

Innovative Approaches in Bleaching of Lignocelluloses- A Review

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ABSTRACT

Improved ClO₂ pulp bleaching, oxygen bleaching, hydrogen peroxide bleaching, ozone bleaching, peracid bleaching, dimethyldioxirane and activated oxygen bleaching, catalytic oxidative yield bleaching Biobleaching, bleaching of high yield pulp, photochemical bleaching, electrochemical bleaching and some other minor bleaching methods are reviewed in this paper.

INTRODUCTION

Methods

Both environmental legislation and market pressure have forced the pulp and paper industry to make efforts towards reduction and/or elimination of chlorinated organic compounds in bleaching effluents. Many countries have enacted legislation to limit the levels of specific compounds in bleach plant effluents. They govern the levels of adsorbable organic halide (AOX), biochemical oxygen demand (BOD), total suspended solids (TSS), chemical oxygen demand (COD) and colour (1, 2).

Elemental chlorine free (ECF) process, in which elemental chlorine is substituted by chlorine dioxide in bleaching process, and the total chlorine free (TCF) process in which bleaching is carried out essentially by using oxygen compounds were introduced into pulp and paper industry to satisfy governments and public demands. The capital investment needed to retrofit and existing mill for TCF production is high and may not achieve any significant additional environmental benefit than ECF process. Numerous studies showed that the discharges are fairly similar in ECF and TCF. Toxicity measurements and biotests neither indicated any marked differences between ECF and TCF mill effluents. Today the ECF bleaching concept is preferred by most mills due to lower capital costs compared with the TCF concept, although the later provides nearly zero AOX in the effluent (3,4)

Improved ClO₂ pulp bleaching

The goal of safeguarding the environment from the

toxic effect of chlorinated organics and other chemical discharges forced industry to develop the bleaching process. ECF grades of bleached pulp now could be successfully produced by using chlorine dioxide (ClO₂) bleaching (5-8). ClO₂ bleaching produces good pulp accompanied by an improvement in effluent quality (9). Kinetics of chlorine dioxide delignification [10] and fundamental parameters contributing to improved ClO₂ pulp bleaching has been investigated [11]. The relationship between specific bleach plant parameters and chloroform generation during ClO₂ bleaching of pulp (12), and the impact of methanol-based by-products in chlorine dioxide solution on pulp bleaching (13) were studied. The principal source of the adsorbable organic halides (AOX) that is formed during ClO₂ bleaching is hypochlorous acid (14). The control of pH profile minimizes the AOX level (15), and improves bleaching efficiency of chlorine dioxide delignification (16). Modification of the first ClO₂ stage in a modern OD>(EPO)<DD sequence for bleaching softwood kraft pulp reduced AOX and biological effects (17). High temperature 95°C ClO₂ delignification is shown to be more efficient than conventional D stage (18).

There is a substantial decrease in chlorine dioxide required to achieve target brightness when using oxygen delignification prior to ClO₂ bleaching (19). Addition of hydrogen peroxide to a ClO₂ stage reduces the organochlorine formation (20). Combination (21) and changing the order (22) of the hydrogen peroxide (P) and chlorine dioxide (D) stages in an ECF improves the bleaching process.

In kraft pulping xylan chains in hemicelluloses are degraded, and hexenuronic acid groups are formed during pulping. Hexenuronic acid groups react with

bleach chemicals such as chlorine dioxide and ozone. These reactions increase the consumption of bleaching chemicals and decrease the final brightness. With an acid treatment, the hexenuronic acid groups can be selectively removed before bleaching. As a result of using acid treatment also improves the brightness stability of bleached kraft pulps (23).

Oxygen bleaching

The discharge of bleach plant pollutant and the operating cost of bleaching are reduced by use of an oxygen delignification system. The technology is compatible with new developments aimed at reducing the discharge of bleach plant effluent (24).

The effluent load from an ECF bleaching sequence depends on the kappa number of the pulp going to bleach plant (25), an effective oxygen delignification stage will be obvious solution to reduce the demand for bleaching chemicals and the effluent load. In conventional oxygen delignification it is possible to reach about 50% delignification with retained pulp quality (26). A 70% delignification could be attained by combination of longer retention time, pretreatment with chelating agents peroxide reinforcement or by multi-stage performance of the oxygen delignification (27). Oxygen delignification and bleaching are integral parts of the closed mill concept; total closure can be achieved with high yield, high kappa pulping and extended oxygen delignification (28). AOX loadings in biologically treated effluents were lower at mills with extended and/or oxygen delignification than at mills that use conventional delignification (29).

Oxygen delignification following pretreatment with nitrogen dioxide, permits removal of more than 85% of the lignin from kraft pulp without severe attack to the carbohydrates. The nitrogen dioxide treatment (0.5%) between two oxygen stages followed by formamidine sulfinic acid (FAS) and hydrogen peroxide, produces TCF fully bleached pulps (30). Oxygen delignification could be improved with interstage peroxy monosulfuric acid treatment (31, 32), or by treatment with chelating agents, and pressurized peroxide stages (33).

Kraft pulp from softwood, freed from catalytically active transition metals and alkaline earth metals by soaking with SO_2 water and alkaline and EDTA, was oxygen bleached in the presence of different alkali (34). The use of oxidized white liquor as an alkali source in O, EO, EOP, and E_2 bleaching sequences can serve to maintain a kraft mill's chemical balance [35].

Hydrogen peroxide bleaching

Hydrogen peroxide is a mild oxidant, which has been

applied, increasingly in recent years to reduce the use of chlorine chemical in pulp bleaching. Its highest efficiency in bleaching and delignification is observed when the reaction is conducted in alkaline medium. The primary alkali source is usually sodium hydroxide, but in a conventional bleaching system, some alkali is also furnished by sodium silicate, which is used primarily as a peroxide stabilizer and performs as an alkaline buffer (36). It functions as a replacement for hypochlorite, either partially or totally peroxide can be used as a single stage for ASAM bagasse pulp bleaching (37).

