modified by sodium borohydride. An increase in pulp yield and reduction in kappa number was also seen with

Table 7.11 Soda pulping of wheat straw with *C. subvermispora* strains 1 and 2 at reduced alkali charges

Parameters	Control	Strain 1	Strain 2	Strain 3
EA (%)	12	10	10	9.0
Kappa no.	28.6	28.6	26.7	28.3
Yield (%)	45.9	48.1	45.9	46.7
Brightness (% ISO)	34.6	34.6	35.7	34.7
Residual alkali (g/L)	1.9	2.1	2.2	1.9

Based on Bajpai et al. (2004a)

biokraft pulp. The addition of AQ and sodium borohydride into biopulping gave positive results in terms of pulp yield and kappa number compared with biokraft pulp. There was a significant increase in pulp brightness when biokraft pulping was modified with 2% sodium borohydrate. Biotreatments resulted in pulps that were easier to refine and the refined bio-kraft-AQ pulps had the highest tensile index. However, biopulps had a lower tear but higher burst index compared to the control kraft pulp.

Recently research has been carried out by Garmaroody et al. (2011) in which poplar chips were pretreated by *Trametes versicolor* for 1, 2, and 3 weeks and then after washing, the chips were air-dried for kraft pulping to achieve pulp kappa number of around 20. Analysis of the pulp samples indicated that fungi pretreatment of chips can degrade lignin and carbohydrates and affect kraft pulping and fiber characteristics. In pretreated pulp samples, higher chemical charge in pulping was observed, together with lower fine and higher long fiber fraction. Increasing pretreatment time increased the fiber length, cross-sectional area, width, cell wall thickness, and volume index, while fine length, fiber coarseness, and curl were reduced. It has been recommended that 2-week pretreatment of chips would produce acceptable overall fiber properties in kraft pulping.

Bajpai et al. (2004a) also studied pretreatment of wheat straw with lignin-degrading fungi to study its effect on chemical pulping. Treatment with *C. subvermispora* reduced the lignin and extractive content of wheat straw by 16.5 and 44.3%, respectively. For chemical pulping, pretreatment reduced the kappa number by 22–27% at the same alkali charge, reduced the alkali charge by 30 kg/ton of raw material for the same kappa number (Table 7.11), or reduced the cooking time by up to 30% for the same kappa number. The biopulp had higher brightness and whiteness than the pulp obtained from feedstock without any fungal treatment (Table 7.12). The COD load in the effluent was lower for biopulping than for conventional pulping. Biopulping benefits obtained with other white-rot fungal cultures, *P. subserialis* and *P. brevispora*, were less pronounced than the benefits obtained with *C. subvermispora*.

Bajpai et al. (2004b) also studied the pretreatment of bagasse with *C. subvermispora* strains and its effect on chemical pulping. Treatment of depithed bagasse with different strains of *C. subvermispora* reduced the kappa number by 10–15% and increased unbleached pulp brightness by 1.1–2.0 ISO points on chemical pulping at the same alkali charge. Bleaching of biopulps at the same chemical charge increased final brightness by 4.7–5.6 ISO points and whiteness by 10.2–11.4 ISO points. Fungal treatment did not result in any adverse effect on the strength properties of pulp.

Table 7.12 Effect of cooking time on soda pulping of *C. subvermispora*-treated wheat straw

	Cooking time (min)	Kappa no.	Yield (%)	Brightness (% ISO)
Control	60	28.1	45.9	34.1
	45	30.1	46.5	33.9
	30	31.5	47.1	33.1
	15	Ellipsis	–	–
C. subvermispora, Strain 2	60	21.9	46.1	38.2
	45	22.5	47.2	37.6
	30	24.1	47.8	37.1
	15	26.1	48.1	36.2

Based on Bajpai et al. (2004a)

Treatment of birch, maple, oak, sycamore, or pine chips with an enzyme mixture containing cellulase and hemicellulase for 24 h disrupted the pit membranes blocking pores between cells and increased the longitudinal and transverse diffusion rates of sodium hydroxide in the chips (Jacobs-Young et al. 1998). Kraft pulping experiments with enzyme-treated sycamore chips confirmed the expected improvement in delignification; addition of pectinase to the enzyme mixture further lowered kappa numbers without reducing yield (Jacobs et al. 1998). The pulps produced from enzyme-treated chips were easier to bleach with chlorine dioxide than control pulps, and had comparable strength properties. Reduced bleaching chemical use should result in lower effluent BOD, COD, and chloroorganic loadings.

