

## **New Technology in Pulping and Bleaching**

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### **Introduction**

Innovation in advancing technologies for production of pulp and paper has been driven, by and large, by the needs to reduce the environmental impact of pulp mills or to enhance the yield in processes of conversion of wood to fibers. "Fiberization" of wood chips is carried out in two categories of processes. One, chemical pulping relies on removing the lignin that binds the cellulose fibers together by chemical delignification processes. The other is based on mechanical fiberization of the wood while retaining much of the lignin. The resulting pulps have significantly different properties. The chemical pulps are used in the manufacture of paper or packaging materials that require the fibers to have excellent mechanical properties or to have high brightness for the manufacture of fine papers. The mechanical pulps are used as fillers or in the manufacture of papers that do not require fibers of high strength. Some chemical pulps are also used as a source of high-purity cellulose for the manufacture of cellulose derivatives or for the production of regenerated cellulose fibers. We will touch upon some advances in both arenas.

Much of the chemical pulping industry is focused on use of the kraft pulping process, and efforts to make the process more efficient continue; both pulping and bleaching operations have been modified and improved.

Pulping and bleaching processes are subjects of separate articles (*see* Pulping: Bleaching of Pulp; Chemical Pulping; Mechanical Pulping). Since both involve delignification of wood fibers, there is some continuity in the processes and the boundary between them can occur at different levels of delignification, depending on the conditions and operational choices at each mill. It is well to consider the operational differences between them however.

The pulping process begins with wood chips and delignifies them to a point where the individual fibers that make up the chips are free to separate from each other. Pulping operations are intended to fiberize the wood by removing much of the lignin. If the pulp is to be used for the manufacture of container board, it can be used at the point where the lignin content has been reduced to between 8% and 10%. The kraft process (*see* Pulping: Chemical Pulping) is based on using a mix of NaOH and NaSH in the white liquor to digest the wood in an alkaline anaerobic environment. The lignin and polysaccharide degradation products solubilized in the process are then burned, after concentration of the black liquor, to recover both the energy content and the inorganic components. The inorganics are then causticized again and recycled into the digesters.

When the pulp is to be used to manufacture white papers, it is necessary to continue the delignification until the pulp has less than 1% lignin. At that point it is subjected to a bleaching process, often thought of as brightening, that removes the remaining lignin and oxidizes residual color bodies so they can be solubilized during extraction to give a white pulp of high brightness. These processes are usually based on creating an oxidizing environment that can both delignify and bleach. The transition from pulping in an anaerobic alkaline environment to bleaching in an oxidizing environment can occur at different levels of lignin content. It can be as high as 10% lignin, where the early oxidative delignification step is thought of as an extension of the pulping or a pretreatment prior to bleaching. But it can also be as low as 3% when the extended cooking of the pulp under anaerobic alkaline conditions is used to achieve the maximum delignification prior to the entry into the oxidizing environment.

The innovations to be described in this article are in processes at different points in the delignification. Some are intended to improve the efficiency and selectivity of the alkaline anaerobic pulping environ-

ment while also reducing the need to use sulfur or eliminating it entirely. Others are based on the application of oxidative environments in manners that require little or no chlorine-based bleaching agents or create a more selective environment. Selectivity is defined as the removal of lignin and its degradation byproducts, with minimal damage to cellulose and other cell wall polysaccharides.

Some important advances in the technology of mechanical pulping will also be described, as will be some innovations with respect to preparation of fibers and pretreatments applied prior to transfer to the paper machine.

## Chemical Pulping

### Kraft Process

As noted earlier, the kraft process is the most common chemical pulping process (*see* Pulping: Chemical Pulping). The chipped wood is introduced into an anaerobic alkaline environment under conditions that result in maximizing the solubilization and removal of lignin, while minimizing the degradation or removal of cell wall polysaccharides, principally cellulose. The pulping process is usually stopped at a lignin content of 4–5% because further treatment under these conditions results in unacceptable losses in cellulose or degradation of the mechanical properties of the fibers. In recent years, however, ways have been found to extend the kraft pulping process to somewhat lower lignin contents without extensive reduction in pulp strength. For continuous digesters, the system is called modified continuous cooking (MCC); for batch digesters, one version of the system is called rapid displacement heating (RDH). In these systems the alkali concentration in the digester is manipulated so as to reduce the damage to the cellulose and hemicelluloses during pulping. The guiding principle in these systems is creation of a countercurrent flow of the pulping chemicals and wood chips. Their aim is to keep the concentration of alkali lower and more uniform throughout the cooking process and also to minimize the concentration of dissolved lignin at the end of the cook. A major problem with these systems is that pulp yield can be substantially reduced. This is in contrast to oxidative delignification, where delignification to the same lignin content results in significantly higher pulp yields. The use of MCC or RDH to reduce the lignin content results in reduction of the organics in the effluent stream as much of the lignin removed in the later delignification is sent to the recovery boiler. This of course is also true of the oxidative delignification processes. Both MCC and RDH systems are

employed in many mills. Others rely on oxidative delignification using either oxygen or ozone to carry out the delignification from about 5% to less than 1% before transfer to the bleach plant.