Many investigators have reported that if oxygen and/or chlorine dioxide and alkali H_2O_2 were combined in bleaching better pulps with a scope to reduce the pollution load is obtained (38, 39). Hydrogen peroxide continues to reduce demands for chlorine dioxide in ECF bleaching. Today, hydrogen peroxide is used in virtually all ECF (40) and TCF (41) bleaching sequences. Ozone or chlorine dioxide bleaching prior to hydrogen peroxide bleaching greatly improves the performance of the hydrogen peroxide stage (41). TCF bleaching of kraft pulp to high brightness value could be attained with hydrogen peroxide and peracetic acid (42). On-site-produced alkaline peroxide for pulp bleaching is a lower-cost peroxide source that can result in significant saving in bleaching cost (43).

It was confirmed that perhydroxyl anion is the primary bleaching moiety in alkaline hydrogen peroxide systems. The rate of bleaching on cotton fabric was shown to be a first order reaction in concentration of perhydroxyl anion. Activation energy of 17 kcal/mole was estimated (44). Formation and involvement of superoxide ($\text{O}_2^-/\text{HO}_2^-$) and hydroxyl radical in TCF bleaching processes has been reviewed (45).

Temperature control is vital to maximization of the peroxide bleaching process (46). Hot peroxide bleaching (46, 47) and pressurized H_2O_2 bleaching provides a Kraft of benefits for pulp bleaching (48). Sodium carbonate solutions were used as the alkali source to increase hydrogen peroxide stability in bleaching (49).

It is well known that use of additives as sodium silicate, magnesium sulphate and chelating agents play important roles in the peroxide bleaching of kraft pulps (50), the most commonly accepted of which is the stabilization of hydrogen peroxide solutions. Magnesium improves the selectivity of oxygen delignification and reduces fibre damage by binding the radicals in oxidative treatment. It also prevents breakage of the carbohydrate chains catalyzed

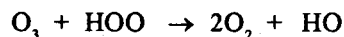
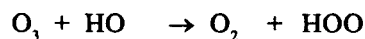
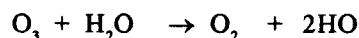
by the metal ions. The effect of magnesium ions is based on the fact that they react in suspension to form magnesium hydroxide. This absorbs the metal ions, making them unable to decompose peroxides. An increase in magnesium therefore helps maintain pulp viscosity. Catalysis and activation of oxygen and peroxide delignification of chemical pulps has been reviewed (51). A combination of zeolites and sodium citrate is an effective alternative to DTPA addition in alkaline peroxide bleaching (52). Cyanamide (H_2NCN) addition on hydrogen peroxide significantly increases the oxidation rate of lignin model compounds (53).

Transition metal ions, especially manganese induces peroxide decomposition under alkaline conditions, so transition metal removal is recommended (54). Unlike Mn (III), Mn (II) is not catalytically active towards peroxide decomposition. Peroxide bleaching performance could be improved by reducing the manganese in the pulp fibres from its high oxidation state and then stabilizing the reduced manganese with additives such as DTPA (55).

Ozone bleaching

Increasing attention is being focused on the use of oxygen-based agents. These chemicals produced no chlorinated organic materials in the bleaching effluent; the effluent is also free from corrosive compounds and can be completely recycled to the mill chemical recovery system. Although it is mainly the lignin component, which responds to bleaching the other constituents of pulp, as cellulose and hemicellulose are also affected to a certain extent, which may cause an unacceptable decline in strength properties. This is especially true when ozone is used as bleaching agent (56). Ozone is a strong electrophile that attacks many lignin structures and now is being used commercially as a partial replacement for the chlorine containing compounds. The drawback of the oxidant bleaching is cellulose degradation if large amount of oxidants are consumed by the pulp. Hydroxyl radicals generated by the lignin-ozone reactions are mainly responsible for the degradation of cellulose (57). Carbohydrates degradation must be suppressed by application of appropriate parameters. This is possible by pre-acidification of the pulp, low temperature bleaching, slow addition of ozone to the pulp and proper mixing. By application of these conditions 0.1% o.d. pulp is required to reduce the pulp kappa number by one unit (58). In water, ozone undergoes a decomposition catalyzed by hydroxyl ions forming hydroxyl perhydroxyl radicals as intermediates and

oxygen as the final product.



Hydroxyl radicals are dominating and they react in a very unspecific way. The formed $HOO\cdot$ radicals have only a limited oxidation power and do not take part in cellulose degradation processes. The cleavage of β -O-4 bonds between the lignin phenol propane units renders lignin soluble. Ozone splitting off β -O-4 bonds either from the aryl or the alkyl side. Double bonds in the aliphatic side chain are also attacked forming carbonyl and peroxide structures. Beside lignin, cellulose is degraded by ozone attacking the acetalic oxygen atom or the C-H linkage of the anomeric C_2 -atom, cleavage of the glucosidic linkages takes place (58). Ozonation studies of pulp with varying contents of lignin show that lignin protects, at least partly cellulose from being attacked by ozone (59) Without a cellulose protector, a maximum ozone charge of only 1% can be applied to kraft pulp without serious carbohydrate degradation (57, 60).

The effect of the main variables, consistency, pH, time, temperature, ozone concentration, ozone charge, pretreatment of chemicals and chemical additives on the properties of kraft and kraft-oxygen pulps are reviewed (60, 61). Results on high consistency ozone bleaching show that the optimum pH for an ozone stage is between pH 2 and 3. The best ozone consumption of pulp is between 25% and 46% consistency (61). Another review with 105 references, covered in details the following categories; studies on ozone bleaching according to pulp type, the effect of main reaction variables (effect of pulp consistency, pH, time, and temperature on the ozonation of pulps), studies on carbohydrates-preserving additives and pretreatments, studies of bleaching sequences containing ozone and pilot plant studies (62).