Franco et al. (2006) studied the potential of *Drimys winteri* for the conventional kraft and biokraft pulp production. For biokraft pulping, wood chips were biotreated with the white-rot fungus *Ganoderma australe*. During the biotreatment, a selective pattern of biodelignification was observed and the wood chips biotreated for 15, 30, and 45 days were submitted to kraft cooking. At low cooking severity (*H*-factor below 1,500/h, 15% active alkali and 25% sulfidity), all biopulps presented lower kappa numbers than control pulps and approximately the same screened pulp yield. Biopulps were easily refined in a PFI mill, requiring less PFI revolutions to achieve the same fibrillation degree. The strength properties of the biopulps were similar to those of the control pulps.

Eucalyptus nitens requires more severe cooking conditions to produce bleachable kraft pulps. Mardones et al. (2006) attempted to find out whether a pretreatment of *E. nitens* with *C. subvermispora* would improve its performance during kraft pulping and improve the pulp properties. The biotreatment of the chips carried out for a period of 15 days resulted in 13.3% lignin loss and a limited glucan degradation (2%). The pulping of biotreated samples required lower active alkali charge to reach the target kappa number compared to the control untreated sample and exhibited better pulping selectivity. The pulp yield increased by 3 and 1.5% for the pulps of 22 and 16 kappa numbers, respectively. The biotreated pulp's strength properties were improved and were similar to those of *Eucalyptus globulus* reference pulp (Table 7.13).

Table 7.13 Properties of kraft pulps[a] prepared from *Eucalyptus nitens* and *Eucalyptus globulus*

Sample	Burst index (kPa m^2/g)	Tensile index (Nm/g)	Tear index (m Nm^2/g)
(a) Physical strength properties			
Control			
E. nitens	5.9	110.2	6.6
Biotreated			
E nitens	6.2	113.8	7.1
E. globulus	6.5	114.6	7.4

Sample	Opacity (%)	Brightness (%)
(b) Brightness and opacity		
Control		
E. nitens	96.2	39.4
Biotreated		
E nitens	94.2	41.3
E. globulus	93.4	39.5

Sample	Coarseness (mg/100 m)	Average fiber length (mm)	Fines content (%)
(c) Fiber properties			
Control			
E. nitens	5.79	0.63	6.08
Biotreated			
E. nitens	5.39	0.64	7.06
E. globulus	5.81	0.68	5.98

Based on Mardones et al. (2006)

[a] Kappa number 16 ± 1

Pretreatment of chips with while-rot fungi increases the rate of their delignification in sulfite pulping also (Messner et al. 1997). In magnesium-based sulfite pulping, treatment of birch and spruce chips with *P. tremellosa, P. brevispora, Dichomitus squalens,* and especially *C. subvermispora* for 2–4 weeks significantly reduced pulp kappa number. However the fungal treatments also reduced pulp strength and brightness. Pretreatment of loblolly pine chips with *C. subvermispora* for 2 weeks increased the rates of lignin and yield loss to the same extent in sodium bisulfite pulping, but preferentially enhanced delignification in calcium-acid sulfite pulping, and decreased shives production. The fungal treatment darkened the chips, so that equal amounts of bleaching chemicals were needed to brighten the treated and control pulps. BOD and COD levels were the same in effluents from the fungus-treated and control pulps, but the Microtox toxicity in the effluent from the fungus-treated chips was less than half that of the control. The reduced toxicity was attributed to biodegradation of RFAs by the fungus (Messner et al. 1997).

7.5 Biopulping with Laccase Mediator System

The bulk of biopulping research on lignocellulosics has focused on the utilization of the white-rot fungi. Some researches have also used laccase mediator system to study biopulping (Widsten and Kandelba 2008; Dyer and Ragauskas 2004; Petit-Conil et al. 2002; Vaheri et al. 1991). Softwood (pine) chips were treated with laccase together with an ABTS, HBT, or VA mediator by Dyer and Ragauskas (2004) before kraft pulping. Laccase/HBT was found to be the most beneficial LMS in terms of enhancing delignification and pulp yield. Petit-Conil et al. (2002) treated softwood (spruce) chips with laccases obtained from three fungi with a mediator (HBT) prior to TMP. Laccase/HBT saved refiner energy with two of the laccases by up to 20%, but the third laccase increased it. The effect on pulp properties in terms of mechanical strength and brightness of handsheets was mostly positive. The improved pulp properties were attributed to a modification of the fiber surface chemistry, and increased external fibrillation and bonding potential. A decrease of 15% in peroxide consumption during subsequent bleaching to equal brightness was achieved with one of the laccases without mediator compared to bleaching without laccase pretreatment. The patent by Vaheri et al. (1991) describes the use of laccase pretreatment for reducing energy consumption during mechanical pulping. The treatment also boosts the pulp strength properties and blue reflectance factor.

