Catalysis and activation of oxygen and peroxide delignification of chemical pulps: a review

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ABSTRACT: Oxygen and hydrogen peroxide have always been technologically attractive oxidants to the pulp and paper industry, with their significance becoming of increasing importance as environmental regulations become more stringent. The fact that molecular oxygen has a triplet ground state whose direct interaction with single-state organic molecules is a spin-forbidden transition, limits its oxidative selectivity. Industrially, it will be extremely beneficial to fix molecular oxygen within organic or inorganic compounds capable of transferring it selectively to an organic substrate such as lignin. Since a variety of research endeavours have already been made to catalyse oxygen delignification and activate peroxide delignification of chemical pulps this paper initially attempts to critically review them. In addition, this effort covers peracids, which can be considered as organic molecules containing active oxygen. Another example of an inorganic molecule containing active oxygen is peroxymonosulfuric acid, which was shown to improve oxygen delignification of kraft pulps. Dioxiranes have also been shown to possess the ability to transfer a single activated oxygen atom onto aromatic and unsaturated substrates. As such, dimethyldioxirane is reviewed for its potential as a novel and selective non-chlorine containing bleaching agent for the production of fully-bleached totally chlorine-free pulp. Another form of activated oxygen may also be present within peroxycarboximidic acid, which is thought to be an intermediate in the interaction of cyanamide with peroxide, proposed as a peroxide activator for the bleaching of sulfite pulps. Finally, our critical review covers the recent scientific and patent literature which contains a number of examples where transition metals have been used as additives in peroxide and oxygen delignifications i.e. tungsten, molybdenum, certain manganese complexes, silicomolybdates and polyoxometalates.

Application: This review serves as a guide to recent research and patents pertaining to oxygen and peroxide delignification, peracids, and dioxiranes.

Environmental regulations coupled to market pressures have forced the pulp and paper industry to explore alternatives to chlorine based bleaching practices for the production of bleached kraft pulp. Various technologies and bleaching chemicals have been suggested as answers to kraft pulp bleaching concerns, from which oxygen, ozone and peroxides are the leading candidates for chlorine replacement. Unfortunately, these chemicals are not without drawbacks.

Oxygen delignification is effective but its delignification effectiveness is limited to about 50% after which a severe loss of pulp strength occurs. Hydrogen peroxide under alkaline or acidic conditions is not an effective delignifying agent while ozone is considerably more effective but it promotes aggressive radical reactions which cause undesirable carbohydrate degradation.

High brightness pulps appear to be difficult to produce only by applying suc-cessive oxygen and peroxide stages. Repeating the same chemistry, stage after stage, gives diminishing returns, with the necessity to introduce stages that activate the pulp or catalyze the chemical used, before additional oxygen or peroxide becomes effective. Devising methods for such activation or catalysis has been the subject of many research endeavors whose specifics are reviewed in this paper.

Activation of oxygen delignification

Oxygen delignification can be considered as an intermediate step between kraft pulping and bleaching since up to about 50% of the residual lignin in kraft pulp can be removed at this stage. Extending a conventional oxygen delignification stage beyond its current limits would decrease bleach chemical demand with serious environmental benefits and significant increases on return on investment.

Recent efforts to augment the efficiency of oxygen delignification fit the fol-lowing classifications:

- Reinforcement, using peroxide or peracids
- Addition of activators or catalysts
- Pulp pretreatment prior to oxygen delignification
- Two-stage oxygen delignification with or without interstage treatment, where the oxygen and alkali charges are split in two stages.

Peroxide and peracids reinforced oxygen delignification

Combining the effects of hydrogen peroxide and oxygen for the bleaching of chemical pulps was first reported in the 1980s. More specifically, a synergy between oxygen and peroxide was reported when peroxide was used for the reinforcement of alkaline extraction stages carried out under moderate oxygen pressures (Eop) (Lachenal *et al.* 1986a, Klein *et al.* 1990). These data showed reduced kappa numbers and improved viscosities. Consequently, in an