### Other Alkaline Pulping Processes

While it can no longer be regarded as a recent innovation, the use of anthraquinone (AQ) as a pulping catalyst has been developed further in recent years. It is usually used to enhance the effectiveness of kraft pulping; in some instances it has also been used with soda pulping, that is, without sulfur.

Recently, it has been shown that octahydro-dimethyl-anthraquinone (ODiMAQ) is a much more effective delignification catalyst than is AQ. It is thought that ODiMAQ can be produced for about the same cost per unit weight as AQ. It is anticipated that soda-ODiMAQ cooking will be more attractive economically than soda-AQ. If oxidative delignification is introduced early in the delignification process, at the level of 8–10% lignin content, it may well be that the soda-ODiMAQ treatment is more effective than soda-AQ. If followed by oxidative delignification, it may become an option for sulfur-free pulping.

### Polyoxometalates in Pulping

Over the past decade a new oxidative delignification system has been developed. Although it has been developed primarily in the context of bleaching, it is likely to be useful in early delignification. Here it would be a replacement for MCC, RDH, oxygen, or ozone delignification. It is based on the use of polyoxometalates (POMs) as regenerable selective oxidants.

The POMs are designed to mimic the action of oxidative enzyme systems that can oxidize and solubilize lignin without damaging the cellulose. They are inorganic cluster anions that are similar to the structures of many minerals. Certain of these POMs in aqueous solution are very selective in oxidizing the lignin of kraft pulp under conditions that result in little damage to the cellulose and hemicelluloses. To minimize damage to the pulp, the delignification must be carried out under anaerobic conditions. After reaction with the pulp, the solution can be filtered off and regenerated. Some of the POMs that are very effective in delignification can also be readily regenerated with oxygen under relatively mild conditions. During the regeneration, these same POMs act as oxidation catalysts for the wet oxidation of the solubilized lignin and carbohydrate fragments to carbon dioxide and water. The reduced POMs are readily washed from the pulp and can be recovered for regeneration with very little

loss. Thus, the overall POM delignification process is a two-stage process that selectively delignifies pulp in water using oxygen as the only consumable in the regeneration process; there are no liquid waste or toxic byproduct streams. Of the POMs studied to date,  $\text{Na}_6[\text{SiV}_2\text{W}_{10}\text{O}_{40}]$  best fulfills the requirements of both the delignification stage and the regeneration and wet-oxidation stage. In multicyclic experiments, it has been found to be thermodynamically stable in both stages. Other POMs are currently being synthesized and evaluated for their effectiveness.

In studies of high-lignin pulps, it has been shown that significant increases in yield can be achieved by stopping kraft or soda-AQ cooks at relatively high lignin content (8–10%) and delignifying the pulps further to bleachable levels with aqueous solutions of a POM. POM delignified kraft pulp was found to give higher yield and stronger pulp than did POM-delignified soda-AQ pulp. It was thought that a higher level of AQ than that used (0.20%) might yield results equivalent to those of kraft pulp.

In a recent study, lodgepole pine chips were cooked to a lignin content near 9% with soda-ODiMAQ and then further delignified to a lignin content of about 4% with aqueous solutions of POM. The yield and strength results from these pulps were then compared with previous results from kraft and soda-AQ cooking of the same wood followed by delignification to the same lignin levels with the same POM. Favorable comparisons were also made with pulps produced from the same chips and delignified to about 4% lignin content by single-stage kraft, soda-AQ, and soda-ODiMAQ methods.

Although a considerable amount of work has been done on suppressing the odor emitted from the kraft process, the problem still persists. At some future date, the public is likely to demand that the kraft process be abandoned. Then the soda-ODiMAQ pulping followed by the POM delignification system is a feasible alternative. The pulp yield is significantly higher than that of the kraft process and the pulp strength, although somewhat less than that of kraft pulp, is more than adequate. Soda-AQ followed by POM delignification may also be feasible, although since AQ and ODiMAQ are equivalent in cost, based on overall yield data available at present, soda-ODiMAQ may be preferred.