7.6 Mechanism of Biopulping

Mechanism of biopulping is not completely understood though extensive investigation has been made over the last decade. Akhtar et al. (1998) examined at the microscopic level the fungal growth patterns of *P. chrysosporium* and *C. subvermispora* in aspen wood chips to gain insight into the mechanism of biopulping. *P. chrysosporium* grew well both across the chip surfaces and throughout the cell walls. The hyphae penetrated the chips through the lumens of wood vessels and fiber cells, as well as through natural wood cell pits and fungal bore holes. Partial degradation of the cell lumen walls was evident. Erosion troughs and localized wall fragmentation or thinning were clearly visible, as was a generalized swelling and relaxing of the normally rigid wood cell wall structure. *C. subvermispom*-treated aspen chips showed packed hyphae within the ray cells. Numerous crystals of calcium oxalate were found on the hyphae, during both the incipient and advanced stages of growth. Physical basis for the biopulping efficacy of the fungal treatment is likely to involve an overall softening and swelling of the cell walls, as well as thinning and fragmentation in localized areas (Sachs et al. 1989). Use of scanning electron microscopy revealed increased fibrillation on biomechanical pulp as compared with RMP (control). The biomechanical pulp fibers appeared more woolly, looser, and more uniform in length than the conventional mechanical and chemimechanical pulp fibers. Fiber bonding in handsheets produced from biomechanical pulp fibers appeared to be similar to that observed in handsheets produced from chemical pulps. Handsheets made from mechanically processed pulps showed uncollapsed fibers, leading to poor conformability and reduced bonding. The kraft pulps yielded handsheets that exhibited fibers of enhanced compressibility and conformability. Handsheets prepared from biomechanical pulps visually resembled the kraft handsheets, exhibiting good compressibility and conformability of the fibers.

Beneficial effects of wood pretreatment with white-rot fungi are obtained in the initial stages of biodegradation when weight losses are lower than 5% (Akhtar et al. 1998). Within biodegradation periods as short as 1 week, biotreated wood chips become softer and easier to disrupt along the fiber axes. This softening effect has been the basis for initial proposal of biological pretreatment of wood chips for mechanical pulping. In mechanical pulping, wood chips are disrupted in disk refiners to produce fibers suitable for papermaking. The process is energy intensive and pulp quality depends on several variables including the refiner design, wood species, and the desired refining level. In this way, wood chips that disrupt along fibers by requiring less mechanical strain would save energy and provide stronger pulps simply because fibers would suffer less damage during refining steps.

Guerra et al. (2002, 2003, 2004) have pointed out for two different types of wood transformations considering the chemical changes induced by the fungus in wood. One of them involves intense lignin depolymerization in short biotreatment periods, while the other indicates that esterification of oxalate secreted by the fungus on the polysaccharides chains increases the water saturation point of the fibers (Hunt et al. 2004). Both transformations are expected to affect the fiber–fiber bonding and, consequently, the physical resistance of wood. Obviously, these changes in wood structure are not isolated events and the overall change in the wood structure and ultrastructure would affect the behavior of biodegraded wood chips during mechanical or chemical pulping processes. Lack of correlation is found between the biopulping benefits and the extent of wood weight or component losses (Leatham et al. 1990a, b; Hunt et al. 2004; Ferraz et al. 2000; Mendonca et al. 2002). For example, the extent of lignin removal during fungal pretreatment is not related to the energy savings in biomechanical pulping or to the increase in delignification rates observed in kraft pulping.

Extensive removal of extractives during wood biodegradation by some white-rot fungi should provide alkali savings in kraft cooking. Extractive removal can result in unobstructed resin canals, facilitating the liquor penetration and reducing the active alkali consumption by nonlignin components. Actually, this benefit has been reported by Fischer et al. (1994) and Kohler et al. (1997) for seasoning of wood chips as well as for wood chips biotreatment by the nonlignin degrading fungus *O. piliferum*. Pulping experiments with extractive-free wood chips have been useful to evaluate the benefits of extractives removal during biopulping. The residual lignin contents in pulps prepared from extractive-free samples are midway between the undecayed controls and the fungal-treated samples (Mendonca et al. 2002), showing that extractives removal facilitates the subsequent kraft pulping but it cannot explain all the benefits observed in biokraft pulping, since even a sample without extractives is not delignified as easily as the fungal-treated samples. The extent of extractives removal during biopulping confirms this conclusion, since, similar to lignin losses, extractive losses are progressive with biodegradation time, whereas the benefits of the fungal treatment are not (Mendonca et al. 2002). The changes induced in the wood chips that provide benefits for mechanical pulping processes are not necessarily the same ones required for chemical pulping. For example, although correlating with the benefits in biomechanical pulping (Hunt et al. 2004), esterification of oxalate to the fibers is not expected to present a clear benefit for kraft pulping because the oxalate esters would consume part of the active alkali used in the cooking process.