Low-consistency (0.5-3%) bleaching requires ozone gas to be introduced into the pulp suspension and dissolved in the water for reaction. Medium-consistency (5-15%) bleaching requires high-energy mixers, which fluidize the pulp and bring it into intimate contact with the ozone gas. high-consistency (>20%) bleaching is carried out with ozone in gaseous phase, contacting the pulp in a pressurized reactor. Research indicates that High-consistency ozone bleaching is optimized at the pulp consistency of 40-55%, ozone charge 1-2% on pulp and ozone concentration 3-5% in carrier gas (63). In particular, the selectivity of ozone bleaching is not affected by

the consistency applied. Medium consistency ozone bleaching is less efficient than high consistency at a given ozone consumption (64), but the differences are leveled in a subsequent alkaline extraction stage (65). Both oxygen and ozone filtrate loads reduce the efficiency of ozone bleaching. In MC ozone bleaching a six times larger volume of solid loaded water is carried into the ozone reaction than in HC treatment. By lowering the gas/liquid ratio ozone reaction rate in MC ozone bleaching is significantly increased which benefits delignification, but the amount of ozone that can be charged per pulse is considerably reduced (66).

At low consistency ozonation pretreatment with EDTA at 90°C enhanced the rate of delignification dramatically without any adverse effect on cellulose. At high consistency both EDTA pretreatment and addition of oxalic acid improved selectivity mainly because of a lesser degradation of cellulose (67). Treatment with oxalic acid (68) or impregnation of chemical pulps with acidified mixture of 1, 4 dioxane and water (69), improved ozone bleaching due to transition metal ion removal.

Ozone bleaching is being used to produce elemental chlorine free (ECF) (70), and totally chlorine free (TCF) bleached chemical pulps (71). Brightness exceeding 89% ISO was obtained, with lower chemical consumption in TCF bleaching of eucalypt pulp using ozone treatment (71-73). Conventional softwood kraft pulp with a kappa acid bagasse pulp (76) were fully bleached to high brightness based on a TCF ozone bleaching process.

To improve ozone efficiency at reduced charges an electrochemical model was developed (77). A laboratory-scale flow-through reactor that continuously provides accurate, reliable, and rapid on-line measurements of ozone consumption rate during high-consistency bleaching was discussed (78). The structural composition of pulp (79) and reaction medium (80) has an important role on the selectivity of ozone bleaching.

Peracid bleaching

The use of chlorine in bleaching leads to the formation and subsequent discharge of organochlorine compounds. Oxygen and hydrogen peroxide are replacement chemicals that are firmly established in chemical pulp bleaching. However, due to their low reactivity with certain lignin structures, they are unable to completely replace the chlorine containing chemicals. Peracids have recently emerged as a potential alternative to chlorine containing chemicals for bleaching of chemical pulps (81). Peracids are

used as replacement for chlorine or chlorine dioxide in the chlorination stage and for increasing final brightness. In contrast to some nonchlorine technology options for cluster rule compliance, peracids require low investment, are easily retrofit, and can be used to both delignification and bleaching (82). Peracetic acid has high reactive ability with lignin and almost does not react with carbohydrates. It provides an ecological reliability of bleaching technology and at the same time providing high selectivity of pulp delignification and high brightness stability (83). It has been shown that peracetic acid is a good delignifier when used in the prebleaching stages. In addition, peracetic acid can also be applied in the latter brightening stages as a substitute for chlorine dioxide. In order to minimize carbohydrate degradation, the peracid solutions should contain low concentrations of hydrogen peroxide whose decomposition can generate high concentrations of the hydroxyl radical. The halide, preferably chloride is added to the caroate stage (peroxymonosulfate) to accelerate lignin degradation and simultaneously retard cellulose depolymerization (84). Viscosities of pulps treated with peracids in the different stage of bleaching were not adversely affected and strength of pulps was similar to unbleached or conventionally bleached pulp (85). Oxalic acid formed in the pulping and bleaching of chemical pulp can create problematic deposits on bleach-plant equipment, limiting the feasible degree of mill closure. Bleaching with peracetic acid produces less oxalic acid than the other bleaching agents (86).

Peracetic acid could be used in ECF and TCF bleaching (87). Peracetic acid was applied with oxygen and hydrogen peroxide to produce high quality TCF pulp while maintaining pulp viscosity. Good metals management is essential for producing high quality TCF pulps (88). Sequence of four-stage bleaching with the peracetic acid and hydrogen peroxide allowed receiving high brightness (82-86%) for organosolv aspen wood pulp (83). An improved peracetic acid bleaching process is applied to oxygen and ozone delignified softwood kraft pulps as well as a spruce CTM pulp. Initial pH of this method is 7 and final pH is 5-5.5, it leads to higher brightness than normal peracetic acid bleaching process whereas the carbohydrate degradation during the treatment is unaffected (89).

To increase chemical pulp brightness Caro's acid can be used in an alkaline medium as an extraction stage (E) of DEopDED bleaching (90). Caroate delignification is combined with ozone in TCF bleaching process (91). Non-wood fibres are easily bleached to high brightness level with

peroxymonosulphate (92). The most serious drawback of carote delignification is cellulose depolymerization by free radicals in the lower pH range (1.0-2.0). The cellulose can be partially protected of compounds that scavenge the sulphate radical anion as halides (93).

Dimethyldioxirane and activated oxygen bleaching

A class of oxidant, termed dioxiranes, more specifically dimethyldioxirane (DMD), was isolated and characterized as an electrophilic oxidant. DMD, cyclic peroxide, is an intermediate in the decomposition reaction of peroxymonosulphate mixed with acetone, water and sodium bicarbonate (94). The oxygen linkage breaks very easily; so that DMD serves as very powerful oxygen atom (active oxygen) donor regardless of whether in situ generated [95] or isolated DMD is used [96].

Activated oxygen renders the residual lignin soluble in the following caustic extraction stage in a way similar to elemental chlorine/chlorine dioxide. A kappa number reduction of greater than 80% was accomplished by activated oxygen and extraction stages. All pulp strengths and viscosity remained virtually the same as conventionally bleached pulps. Activated oxygen treatment can effectively and selectively delignify softwood kraft pulp to a kappa number less than 3, makes a TCF bleaching to 90% ISO brightness possible (97). Softwood and hardwood kraft pulps were pretreated with xylanase followed by treatment with activated peroxide species such as DMD or nitrilamine reinforced peroxide followed by chlorine dioxide bleaching allowed 2-5% ISO brightness gains (98).