effort to improve the oxygen delignification stage itself, peroxide reinforced oxygen delignification was proposed aimed at enhancing the efficiency of lignin removal. Parthasarathy and coworkers showed that peroxide had an additive effect with oxygen on the delignification of pine kraft pulps, resulting in improved selectivity and delignification efficiency (Parthasarathy *et al.* 1990). For example, the addition of 0.5% hydrogen peroxide into an oxygen delignification stage, caused a 60% kappa number reduction as compared to a 50% maximum kappa number reduction possible for one stage oxygen delignification. Compared to conventional oxygen delignification, peroxide reinforcement (at lower alkali charges) produced delignified pulps of the same kappa number with higher viscosity than those obtained in its absence. In addition, peroxide reinforced oxygen delignification was found to allow the use of lower temperatures with similar kappa number reductions.

Parthasarathy and coworkers also examined the peroxide reinforcement of a double-stage oxygen delignification process (Parthasarathy *et al.* 1990). Using a (PO)(PO) process, kraft pulps were shown to be delignified to about 73% of their original kappa number as compared to 61% for a double oxygen delignification process, in the absence of peroxide. Once again, at similar kappa numbers, peroxide reinforced double oxygen delignification produced pulps with higher viscosities and better strength properties. It was also postulated that peroxide has to be added during the first stage of a double-stage oxygen bleaching to realize potential benefits from the second oxygen stage which may or may not be reinforced with hydrogen peroxide.

In another effort, Odermatt and coworkers investigated the effect of adding hydrogen peroxide and activated hydrogen peroxide on the selectivity and delignification efficiency of oxygen delignification (Odermatt *et al.*1994). By controlling the peroxide decomposition with diethylenetriamine pentaacetic acid (DTPA) and an acid pretreatment, oxygen delignification in the presence of cyanamide activated hydrogen peroxide, resulted in pulps of low lignin content (kappa numbers below 10, with over 60% delignification), while maintaining good selectivity. Applying two oxygen treatments reinforced with cyanamide activated hydrogen peroxide, i.e. an (OP)(OP) sequence, a pulp of kappa number 4.4 (amounting to an 82% overall delignification) was produced.

Investigations of peroxide activated with polypyridines (Jachinski and Patt 1998) as well as peracids, as potential systems for reinforcing oxygen delignification will be described in detail in other sections of this paper.
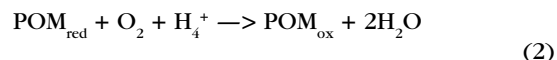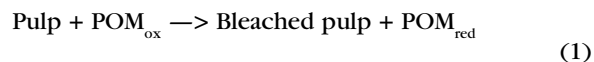
Oxygen delignification of kraft pulp in the presence of acidic peroxide was originally described by Suss and Helmling in 1987 (Suss and Helmling 1987). Such a treatment improved the delignification rate of a subsequent alkaline stage. Further efforts addressed the addition of molybdate ions in acidic peroxide assisted oxygen delignification (Agnemo 1997).An addition of a 1% peroxide together with molybdate (300 ppm as Mo) was found to reduce the kappa number to 10.3, as compared to a kappa number of 16.8 of the control experiment. Serious viscosity losses, however, accompanied these effects.

Liebergott studied peracid/oxygen treatment of kraft pulp (Liebergott 1996).Acidic peroxide (AP), peracetic acid (Pa), peroxymonosulfuric acid (Px) and mixed peracids solution (Pxa) were tested under acidic conditions with oxygen on an oxygen delignified softwood pulp (kappa 20). Px/O and Pxa/O treatment followed by Eop extraction resulted in a delignification of 63% (kappa 7.5) and 67% (kappa 6.7) respectively.

Polyoxometalates and other transition metal based activators

Extensive research on polyoxometalates (POM) bleaching commenced in 1992 by the USDA Forest Service, Forest Product Laboratory (Weinstock and Hill 1994; 1996). In 1995, the group claimed a highly selective closed mill technology (Weinstock *et al.* 1995a; 1995b; 1995c).The process cycle starts with the reaction of fully oxidized POM with unbleached kraft pulp under anaerobic conditions (eq. 1).At this stage, the POM complexes are reduced, and oxidized residual lignin fragments are dissolved in the bleaching liquor.After the bleaching, the reduced POM liquor can be re-oxidized in a separate stage (eq. 2) using oxygen. During the regeneration of the POM complexes the dissolved lignin fragments are converted to carbon dioxide and water. The recycling potential of the POM liquor has been demonstrated (Weinstock *et al.* 1995a).