Schwanninger et al. (2004) have reported that some near infra-red (NIR) bands from wood change significantly in biodegradation periods as short as 4 days. These changes in NIR band intensities prove that structural changes in wood components initiate very early during biodegradation. More relevant is that NIR bands can reflect not only changes in the covalent bonds of wood components, but also changes in fiber–fiber interactions such as hydrogen bonds. It is possible that minor changes in hydrogen bonding between fiber surfaces would be responsible by the softening effect observed in wood chips biotreated by white-rot fungi that facilitates disruption of the lignocellulosic matrix by disk refiners. To arrive at a comprehensive description of the biopulping chemistry, wood transformations occurring during biodegradation need to be explored in detail.

7.7 Advantages of Biopulping

Biomechanical pulping saves substantial amount of electrical energy or increases mill throughput significantly. It also improves paper strength compared to conventional RMP. Studies suggest that fungal treatment is also effective for depitching wood chips. It decreases dichloromethane extractable resin by about 30% (Fischer et al. 1994) including a 60% reduction in triglycerides which are responsible for sticky deposits on the paper machine (Fischer and Messner 1992). The cost of incorporating the fungal treatment process into existing mills is minimal. It is a relatively simple process that can be carried out in any woodyard.

Biochemical pulping reduces the amount of cooking chemicals, increases the cooking capacity, or enables extended cooking, resulting in lower consumption of bleaching chemicals. Increased delignification efficiency results in an indirect energy saving for pulping, and reduces pollution (Kirk et al. 1994). The waste load produced by biopulping should be considerably lower and more benign than effluents currently produced by commercial CTMP mills. In fact, the effluents from fungus-treated mechanical pulps have been found to be less toxic (Sykes 1994) although sometimes they may contain slightly higher BOD and COD than effluents from untreated pulp. These findings suggest that biopulping is environmentally compatible. Biopulping technology has advanced rapidly within recent years and pilot mill trials have been started worldwide (Reid et al. 2010).

7.8 Limitations and Future Prospects

A biopulping process would require inoculum on a regular basis for commercial scale applications, which would involve additional work and expense. Large-scale production of basidiomycetes is usually difficult. The fungal treatment is lengthy; a minimum of 2-week incubation is required to get the desired benefits. At first glance, the long reaction time needed for the fungal process seems to be a great disadvantage. However, considering that wood chips are often stored at the mill for at least 2 weeks, time and space should be available in the pulp mill to introduce this process. In fact, this type of bioprocess is already familiar to the pulp and paper industry as a similar process based on Cartapip® has been used commercially in many US mechanical pulp mills since 1990 (Farrell et al. 1992; Brush et al. 1994; Wall et al. 1994). The success of the Cartapip process shows that mills are able and willing to insert a biological step into their existing operations. Nevertheless it is desirable to apply classical or molecular genetic methods to improve the effectiveness of the biopulping fungi, leading to shorter reaction treatment times.

Although a chip pile-based biopulping system has been designed and evaluated on a pilot scale, the process requires demonstrated long-term operation at mill scale.

Fungal treatment reduces the brightness of resulting mechanical pulps by as much as 15–20 Elrepho brightness points in 4 weeks and 8–10 points in 2 weeks. However, aspen biorefiner mechanical pulp (BRMP) could be readily bleached to 60% Elrepho brightness with 1% sodium hydrosulfite, and 80% brightness with a two-step bleach sequence using sodium hydrosulfite and alkaline hydrogen peroxide. Based on the accelerated thermal and photoaging tests, the brightness stability of BRMP was found to be slightly lower than that of RMP but slightly higher than that of CTMP (Sykes 1993).

Although biomechanical pulping seems to have a high potential to reduce pollution problems, very few data on the environmental performance of biomechanical pulping vis-à-vis CTMP and other high yield pulping processes are available. These data need to be generated from systematic studies comparing biomechanical pulping to other pulping processes, for equivalent quality and yield of pulp.