Unbleached and oxygen-delignified softwood kraft pulps were delignified to more than 80% kappa reduction with DMD. The bleached pulps showed the same pulp strengths as those obtained by conventional bleaching methods. The electrophilicity measured for dimethyldioxirane (DMD), methyl (trifluoromethyl), dioxirane (TFD) and diethyldioxirane (DED) follows the descending order, (TFD>DMD >DED). Excellent bleaching selectivities were found for all three dioxiranes tested. DMD demonstrated better effectiveness of delignification than TFD followed in turn by DED. The reduced performance of TFD could be due its thermal decomposition during bleaching (99).

DMD has demonstrated superb selectivity and reactivity in pulp bleaching. It can completely replace chlorine/chlorine dioxide in the chlorination stage, and it bleaches both hardwood and softwood kraft pulp and results in little yield loss (100). DMD can degrade lignin by hydroxylation and oxidative rupture

of the aromatic ring; it reacts with residual lignin via electrophilic oxidation and renders the residual lignin soluble in the following caustic extraction (101). DMD (T) (at 25°C) and chlorine dioxide (D) (at 74°C) provided the same total brightness gain and kappa number reduction after the second oxygen stage in sequences ODO and OTO. As an interstage treatment DMD showed a greater brightness gain per kappa unit reduction than chlorine dioxide (102).

Model compounds with DMD undergo ortho- and para-hydroxylation reactions that are likely to proceed via oxygen insertion into C-H bonds. DMD may also cause the demethylation of a totally etherified phenolic structure creating free phenolic hydroxyl groups, which in turn activate the molecule towards further reactions. It was demonstrated that DMD electrophilically oxidizes the aromatic rings of both etherified and non-etherified softwood lignin model compounds (103). DMD reacts with electron-rich C=C double bonds in aliphatic side chains to form epoxides or aromatic rings to form arene oxides. These epoxides are readily hydrolyzed to diols in aqueous solution; diols undergo a facile ring opening reaction with dioxiranes (100).

DMD is a stereospecific electrophilic oxygen transfer agent that allows epoxidation of unsaturated centers at room temperature. DMD appears to be more reactive towards etherified structures, which is the majority in almost all residual lignins, than other oxidative reagents. DMD is quite stable (half life > 25 h) at room temperature in acetone or acetone-water solution as long as the pH is kept below 4. The decomposition of DMD is first order and is unaffected by the ionic strength of the solution. The decomposition of DMD is accelerated by the presence of transition metal ions but seems to be protected by the presence of Mg^{+2} (104). The guaiacyl phenolic units, present on the lignin, were found to be the major sites of attack for all oxidative treatment. Low charges of DMD may act as activating stage prior to another bleaching stage. Most of the condensed phenolic units present in residual kraft lignin react with the oxidative bleaching reagents (105).

About 90% of colour and 50% of BOD in wastewaters come from bleaching plants. Singlet oxygen, with its specific oxidation properties reacts through quite a different reaction mechanism than the common oxygen. The singlet oxygen can be generated by the reaction of sodium hypochlorite and hydrogen peroxide. Singlet oxygen exhibits higher selective delignification effects, about 5 times more than the normal oxygen delignification, and the AOX value becomes 10-15 times lower (106).

Catalytic Oxidative bleaching

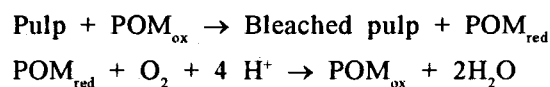
The manufacture of totally chlorine free (ECF) pulps has stimulated interest in multi-stage bleaching with oxygen containing chemicals such as oxygen, ozone, hydrogen peroxide and peroxyacids. A highly selective oxygen-based polyoxometalate bleaching technology compatible with mill closure has been developed (107).

Heteropolyacids or heteropolyanions (HPA) are inorganic compounds composed primarily of the early transition metal cation (mostly W, Mo, and V) and a central heteroatom (Si, P, Ge, etc). HPA are easy to prepare as they are spontaneously formed when water-soluble metal oxoanions and suitable heteroatoms are combined under acidic conditions (108). HPA have many special properties, such as stabilization of the metal ion in aqueous solution, selection, selective degradation of lignin, resistance to oxidative degradation, possibility of reoxidation and so can be employed as a reusable agent in repeated cycles of pulp bleaching. HPA in combination with H₂O₂ efficiently bleach hardwood kraft pulp to low kappa numbers (109).

Eucalyptus kraft pulp was bleached by different TCF sequences using oxygen and ozone stages catalyzed by [Pm₇V₅O₄₀]⁸⁻ heteropolyanions. In the catalyzed oxygen pre-bleaching stage, performed under acidic conditions, the kappa number decrease both due to the lignin oxidation (about 65% contribution) and hexenuronic acids elimination (about 35% contribution). The pulp bleached with catalyzed ozone stages shows a significant improvement of strength properties (compared with unanalyzed bleaching) due to polysaccharides protection towards undesirable oxidative destruction (110). The use of an organic solvent, such as ethanol in the pulping solution favours the oxidative delignification, protecting the lignin against competing reactions (condensation) (111). Heptamolybdopentavanado-phosphate heteropolyanion (Pm₇V₅O₄₀]⁸⁻ (HPA-5) was used as a POM (polyoxometalates) catalyst in kraft pulp oxidative bleaching under acidic conditions. When compared to alkaline oxygen delignification, POM delignification results in an increase in oxidation selectivity and a decrease in the required processing temperature and oxygen pressure (112). A delignification degree of 40% in the PHA/O system may be attained with a viscosity drop of only 5% (113).