### Bleaching Chemical Pulps

The increased emphasis on reducing the environmental impact of pulp bleaching has led to exploration of the use of enzyme systems. In an effort to achieve this goal, research has increased toward enzymatic treatments. There are two fundamental

approaches: the first is to enhance the removal of lignin by traditional bleaching chemicals. The application of xylanases in commercial systems is indicative of the promise of this approach. The second approach has been to use enzymes that act directly on lignin. The work here has focused largely on manganese peroxidase- and laccase-mediator systems. There are currently economic limitations to their commercial implementation. Additionally, POMs are being developed as inorganic analogs to enzymes in the direct oxidation of lignin.

### Polyoxometalates in Bleaching

It has been shown that POMs can be used to delignify even high-lignin pulps to very low-lignin contents without excessive damage to the pulp. Only a single brightening stage would be required to attain high brightness after POM delignification. Based on present knowledge, it seems that the POM bleaching process is well adapted to facilitate the TCF kraft mill and bleach plant. Only effluent from the final brightening stage would go to the kraft recovery cycle. The POM delignification and regeneration/wet-oxidation cycle would be self-contained and would not contribute effluent to the kraft recovery cycle. This would either increase pulp mill capacity or reduce the size of the required kraft recovery furnace. POM bleaching is a novel technology that may revolutionize the bleaching of chemical pulps.

### Xylanase Treatment

The application of xylanases to fibers between chemical pulping and the bleaching sequence is being rapidly implemented in mills worldwide. This has occurred for many reasons. Xylanase treatments can be implemented successfully with softwood, hardwood, and other lignocellulosic pulps. Reduced chemical loads are required for the bleaching sequence; if chlorine or chlorine dioxide is used, effluent properties, such as aromatic organic halides (AOX), chemical oxygen demand (COD), and color are reduced. Higher-brightness ceilings can be reached. Implementation of xylanase treatment into current industrial bleaching sequences can be done without extensive capital costs.

In general, the xylanase treatment is placed after the pulping and oxygen delignification steps and prior to chlorine, chlorine dioxide, and hydrogen peroxide steps; mills have implemented xylanase before or after ozone bleaching stages. In general, the higher the lignin content is prior to the xylanase application, the greater the reduction on subsequent chemical consumption or brightness gain. If hydrogen peroxide will follow, the xylanase treatment can be combined

with chelation. Although the optimum reaction conditions vary with different xylanases, the pH generally lies between 4 and 9, with the temperature between 40 and 80°C. The xylanase is generally applied as a concentrated liquid at a rate near 100 ml per ton of pulp; too much can cause yield losses. Recent work has also found that mixtures of xylanases can have an improved effect. Most of the problems encountered with the xylanase treatment in mills have been due to poor mixing, reactor channeling, or poor pH and temperature control.

There are several proposals for the mechanism of xylanase efficacy. Xylanase may remove from the pulping process the reprecipitated xylans that have covered the lignin and limited access of subsequent bleaching chemicals. Or the removal of residual xylan in the cell walls may allow entrapped lignin to diffuse more easily out of the pulp fiber. Additionally, xylanases may play a role in altering lignin-carbohydrate bonding or in removing hexyneuronic acid groups.

### Oxidative Enzyme Treatments

The extracellular ligninolytic enzymes of white-rot fungi have been the focus of significant development efforts over the past several years. These include lignin peroxidases (LiP), manganese peroxidases (MnP), and laccase, which can be used to replace chemical bleaching stages. While these enzymatic treatments do not usually brighten pulp (the pulp, in fact, often becomes darker after treatment) they do increase the effectiveness of subsequent brightening stages.

Manganese peroxidases are used in conjunction with hydrogen peroxide and manganese. Some pulps do not require additional manganese as they either already contain a sufficient amount of accessible manganese or chelators can be added to liberate sufficient amounts for full activity. Manganese and lignin peroxidases need a hydrogen peroxide source to be effective. Problematically, however, too high a level of hydrogen peroxide can inactivate these peroxidases, so glucose oxidase systems have been studied recently in order to generate low levels of hydrogen peroxide continuously. While these enzymes have become more available, an economical source for industrial application in pulp and paper has yet to be found.

Laccases work with oxygen and a mediator, a low-molecular-weight compound. These laccase-mediator systems (LMS) can achieve 40–60% delignification of kraft pulps. Researchers have commonly used 2,2'-azinobis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS), 1-hydroxybenzotriazole (1-HBT), and violuric acid (VA) as mediators, but

they are very expensive and may deactivate the laccase over time. Other mediators, such as extractives from wood and transition-metal complexes, are currently being studied. Furthermore, different laccases react differently with mediators and multistage laccase treatments, each with different mediators, will remove more lignin.