References

Akamatsu I, Yoshihara K, Kamishima H (1984) Influence of white-rot fungi on poplar chips and thermo-mechanical pulping of fungi-treated chips. Mokuzai Gakkaishi 30:697–702

Akamatsu IH, Ueshima KY, Umeda TA (1988) Biological pulping apparatus for wood chips. Japanese Patent Application 63/83537

Akhtar M (1994) Biomechanical pulping of aspen wood chips with three strains of *Ceriporiopsis subvermispora*. Holzforschung 48:199–202

Akhtar M (1997) Method of enhancing biopulping efficiency. US Patent 5,620,564

Akhtar M, Attridge NC, Myers GC (1992a) Biomechanical pulping of loblolly pine with different strains of the white-rot fungus *Ceriporiopsis subvermispora*. Tappi J 75(2):105–109

Akhtar M, Attridge MC, Blanchette RA (1992b) The white-rot fungus *Ceriporiopsis subvermispora* saves electrical energy and improves strength properties during biomechanical pulping of both hardwood and softwood chips. In: Kuwahara M, Shimada M (eds) Biotechnology in the pulp and paper industry. UNI Publishers, Kyoto, pp 3–8

Akhtar M, Attridge MC, Myers GC (1993) Biomechanical pulping of loblolly pine chips with selected white-rot fungi. Holzforschung 47:36–40

Akhtar M, Blanchette RA, Burnes T (1995a) Using Simons stain to predict energy savings during biomechanical pulping. Wood Fiber Sci 27(3):258–264

Akhtar M, Attridge MC, Koning JW et al (1995b) Method of pulping wood chips with a fungi using sulfite salt-treated wood chips. US Patent 5,460,697

Akhtar M, Blanchette RA, Kirk TK (1996) Biopulping: an overview of consortia research. In: Srebotnik E, Messner K (eds) Biotechnology in the pulp and paper industry. Recent advances in applied and fundamental research. Facultas-Universitatsverlag, Vienna, pp 187–192

Akhtar M, Blanchette RA, Kirk TK (1997a) Fungal delignification and biomechanical pulping of wood. Adv Biochem Eng Biotechnol 57:159–195

Akhtar M, Lentz MJ, Blanchette RA (1997b) Corn steep liquor lowers the amount of inoculum for biopulping. Tappi J 80(6):161–164

Akhtar M, Blanchette RA, Myers G (1998) An overview of biomechanical pulping research. In: Young RA, Akhtar M (eds) Environmentally friendly technologies for the pulp and paper industry. Wiley, New York, pp 309–340

Ander P, Eriksson KE (1975) Influence of carbohydrates on lignin degradation by the white-rot fungus *Sporotrichum pulverulentum*. Sven Papperstid 78:643–652

Arppe M (2001) Mechanical pulp: has it got a future or will it be discontinued? Int Papwirtsch 10:45–50

Bajpai P, Bajpai PK, Kondo R (1999) Biotechnology for environmental protection in pulp and paper industry. Springer, Berlin, pp 141–170

Bajpai P, Bajpai PK, Akhtar M (2001) Biokraft pulping of *Eucalyptus* with selected lignin-degrading fungi. J Pulp Pap Sci 27(7):235–239

Bajpai P, Bajpai PK, Akhtar M (2003) Eucalyptus biokraft pulping process. US Patent 6,613,192

Bajpai P, Mishra SP, Mishra OP, Kumar S, Bajpai PK, Singh S (2004a) Biochemical pulping of wheat straw. Tappi J 3(8):3–6

Bajpai P, Mishra SP, Mishra OP, Kumar S, Bajpai PK (2004b) Biochemical pulping of bagasse. Biotechnol Prog 20(4):1270–1272

Bar-Lev SS, Kirk TK, Chang H-M (1982) Fungal treatment can reduce energy requirements for secondary refining of TMP. Tappi J 65(10):111–113

Blanchette RA, Burnes TA, Leatham GF (1988) Selection of white-rot fungi for biopulping. Biomass 15:93–101

Blanchette RA, Leatham GF, Attridge M (1991) Biomechanical pulping with *C. subvermispora*. US Patent 5,055,159

Blanchette RA, Akhtar M, Attridge MC (1992a) Using Simons stain to evaluate fiber characteristics of biomechanical pulps. Tappi J 75(11):121–124

Blanchette RA, Burnes TA, Eerdmans MM (1992b) Evaluating isolates of *Phanerochaete chysosporium* and *Ceriporopsis subvermispora* for use in biological pulping processes. Holzforschung 46:109–115

Brush TS, Farrell RL, Ho C (1994) Biodegradation of wood extractives form southern yellow pine by *Ophiostoma piliferum*. Tappi J 77(1):155–159

Çöpür Y, Tozluoğlu A (2007) The effect of AQ and NaBH4 on bio-kraft delignification (*Ceriporiopsis subvermispora*) of brutia pine chips, International Biodeterioration & Biodegradation 60(2):126–131

Dyer TJ, Ragauskas AJ (2004) Laccase: a harbinger to kraft pulping. ACS Symp Ser 889:339–362

Eaton DC, Chang H-M, Joyce TW (1982) Method obtains fungal reduction of the color of extraction stage kraft bleach effluent. Tappi J 65(6):89–92

Environment Canada Report (1988) WTC Bio-07-1988

Eriksson KE (1985) Swedish developments in biotechnology related to the pulp and paper industry. Tappi J 68(7):46–55