The aerobic lignin oxidation in the presence of heptamolybdopentavanadophosphate anion [Pm₇V₅O₄₀]⁸⁻ POM allows to oxidize lignin and regenerate the catalyst (re-oxidize) in the same process stage

(114). POM acts as inorganic regenerable electron transfer catalysts used as oxidative reactants in the absence of oxygen (anaerobic conditions) (115). In the presence of low concentrations (1-3 mmol/l) of POM, a high delignification of hardwood kraft pulp can be achieved in 1.5-2.0 h of treatment. The involving of POM in DEDED process allows decrease in the consumption of ClO₂ on 50-60% to reach 90% brightness without strong decrease in the pulp strength. The extended delignification (higher than 60%) in POM bleaching stage with the minimal polysaccharides damage is possible by using POM species which are stable at pH>2.5 (116). The VO₂⁺ ions produced via the dissociation of HPA in acidic conditions are suggested to have a much stronger catalytic effect on the oxidation of lignin than parent HPA. Kinetic studies show that the catalysis diffusion in the wood tissue is the rate-limiting step of delignification, while the lignin oxidation rate is determined by the HPA/VO₂⁺ catalytic oxidation step (117). In bleaching, fully oxidized POM complexes are reacted with unbleached pulp under anaerobic conditions. During oxidative bleaching the POM complexes are reduced and the bleaching liquor dissolves oxidized residual lignin fragments. Afterwards, the reduced POM liquor is deoxidized by oxygen, thus the POM liquor can be continually reused with mill closure achieved by use of a recovery system (118).



The effects of ammonium triperoxo-phenanthroline vanadate (ATPV) were examined under hydrogen peroxide bleaching conditions. The presence of 0.5% ATPV in the bleach liquor improved the delignification efficiency and pulp brightness. Possible mechanisms for this activation could involve hydroxylation and epoxidation reactions occurring between the peroxide and the residual kraft lignin. At the same kappa number, the viscosity values for an activated and a control pulp were approximately the same (119). A series of porphyrin and phthalocyanine complexes of Co, Fe and Mn have long been studied for their ability to mediate the transfer and hence improve the reactivity and selectivity in the oxygen bleaching of softwood kraft pulp. The Mn (III) complex of meso (tetrasulfonatophenyl) porphyrin is shown to promote delignification and suppress cellulose degradation. The degradation rate of the lignin model compound in the presence of 0.23 mmol catalyst was up to ten times than that in the absence of the catalyst (120).

Biobleaching

Chlorinated phenolic compounds produced during conventional pulp bleaching are toxic and very resistant to biodegradation. It thus seems urgent to reduce or eliminate the use of elemental chlorine in pulp bleaching, and at the same time, develop alternative bleaching techniques, which do not give rise to formation of environmental hazardous compounds. New research efforts have been directed towards developing new biotechnology solutions to reduce environmental effluents impact or to alter pulp properties (121). They can be classified as either microbial, in which growing cells are used (bacteria, yeast, fungi or algae), or enzymatic, in which pre-formed enzymes are employed (122, 123). Microbial and enzymatic processes can be combined. Hemicellulase aided bleaching, the most well established economically feasible techniques in pulp and paper industry, can offer an alternative approach to biological bleaching (124, 125). Several studies using various hemicellulases, xylanases in particular, have been published (126, 129).

The enzymatic treatments based on hemicellulases introduce modifications in carbohydrate structures, leading to enhanced delignification in subsequent chemical bleaching operations. The mechanism is based on the partial depolymerization of hemicelluloses, which impede the chemical removal of residual lignin from pulp fibres, leading to the free flow of bleach chemicals into the fibre (130). The enzyme is proposed to work on other way in which it may cleave lignin-carbohydrate bonds and facilitate lignin removal from pulps, which reduce about one quarter from active chlorine consumption during bleaching (131).

Many reviews in biotechnology illustrate the subjects on pulping and bleaching as production, properties and applications of *Trichoderma* xylanases (132), Applications of xylanases to the bleaching of kraft pulp (133, 134), mechanisms of xylanase aided bleaching of kraft pulp (135, 136), basic and applied research on microbial cellulases, hemicellulases and pectinases (137), production of oxidative enzymes, laccase manganese peroxidase and lignin peroxidase by the fungus to partially delignify kraft pulp (138, 139) and many other interesting subjects in the pulp and paper industry as enzymatic hydrolysis and sugar production, fibrillation, drainage, retting, contaminant removal, enhancement of auto adhesion of fibers and bonding immobilization of enzymes, biodegradability of cellulose derivatives, etc. (139, 144).

In general, treatment of kraft pulp with various

xylanases under mild conditions, i.e., temperatures of 40-50°C, pH values of 4-9 and treatments time less than 10 h, has led to a substantial reduction in bleaching chemical consumption in subsequent bleaching stages. The fully bleached kraft pulps resulting from enzyme treatment, possessed physical strength properties comparable to those in conventionally bleached pulps. Additionally, the AOX levels in the effluents have been substantially reduced. The enzymatic pretreatment method can be applicable to any traditional or modern bleaching sequence in existing plants without significant investments. The objectives of the enzymatic treatment are to decrease chemical consumption to reduce the environmental load and to increase final pulp brightness. Xylanase enzymes are the most effective for the prebleaching of kraft pulp on most acidic bleach treatments, such as those with chlorine, chlorine dioxide and ozone. Reduction in bleach chemical demand to achieve target brightness can range from 10 to 30%. Enzyme aided bleaching is therefore both environmentally safe and economically attractive (142-151).