Laccases have also been used for reducing the energy of mechanical pulping. Peroxidases and laccases have also been used to polymerize and copolymerize materials with lignocellulosic fibers.

### Mechanical Pulping

Mechanical pulping includes all processes that fiberize the wood chips with little or no application of chemicals. Not surprisingly, they require a considerable amount of energy, and they generally result in damage to the fibers. Thus two important goals are sought in advancing this technology. The first is to reduce the energy consumption in the mechanical refining. The second is to reduce the damage to the fibers. Recent developments have resulted in advances in both areas.

### Biopulping

Biopulping is a process developed to improve the quality of mechanical pulps and significantly reduce the electrical energy required to pulp wood chips. High-yield mechanical pulps use wood resources efficiently, but consume considerable electrical energy during refining. The resulting pulp is considerably weaker than pulps produced by chemical pulping methods.

When wood chips are pretreated with an inoculum of fungi prior to relining, the wood chips become softened and more porous. Consequently, these treated chips are more easily broken apart when they are refined. The primary advantage of biopulping is the substantial savings in refining energy - as much as 30% depending on the wood species.

The biopulping procedure involves decontaminating wood chips with steam to eliminate competitive naturally occurring bacteria and fungi. Next they are sprayed with a dilute inoculum of a select fungus. Inoculated chips are incubated in an aerated chip pile for 2 weeks. Under warm, moist conditions the lignin-degrading fungi colonize chip surfaces and penetrate chip interiors with a network of hyphae. These treated chips are more readily broken apart during subsequent refining, saving as much as 30% of the electrical energy while producing more flexible, intact fibers compared to refining untreated chips. Various white-rot fungi have been used for biopulping; however,

*Ceriporiopsis subvermispota* has proven to be very competitive both on softwoods and hardwoods and is one of the best energy conservers. Because this fungus consumes some of the pitch contained in the wood chips, both the toxicity and biological oxygen demand (BOD) content of mill process water are decreased and these pulps are more responsive to oxidative and reductive bleaching chemicals.

Because biopulping produces a superior mechanical pulp, it can be considered a viable alternative to chemical pulping and is a less costly alternative for constructing new mills because it requires simpler equipment and produces an effluent with reduced BOD. No additional equipment is required for biopulping in mechanical pulping mills. However, equipment for asepsis and inoculation, such as a conveyor system, steam, and inocula delivery, is needed.

Paper made from pretreated wood chips is stronger than paper made from conventional mechanical pulp and displays better optical properties, except brightness. Biopulping has been demonstrated successfully in mill trials in the USA and currently is being extensively trialed in a South American mill.

### RTS

Thermal mechanical pulp (TMP) is the most common way to produce mechanical pulp. Wood chips are presteamed and passed through a pressurized refiner at high consistency. While this conventional process produces an acceptable mechanical pulp, considerable energy is required and pulp brightness is decreased. Recently a new refining process has been perfected. It has been termed RTS; it shortens the retention time, lowers the temperature of chip pretreatment, which is followed by rapid speed refining through specially configured refiner plates. Use of this process significantly reduces the energy requirement and improves the brightness and quality of the resulting pulp. Savings are realized primarily from decreased energy consumption, but the decreased bleach requirement and higher-quality pulp also contribute to the desirability of this process.

### Fiber Modification

In addition to the various innovations in fiberization of wood chips into pulps, a number of advances in the technology of fiber preparation have been reported. A few of these are included here. The first is related to enhancing the opacity of fibers through deposition of pigment particles within the papermaking fibers prior to formation on the paper machine. Two others are related to enhancing the recyclability of pulp fibers.

### Fiber Loading

Fiber loading is a process for incorporating calcium carbonate made *in situ* and deposited within the lumen and cell walls of refined wood fibers during papermaking. This process requires two steps. First calcium hydroxide (hydrated lime) is mixed into moist pulp at high consistency. This alkaline mixture is then reacted with carbon dioxide within a pressurized refiner at ambient temperature. Calcium carbonate precipitates inside and on the surfaces of pulp fibers, where it is held tenaciously during subsequent papermaking.

Calcium carbonate is an important component of printing and writing papers. Papermaker's carbonate contributes opacity, smoothness, and brightness to high-quality paper; this filler also replaces some of the costly bleached kraft fiber.