Eriksson KE, Vallander L (1980) Biomechanical pulping. In: Kirk TK, Higuchi T, Chang H-M (eds) Lignin biodegradation: microbiology, chemistry, and potential applications, vol II. CRC Press, Boca Raton, pp 213–233

Eriksson KE, Vallander L (1982) Properties of pulps from thermomechanical pulping of chips pretreated with fungi. Sven Papperstid 85:R33–R38

Eriksson KE, Ander P, Henningsson B (1976) Method for producing cellulose pulp. US Patent 3,962,033

Eriksson KE, Grunewald A, Vallander L (1980) Studies of growth conditions in wood for three white-rot fungi and their cellulaseless mutants. Biotechnol Bioeng 22:363–376

Farrell RA, Blanchette RA, Brush TH (1992) In: Kuwahara M, Shimada M (eds) Biotechnology in the pulp and paper industry. UNI Publishers, Kyoto, pp 27–32

Ferraz A, Mendonca R, Silva FT (2000) Organosolv delignification of white- and brown-rotted *Eucalyptus grandis* hardwood. J Chem Technol Biotechnol 75:18–24

Ferraz A, Guerra A, Mendonca R, Masarin F, Vicentim MP, Aguiar A (2008) Technological advances and mechanistic basis for fungal biopulping. Enzyme Microb Technol 43:178–185

Firth B, Backman C (1990) Comparison of Microtox testing with rainbow trout (acute) and *Ceriodaphnia* (chronic) bioassays in mill wastewaters. Tappi J 73(12):169–174

Fischer K, Messner K (1992) Reducing troublesome pitch in pulp mills by lipolytic enzymes. Tappi J 75(2):130–134

Fischer K, Akhtar M, Blanchette RA, Burnes TA, Messner K, Kirk TK (1994) Reduction of resin content in wood chips during experimental biological pulping processes. Holzforschung 48:285–290

Franco H, Freer J, Rodrıguez J, Baeza J, Elissetche JP, Mendon R (2006) Kraft pulping of *Drimys winteri* wood chips biotreated with *Ganoderma australe*. J Chem Technol Biotechnol 81:196–200

Garmaroody ER, Resalati H, Fardim P, Hosseini SZ, Rahnama K, Saraeeyan AR, Mirshokraee SA (2011) The effects of fungi pre-treatment of poplar chips on the kraft fiber properties. Bioresour Technol 102(5):4165–4170

Giovannozzi-Sermanni G, Cappelletto PL, D'Annibale A (1997) Enzymatic pretreatment of non-woody plants for pulp and paper production. Tappi J 80(6):139–144

Guerra A, Mendonca R, Ferraz A (2002) Characterization of the residual lignins in *Pinus taeda* biodegraded by *Ceriporiopsis subvermispora* by using in situ CuO oxidation and DFRC methods. Holzforschung 56:157–160

Guerra A, Mendonca R, Ferraz A (2003) Molecular weight distribution of wood components extracted from *Pinus taeda* biotreated by *Ceriporiopsis subvermispora*. Enzyme Microb Technol 33:12–18

Guerra A, Ferraz A, Lu F, Ralph J (2004) Structural characterization of lignin during *Pinus taeda* wood treatment with *Ceriporiopsis subvermispora*. Appl Environ Microbiol 70:4073–4078

Guerra A, Mendonca R, Ferraz A (2005) Bio-chemimechanical pulps from *Eucalyptus grandis*: strength properties, bleaching, and brightness stability. J Wood Chem Technol 25:203–216

Guerra A, Pavan PC, Ferraz A (2006) Bleaching, brightness stability and chemical characteristics of *Eucalyptus grandis*-bio-TMP pulps prepared in a biopulping pilot plant. Appita J 59:412–415

Hall E, Cornacchio LA (1988) Anaerobic treatability of Canadian pulp and paper mill wastewaters. Pulp Pap Can 89:T188–T192

Heden CG, Eriksson KE, Johnsrud K (1988) Japanese Patent Application 152/380

Hunt C, Kenealy W, Horn E, Houtman C (2004) A biopulping mechanism: creation of acid groups on fiber. Holzforschung 58:434–439

Jacobs CJ, Vendetti RA, Joyce TW (1998) Effect of enzyme pretreatments on conventional kraft pulping. Tappi J 81(2):143–147

Jacobs-Young CJ, Venditti RA, Joyce TW (1998) Effect of enzymatic pretreatment on the diffusion of sodium hydroxide in wood. Tappi J 81(1):260–266

Jakko Poyry Inc. (1985) Multiclient report. Lindingo, Sweden, p 2

Johnson I, Butler R (1991) Paper mill effluents: a move to toxicity-based consents. Pap Technol 32(6):21–25