The enzymatic method can be combined to various types of pulping processes and bleaching sequences (152-158). The addition of a xylanase treatment stage, either before or after the peroxide bleaching stage (s), resulted in the enhanced brightening of all pulps (159). Xylanase treatment before the oxygen delignification bleaching stage in TCF bleaching of eucalyptus kraft pulps enables the production of fully bleached pulps with high brightness (90% ISO) and viscosity (above 800 ml/g). The improvement of bleachability produced by the enzyme reduces the quantity of ozone needed in subsequent bleaching stages (160). A xylanase from *Aspergillus kawachii* active at pH 2.0-2.5, was found to be suitable for improvement of bleachability and can be successfully combined with the acidic metal washing stage, the bleaching result is comparable to that obtained by an EDTA treatment. The use of acid-tolerant xylanase is especially beneficial prior to ozone or chlorine dioxide bleaching stages due to the minimization of pH adjustment steps during bleaching (161). Thermostable xylanase of *Dictyoglomus* sp is well suited for pulp treatment at elevated temperatures in neutral and alkaline conditions (162). Manganese peroxidase has synergistic effects in bleaching of kraft pulps with xylanase (163). Isolated fungus from a bagasse storage pile was able to produce xylanase enzyme without any cellulase activity. The crude enzyme produced enhanced the bleachability of the hardwood and bagasse pulps and did not affect the physical properties of pulps (164).

Pulp bleaching with a laccase mediator system has reached the pilot plant stage (165). Kraft pulp was delignified using laccase produced by the white rot fungus *Trametes versicolor*. This enzyme was stable for 6h at 55°C and pH 8.0, allowing its use under conditions very close to those used in industrial bleaching (166). *Trametes versicolor* and laccase enzymes were assessed for their potential to improve the brightness of Douglas-fir heartwood derived TMP. Although the application of laccase without a mediator decreased the unbleached brightness of pulps, after bleaching with H₂O₂ it was found that the laccase treatment increased the bleached brightness from 58 to 61% ISO (167). Pine Kraft-AQ pulp was biobleached with pressurized dioxygen at 40°C in laccase-mediator system (LMS), i.e. in acetate buffer (pH 4.5) containing *Coriolus*-laccase and 1-hydroxy-benzotriazole (HOBT) as a mediator. The NMR studies indicated that intensive degradation of aromatic ring has occurred in the biobleaching. However, pre-methylation of neither benzyl alcohol nor phenolic hydroxyl groups of the residual lignin in pulp before the biobleaching affected the rate of delignification. The latter indicates that phenolic moieties participate not only in oxidative degradation but also dehydrogenative polymerization reactions in the biobleaching (168). The application of laccase-violuric acid systems on high-kappa pulps may be a viable technology that can yield substantial delignification without detrimental ramifications on viscosity (169).

Kraft pulps were delignified using laccase and a various mediators as ABTS (2, 2-azinobis-3-ethylbenzthiazoline-6-sulfonate) (170), 1-hydroxybenzotriazole (171, 173), phthalimide [173], and transition metal complexes (174, 175). Development of new laccase-mediators system enables biobleaching of high lignin content kraft pulps (176, 177).

Bleaching of high-yield pulp

To satisfy increasing pulp demands and to conserve wood resources, there is a great interest in studies on high yield pulping process. For the bleaching of the high yield pulp the sodium dithionite and hydrogen peroxide are the main processes used alone or in combination in single or two-stage process to obtain a final brightness of 50-70% (178, 179). Sodium dithionite, also known as sodium hydrosulphite, will react with the chromophores present in the lignin to make less coloured compounds and consequently, to give a brighter aspect to pulp (180). Mechanical pulps may be bleached to 60-63% ISO brightness using a reducing agent, sodium hydrosulphite [181]. About 50% of bleached mechanical pulp is currently

produced using dithionite bleaching (182).

The potential of a reductive agent, formamidine sulphinic acid (FAS), has been evaluated for the bleaching of mechanical pulp. A ratio of 0.5% sodium hydroxide is suitable for 1% FAS, more than that will increase the yellow shade of the pulp. The results of FAS bleaching are approximately the same obtained by sodium hydrosulphite with improved brightness stability [183]. Formamidine sulphinic acid (FAS) is more effective than sodium hydrosulphite as a reducing agent for removing dyes in the bleaching of recycled fibres (184).

Sequential bleaching with hydrogen peroxide followed by a hydrosulphite bleaching combining the oxidative properties of peroxide and the reductive properties of hydrosulphite and reduced the usage of bleach chemicals. Typically an 8-9 point brightness gain can be achieved with hydrosulphite bleach in a one-stage application. Two-stage sequential bleaching with peroxide and hydrosulphite bleach can achieve a total brightness gain as high as 18 points (185).

Decomposition of hydrogen peroxide is one of the major causes of a loss of bleaching efficiency of mechanical and thermomechanical pulps (186). The addition of aluminum nitrate (up to 100 ppm Al on pulp) to a two-stage acid/alkali hydrogen peroxide bleach of eucalyptus regnans stone groundwood pulp enhance the brightness gain of the pulp. It is proposed that the presence of aluminum ions modifies the catalytic behaviour of the transition metal ions present in the pulp, reducing peroxide consumption, while increasing the brightness of the pulp (187). Different types of alkali could replace sodium hydroxide and silicate and yet give pulp with sufficient brightness and mechanical strength. The results showed that CaO, Ca(OH)₂, NaHCO₃, MgO and Mg(OH)₂ could be used in place of sodium hydroxide. Mg compounds gave the highest brightness increases even without silicate. With Mg compounds the COD of the residual liquor fell to about half its normal value, but the mechanical strength suffered about 20% (188).

A combination of Na-A zeolite or phosphoric acid-treated zeolite with hydrogen peroxide promoted elimination of chromophores. The addition of zeolite to the peroxide enhanced brightening of the pulp by improving the light reflectance at 457 nm, a change potentially attributable to a decrease in chromophoric quinonoid structures (189). A significant decrease in the heavy metal content in pulp was achieved by pretreating TMP with porous zeolite supports of citric acid and pyromellitic acid. Zeolite-supported citric

acid and zeolite-supported pyromellitic acid systems showed synergistic chelation effects over the separate addition of citric acid, pyromellitic acid, and zeolite alone. These supported chemicals demonstrated better chelation and peroxide stabilization efficiency compared to an optimum charge of a conventional DTPA/Na-silicate system. A pretreatment with 2 wt.% Na-cit. zeo of a commercial TMP chelated Mn and Fe effectively under a mildly acidic pH condition. An optimum pretreatment condition of 30 min at 60°C is recommended (190). Metal management to maximize peroxide bleaching by sequestering metal ions improves peroxide bleaching of a commercial thermomechanical pulp (191).