Large paper mills often install a satellite plant on site to manufacture precipitated calcium carbonate (PCC) for their use. In conventional papermaking, a suspension of PCC is added to the pulp slurry prior to entering the headbox of the paper machine. Calcium carbonate added in this manner is located primarily between pulp fibers when made into paper. Fillers, such as PCC, interfere with fiber bonding essential to paper strength. Therefore, there is a limit to how much filler can be added without compromising the strength of paper.

In contrast, pulp fiber loaded with calcium carbonate has several distinct advantages over the conventional method of direct addition of PCC. Because a portion of the calcium carbonate formed during fiber loading is located within pulp fibers, more filler can be incorporated than by direct addition of PCC without losing paper strength. More filler incorporated within a paper furnish also reduces the amount of energy required to dry the paper.

Fiber loading has been demonstrated on mill scale. The only additional equipment required for manufacture is a pressurized chamber for introducing and reacting the carbon dioxide. Because the starting materials, hydrated lime and carbon dioxide, are inexpensive, this method of calcium carbonate production is cost-effective. Fiber loading can be used in small mills where a satellite PCC plant is not economically feasible.

All types of wood fibers can be fiber-loaded; this includes recycled fiber. Another benefit of paper made from fiber-loaded pulp is that the carbonate filler is better retained with the fiber during recycling than conventionally made paper. Disposal of sludge accumulated from paper fillers removed during recycling has become a major disadvantage of recycling mills. Fiber-loaded paper can minimize sludge production.

### Enzymatic Deinking

Xerographic and laser-printed papers need to have the inks removed prior to recycling, but they are difficult to deink using conventional methods. This has resulted in a lower recycling rate for these types of papers at a time when they are being produced at growing rates. Cellulases have been shown to remove these toners and other contaminants from waste-paper pulps. In treatments, they are combined with nonionic surfactants, such as polyethylene oxide, and mechanical action. Cellulases likely improve deinking through several complementary mechanisms. They remove fibrils from the fiber surfaces and facilitate the removal of toner particles. Cellulases also separate fibrils from toner particles, which reduces toner particle size and makes them more hydrophobic for easier removal during the flotation and washing stages that follow. Researchers have recently improved cellulase action by linking surfactants directly on to the enzyme's amino acid groups.

Cellulases have also been shown to increase the freeness and flexibility and reduce the coarseness of dried fibers. They can also improve sheet density and smoothness. Cellulase treatments of recycled fibers may also reduce disintegration time and increase the bleachability of low-quality, recycled paper. However, excessive treatment can erode the fiber surface and ultimately reduce pulp strength.

Cellulase enzymes are commercially available and are used increasingly in the paper-recycling industry.

### Pressure-Sensitive Adhesive Modification

The use of pressure sensitive adhesives (PSAs) has increased dramatically in the last decade. Prompted, in part, by consumer demand, adhesives were formulated to be more user-friendly - at least in their application. The problem caused by many of the PSAs did not surface until they entered the recycled-paper stream. Usually attached to envelopes in the form of self-sealing envelopes, postal stamps, and address labels, the PSAs became commingled with high-quality printing and writing papers. When subjected to high repulping temperature, alkaline pH, and vigorous agitation, many adhesives become plasticized, fragmented, or dispersed, enabling them to pass through pressure screens intended to retain and separate them and other macrocontaminants from recycling furnishes.

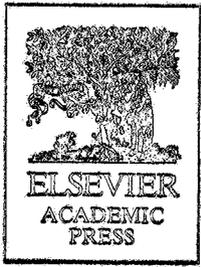
Because the US Postal Service (USPS) is a major user of PSAs in the form of stamps, labels, and postal stationery, it introduced and funded a research initiative to assure that the PSAs used in USPS products were recyclable. A consortium comprising adhesive manufacturers, printers, and recyclers was

formed. A 5-year research program was undertaken to examine the recyclability of numerous PSA formulations. The essential characteristics of PSAs that made them removable under typical recycling conditions were identified. New guidelines for new PSA formulations were developed for adhesive manufacturers. Acceptable PSAs remain intact, thus were removed primarily by pressure screening, under typical warm, alkaline conditions used in recycling. Adhesives that were successfully removed during processing in pilot plant trials by pressure screening, cleaning, and flotation were subsequently confirmed in recycling mill trials. This research resulted in recyclable PSAs for the USPS products. The guidelines are likely to be adopted by other manufacturers of paper likely to be recycled.

See also: **Papermaking:** World Paper Industry Overview. **Pulping:** Bleaching of Pulp; Chemical Pulping; Environmental Control; Mechanical Pulping.

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