Johnsrud SC, Eriksson KE (1985) Cross-breeding of selected and mutated homokaryotic strains of *Phanerochaete chrysosporium* K-3: new cellulase deficient strains with increased ability to degrade lignin. Appl Microbiol Biotechnol 21:320–327

Johnsrud SC, Fernandez N, Lopez P (1987) Properties of fungal pretreated high yield bagasse. Nord Pulp Pap Res J (Special Issue) 2:47–52

Joyce TW, Pellinen J (1995) White rot fungi for the treatment of pulp and paper industry wastewater. In: Proceedings of the Tappi environmental conference, Seattle

Karl W (1990) The 1990's could be the decade for CTMP. Tappi J 73(Suppl 2000 and Beyond):90–92

Kennedy KJ, McCarthy PJ, Droste RL (1992) Batch and continuous anaerobic toxicity of resin acids from chemithermomechanical pulp wastewater. J Ferm Bioeng 73(3):206–212

Kirk TK (1993) Biopulping: a glimpse of the future? Res Rep FPL-RP-523. Forest Products Laboratory, Madison

Kirk TK, Akhtar M, Blanchette RA (1994) Biopulping: seven years of consortia research. In: Proceedings of the Tappi biological science symposium. Tappi Press, Atlanta, pp 57–66

Kobe Steel (1988) Lignin degrading microorganisms having high activity and selectivity (for lignin). Japanese Patent EP295063

Kohler LJF, Dinus RJ, Malcolrn EV, Rudie AW, Farrell RL, Brush TS (1997) Improving softwood mechanical pulp properties with *Ophiostoma piliferum*. Tappi J 80:135–140

Kojima Y (1988) Inoculation of lignocellulosic materials with microbes in delignification. Japanese Patent Application 63/91077

Lawson LR Jr, Still CN (1957) The biological decomposition of lignin – literature survey. Tappi J 40(9):56A–80A

Leach JM, Thakore AN (1976) Toxic constituents in mechanical pulping effluents. Tappi J 59(2):129–132

Leask RA, Kocurek MJ (1987) Mechanical pulping. Joint Textbook Committee of the Paper Industry, Montreal

Leatham GF, Myers GC (1990) A PFI mill can be used to predict biomechanical pulp strength properties. Tappi J 73(4):192–197

Leatham GF, Myers GC, Wegner TH (1990a) Biomechanical pulping of aspen chips: paper strength and optical properties resulting from different fungal treatments. Tappi J 73(3):249–255

Leatham GF, Myers GC, Wegner TH (1990b) Biomechanical pulping of aspen chips: energy savings resulting from different fungal treatments. Tappi J 73(5):197–200

Lo SN, Liu HW, Rousseau S (1991) Characterization of pollutants at source and biological treatment of a CTMP effluent. Appita 44(2):133–138

Mardones L, Gomide JL, Freer J, Ferraz A, Rodrıguez J (2006) Kraft pulping of *Eucalyptus nitens* wood chips biotreated by *Ceriporiopsis subvermispora*. J Chem Technol Biotechnol 81:608–613

Martinez AT, Camarero S, Guillén F (1994) Progress in biopulping of non-woody materials: chemical, enzymatic and ultrastructural aspects of wheat straw delignification with ligninolytic fungi from the genus *Pleurotus*. FEMS Microbiol Rev 13:265–274

Masarin F, Ferraz A (2008) Evaluation of *Eucalyptus grandis* biopulping with *Ceriporiopsis subvermispora* under nonaseptic conditions. Holzforschung 62:1–7

Masarin F, Pavan PC, Vicentim MP, Souza-Cruz PB, Loguercio-Leite C, Ferraz A (2009) Laboratory and mill scale evaluation of biopulping of *Eucalyptus grandis* Hill ex Maiden with *Phanerochaete chrysosporium* RP-78 under non-aseptic conditions. Holzforschung 63:259–263

Mendonca R, Guerra A, Ferraz A (2002) Delignification of *Pinus taeda* wood chips treated with *Ceriporiopsis subvermispora* for preparing high-yield kraft pulps. J Chem Technol Biotechnol 77:411–418

Messner K, Koller K, Wall MB (1997) Fungal treatment of wood chips for chemical pulping. In: Young RA, Akhtar M (eds) Environmentally friendly technologies for the pulp and paper industry. Wiley, New York, pp 385–419

Myers GC, Leatham GF, Wegner TH (1988) Fungal pretreatment of aspen chips improves strength of refiner mechanical pulp. Tappi J 71(5):105–108

Nishida T (1989) Lignin biodegradation by wood-rotting fungi. V. A new method for evaluation of the ligninolytic activity of lignin-degrading fungi. Mokuzai Gakkaishi 35(7):675–677