Mechanical pulps are bleached by treatment with oxygen gas and alkali in the presence of borohydrides. The combined treatment gives brightness gains of 15-20 points comparable with those achieved using stabilized alkaline 4% hydrogen peroxide. Bleaching occurs via the conversion of oxygen molecules to hydroperoxide ions (HOO⁻) by reaction of oxygen with ionized phenolic groups in the lignin where they bleach by reacting with coloured lignin quinone and coniferaldehyde chromophores. Borohydrides are stable to the reaction conditions, its primary role is to regenerate the phenolic groups and prevent its oxidation by oxygen (192).

Bleached mechanical pulps has less resistance to UV rays when irradiated, brightness is decreased and the yellow shade is more pronounced (193). A review on different aspect on photoyellowing of paper made from mechanical pulps has been discussed (194). It was found that 5-hydroxymethyl-2-furaldehyde (HMF), which is readily formed from carbohydrates, has the colour forming ability and cause a severe yellowing of both mechanical and chemical pulps. HMF interacts with pulp components forming adducts leading to the formation of colour (195). Thio additives in thiol-photostabilization of hardwood BCTMP remove chromophores across the fibre wall (196). The use of acyclic thiosulphinates in combination with UV absorbers provided a very effective means of retarding the photoaging process of mechanical pulps (197). Chemical modification with propionic anhydride strongly reduced light induced yellowing up to 80% of the discolouration could be hindered (198). A potential mode of stabilization of mechanical pulps by the hexadienol is triplet quenching of the excited state of lignin chromophores such as the α carbonyl groups of phenacyl aryl ethers. Other pathways of stabilization for hexadienol applied to BCTMP may include termination of free radical propagation by hydrogen atom donation (189). Acetylation was found

to slow down the UV-light induce reaction, could also promote photobleaching reactions when the pulps were subjected to an irradiation source emitting light in the visible range (200).

To address the deficiencies of benzophenone UV screens for preventing brightness reversion in high yield mechanical papers, a new series of such materials were synthesized with enhanced water solubility and compatibility with the lignocellulosic substrate. A series of 2,4-dihydroxybenzophenones (DHB) were synthesized containing various Mannich bases at the C3 position of one of its rings. They possess the UV-screening ability of o-hydroxybenzophenones, and they also contain tertiary nitrogen atoms that may function as radical scavengers. Aqueous solutions of the hydrochloride salt of 3-(dimethylaminomethylene) 2,4-dihydroxybenzophenone, when applied on bleached chemithermomechanical pulps (CTMP) sheets, were significantly more efficient in preventing photoyellowing than the original DHB applied on the sheets from ethanol-water solutions (201). Photostabilization of high yield bleached mechanical pulps could be achieved with mercapto stabilizers (202), thiol additives (203), DTPA treatment (204) or by combining various classes of additives and acetylation (205).

Minor bleaching methods

Photochemical bleaching

Photocatalyzed reactions using semiconductor oxides applied to environmental problems have received a considerable attention in the last years. Increase in colour during irradiation of mechanical pulps was caused by the formation of ortho-quinones, the chromophores produced by UV-radiation were found to be almost completely removed by sodium borohydride reduction. Irradiation at a shortwave length (373 nm) creates a coloured chromophore, while irradiation at the longer wavelength (435 nm) leads to the formation of a colourless product. Methoxylated ortho-quinones could be bleached by 420 nm irradiation (200).

Titanium dioxide and zinc oxide are the most attractive photocatalysts because they are cheap, friendly to the environment and easy to be recovered. The photochemical bleaching based on the generation of oxygen active species appear very promising. The bleaching was attributed to the action of oxygen active species such as superoxide anion, hydroxyl radicals, and singlet oxygen produced by irradiation in alkaline solutions (206). A two-stage process for photochemical bleaching of cellulosic pulp is

presented. The first, based on the generation of oxygen active species by the photocatalytic action of TiO_2 , and the second on the photochemical decomposition of hydrogen peroxide. Both stages are carried out under alkaline pH and at 85°C in aqueous suspension at a consistency of 5%. The UV-visible irradiation (wavelength >300 nm) was involved. The presence of TiO_2 as photocatalyst showed several advantages, such as reduction of reactions time, preservation of the pulp viscosity, increase of selectivity during the photobleaching and decrease of the consumption of the bleaching chemicals (206).

Good quality TCF bleached chemical pulp was produced from eucalyptus grandis wood by combination of peroxyformic acid pulping and photochemical bleaching. Three stages photochemical bleaching in basic medium at 85°C were applied, ground stage oxygen treatment followed by the action of singlet oxygen generated by methylene blue and hydrogen peroxide (2%, 1h) (207). Two stages bleaching of peroxyformic sugarcane bagasse pulp combining photocatalysis and photosensitization are presented. The first stage consists of an irradiation (1h), with tungsten or mercury lamps, of the pulp under alkaline pH with TiO_2 and methylene blue (MB) or 3,4,9,10-perylenetetracarboxylic acid (PTCA) or FE (Ii) 4,4',4'',4'''- tetrasulphophthalocyanine (TSPC) concentration 10^{-5} mol L^{-1} in the presence of bubbling oxygen and hydrogen peroxide (2% pulp basis). The second photobleaching stage performed with hydrogen peroxide (3%) efficiently completed the delignification and the brightness gain, removing completely the sensitizer from the pulp (208).

An alternative bleaching process for cellulose pulp using hydrogen peroxide and ultraviolet light in alkaline media was evaluated. 90% delignification is possible, maintaining good pulp viscosity and strength properties (209). Three stages photochemical bleaching in basic medium at 85°C were applied for photodelignification of eucalyptus grandis organosolv chemical pulp (210). Up to 75% delignification was observed for photoreactions conducted at room temperature and atmospheric pressure during oxygen delignification of softwood kraft pulp (211).