Nishida T, Kashino Y, Mimura A (1988) Lignin biodegradation by wood-rotting fungi. l. Screening of lignin-degrading fungi. Mokuzai Gakkaishi 34:530–536

Oriaran TP, Labosky P Jr, Blankenhorn PR (1990) Kraft pulp and papermaking properties of *Phanerochaete chrysosporium* degraded aspen. Tappi J 73(7):147–152

Oriaran TP, Labosky P Jr, Blankenhorn PR (1991) Kraft pulp and papermaking properties of *Phanerochaete chrysosporium* degraded red oak. Wood Fiber Sci 23:316–327

Otjen L, Blanchette R, Effland M (1987) Assessment of 30 white rot basidiomycetes for selective lignin degradation. Holzforschung 41:343–349

Petit-Conil M, Semar S, Niku-Paavola M-L, Sigoillot JC, Asther M, Anke H (2002) Potential of laccases in softwood-hardwood high-yield pulping and bleaching. Prog Biotechnol 21:61–71

Reid ID, Bourbolnnais R, Paice MG (2010) Biopulping and biobleaching. In: Heitner C, Dimmel DR, Schmidt JA (eds) Lignin and lignans: advances in chemistry. CRC Press, Boca Raton, pp 521–554

Sabharwal HS, Akhtar M, Blanchette RA (1994) Biomechanical pulping of kenaf. Tappi J 77(12):105–112

Sabharwal HS, Akhtar M, Blanchette RA (1995) Refiner mechanical and biomechanical pulping of jute. Holzforschung 49:537–544

Sachs IB, Leatham GF, Myers GC (1989) Biomechanical pulping of aspen chips by *Phanerochaete chrysosporium*: fungal growth pattern and effects on wood cell walls. Wood Fiber Sci 21:331–342

Sachs IB, Leatham GF, Myers GC (1990) Distinguishing characteristics of biomechanical pulp. Tappi J 73(9):249–254

Sachs IB, Blanchette RA, Cease KR (1991) Effect of wood particle size on fungal growth in a model biomechanical pulping process. Wood Fiber Sci 23:363–375

Schwanninger M, Hinterstoisser B, Gradinger C, Messner K, Fackler K (2004) Examination of spruce wood degradation by *Ceriporiopsis subvermispora* using near and mid infrared spectroscopy. J Near Infrared Spectros 12:397–409

Scott GM, Akhtar M, Lentz MJ (1997) Engineering, scale-up, and economic aspects of fungal pretreatment of wood chips. In: Young RA, Akhtar M (eds) Environmentally friendly technologies for the pulp and paper industry. Wiley, New York, pp 341–383

Setliff EC, Marton R, Granzow SG (1990) Biomechanical pulping with white-rot fungi. Tappi J 73(8):141–147

Springer AM (1986) Industrial environmental control. Pulp and paper industry. Wiley-Interscience, New York

Sykes M (1993) Bleaching and brightness stability of aspen biomechanical pulps. Tappi J 76(11):121–126

Sykes M (1994) Environmental compatibility of effluents of aspen biomechanical pulps. Tappi J 77(1):160–166

Vaheri M, Salama N, Ruohoniemi K (1991) Procedure for the production of pulp. European Patent Application EP429422, 29 May 1991

Wall MB, Cameron DC, Lightfoot EN (1993) Biopulping process design and kinetics. Biotechnol Adv 11:645–662

Wall MB, Brecker J, Noel Y et al (1994) Cartapip 97® treatment of wood chips to improve chemical pulping efficiency. In: Proceedings of the Tappi biological sciences symposium, Madison, pp 67

Wall MB, Stafford G, Noel Y (1996) Treatment with *Ophiostoma piliferum* improves chemical pulping efficiency. In: Srebotnik E, Messner K (eds) Biotechnology in the pulp and paper industry. Recent advances in applied and fundamental research. Facultas-Universitatsverlag, Vienna, pp 205–210

Wegner TH, Myers GC, Leatham GF (1991) Biological treatments as an alternative to chemical pretreatment in high-yield wood pulping. Tappi J 74(3):189–193

Welander T (1988) An anaerobic process for treatment of CTMP effluent. Wat Sci Technol 20:143–147

Widsten P, Kandelba A (2008) Laccase applications in the forest products industry: a review. Enzyme Microb Technol 42:293–307

Wolfaardt JF, Bosman JL, Jacobs A (1996) Bio-kraft pulping of softwood. In: Srebotnik E, Messner K (eds) Biotechnology in the pulp and paper industry. Recent advances in applied and fundamental research. Facultas-Universitatsverlag, Vienna, pp 211–216