Because ultraviolet radiation generates reactive radicals, it has been used in delignification. It has been found that UV radiation enhanced bleaching by chlorine, hypochlorous acid, hypochlorite, chlorine dioxide, hydrogen peroxide and oxygen delignification. Under relatively mild conditions (1% concentration, 32°C), alkaline hydrogen peroxide delignification and brightening of eucalypt kraft pulp were significantly

enhanced by UV irradiation at 254 nm. The pulp was bleached from 41 to 81% ISO with 2% peroxide after 10 hours irradiation. Hydroxyl radicals appear to be the principal active species in the UV/peroxide system. Fibre damage is not appreciable under these bleaching conditions (212).

Non-phenolic α - ether structures in residual lignin are known to be completely stable in the presence of oxygen containing species under alkaline bleaching conditions. It has been shown that in the presence of organic acids, both phenolic and non-phenolic units in residual lignin undergo oxidative degradation. Nitric acid catalyzed peroxyformic acid pretreatment can release residual lignin from eucalyptus krat pulp. Sodium hydroxide extraction is necessary to dissolve the released lignin, and when followed by UV-peroxide bleaching, the pulp can be fully bleached to high brightness (213). The photoreactivity of lignin model ether in alkaline methanol has been investigated on exposure to UV-visible irradiation and in the presence of MB as singlet oxygen sensitizer. An analysis of photoproducts indicates that the oxidation of the benzylic alcohol moiety into a carbonyl derivatives and the cleavage of the β -O-4 bond are minor processes. The structure of the photoproducts indicates that hydroxyl radical and superoxide anion are the main active oxygen species in the photochemical process (214).

Perborate bleaching

A literature review revealed that adding alkaline peroxide to wood chips prior to refining could improve pulp quality in terms of brightness and strength properties. Other alternatives of enhancing the efficiency of the refiner bleaching process include the use of sodium perborate and an activator for peroxide. Sodium perborate is a more powerful bleaching agent than hydrogen peroxide; at an equivalent charge of an oxidizing agent, up to 20 ISO points were gained for perborate compared to a 13-point ISO gain registered for the peroxide. Most of the strength properties have been improved. The use of the activator tetraacetyl ethylenediamine (TAED) is more efficient in terms of strength properties than brightness. The use of sodium perborate in the refiner represents an alternative that could be more economical than hydrogen peroxide (215).

Perborates are of low cost and low toxicity, and usually manufactured from the interaction of borates with hydrogen peroxide (216). The possibility of using peroxyborates, produced in situ by combining aqueous alkaline hydrogen peroxide and borax reach a pilot plant (217). Bleached TMP handsheets were

impregnated at pH 9.5 with a mixture comprised of 2% borax and 1% hydrogen peroxide, the percentage stabilization offered after 33h of cumulative direct indoor sunlight irradiation was about 70%. When a similar solution was used to impregnate unbleached TMP samples, a brightness gain of about 10 ISO points was obtained (218). The possibility of using sodium perborate for bleaching thermomechanical pulp was investigated (219, 220).

Amine boranes bleaching

The presence of carbonyl groups (aldehyde or ketone) in the cellulose polymer makes the acid and alkaline hydrolysis easier, and is in part responsible for the yellowing of the paper. Borane tert-butylamine complex $\{(CH_3)_3CNH_2 \cdot BH_3\}$ gave particularly good results in selective reducing of aldehydes and ketones and it also produces optical bleaching of paper. Its effectiveness has been demonstrated not only on artificially oxidized paper, but also on original prints (221). The bleaching potential for softwood pulp of borane-tert-butylamine and borane-ammonia complexes was examined in relation to their use as potential replacements for sodium hydrosulphite. The materials selectively attack aldehyde structures of the paper. This increases brightness. Amine boranes modify coniferaldehyde chromophores to give chemical species that absorb light below 300 nm. Amine boranes are useful in a multistage bleaching process with hydrogen peroxide. They give an ISO brightness of more than 76% (222).

Nitrous acid delignification

Nitrous acid pretreatment for oxygen bleaching of beech kraft pulp followed by chlorine dioxide and hydrogen peroxide gives pulps with high brightness (87%) and viscosity (20 cP) at an extremely low AOX level (0.1 kg/t pulp) (223).

Nitrosylsulphuric acid pretreatment

Kraft pulp pretreated with nitrosylsulphuric acid (NSA) as a liquid nitrosating agent showed an improvement in delignification with good viscosity protection in the succeeding alkaline oxygen stage. NSA-pretreated pulp required less active chlorine in the C+D stage and also less caustic charge in the EO stage. The effluents exhibited lower AOX content with NSA pretreatment (224).

Electrochemical bleaching

The object of the electrochemical bleaching is to explore the possibility of carrying out the process of bleaching electrochemically, in one stage (in situ bleaching) with a view to reducing the cost of the

bleaching process, to clean the bleaching effluent and also to eliminate the hazards involved in chemical transportation and handling. Sulphite, kraft wood pulp and bagasse (chemical, chemimechanical and mechanical) pulps were successfully bleached to a relatively high degree of brightness with electrochemical process by electrolyzing sodium chloride solution. Bleaching was carried out by using NaCl solution and DC electricity. The rate of electrochemical bleaching was found to increase with increasing current density and salt concentration. The advantages claimed that electrochemical bleaching eliminates the chlorination stage, therefore, resulting in a reduction of AOX. It reduces the bleaching time by half compared to CEH sequences. The electrolyte solution can be used for several bleaching series; it is possible to use three times less energy for the same gain in brightness (225, 226).

At the anode $2Cl^- \rightarrow Cl_2 + 2e^-$

At the cathode $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

In bulk slurry $Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+$

$HOCl \leftrightarrow OCl^- + H^+$

$2HOCl + OCl^- \rightarrow ClO_3^- + H^+$

A novel method for bleaching of pulp with electrochemically activated violuric acid as a water-soluble mediator has been presented (227).

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