$$\text{Pulp} + \text{POM}_{ox} \longrightarrow \text{Bleached pulp} + \text{POM}_{red} \tag{1}$$

$$\text{POM}_{red} + O_2 + H_4^+ \longrightarrow \text{POM}_{ox} + 2H_2O \tag{2}$$

Recently, two different POM anions ("-[SiVW$_{11}$O$_{40}$]$^{5-}$ and "-[PV$_2$Mo$_{10}$O$_{40}$]$^{5-}$) were selected as potential catalysts of oxygen delignification and extensive studies of their reactions with phenolic lignin model compounds have been reported (Weinstock *et al.* 1998a; 1998b).
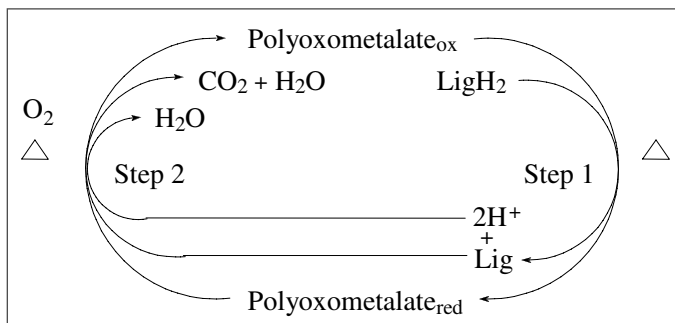

Scheme 1: An effluent free POM delignification process. Step 1: Anaerobic oxidation of lignin in wood or pulp fiber by fully oxidized POM complexes (POMox); Step 2: Aerobic wet oxidation (mineralization) of dissolved organic compounds and regeneration of the reduced POM complexes (POMred) to their fully oxidized, delignification-active form. (Weinstock et al. 1998a).

Another generation of POMs has recently been developed by Atalla and coworkers (Atalla *et al.* 1998). While the first generation was able to operate only at acidic pH, the new POMs are stable at pH levels above neutral. In this respect, the hydrolysis of cellulose is significantly reduced.The group also claimed that

this new generation of POMs is of improved stability due to newly developed synthetic procedures, which allow the POM to be repeatedly recycled in a closed system. More specifically, POM with the formulae $Na_6SiV_2W_{10}O_{40}$ was effective in reducing the kappa number of unbleached kraft pulp from above 30 to below 10 with limited losses in viscosity.

In contrast to the anaerobic reaction conditions required for the use of POMs developed by the Weinstock and Atalla team, Evtuguin and Pascoal Neto (Evtuguin and Pascoal Neto 1997a) have described the possibility of using POM catalysts under aerobic conditions. In this respect, the possibility of oxygen delignifying pulp in mixtures of organic solvents with water in a single-stage aerobic process has been patented (Evtuguin and Pascoal Neto 1997a). The oxidation of lignin under an oxygen atmosphere occurs *via* its reaction with POM while at the same stage the re-oxidation of a reduced form of POM by oxygen takes place. The presence of such a redox cycle could conceivably offer good process efficiencies. Preliminary data of POM assisted oxygen pulping of eucalyptus wood and POM assisted oxygen bleaching of sulfate pulp in organic solvent/aqueous media have been presented (Evtuguin and Pascoal Neto 1997b). More specifically, the hepta-molybdopentavanadophosphate (HPA-5) anion was shown to be promoting oxygen delignification in organic solvent/aqueous media.
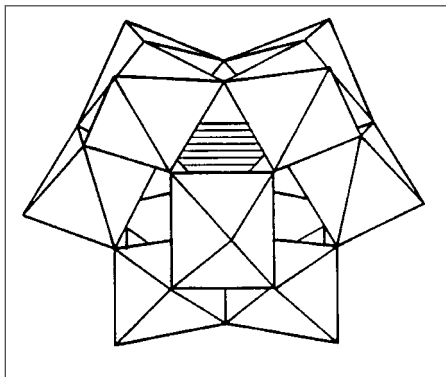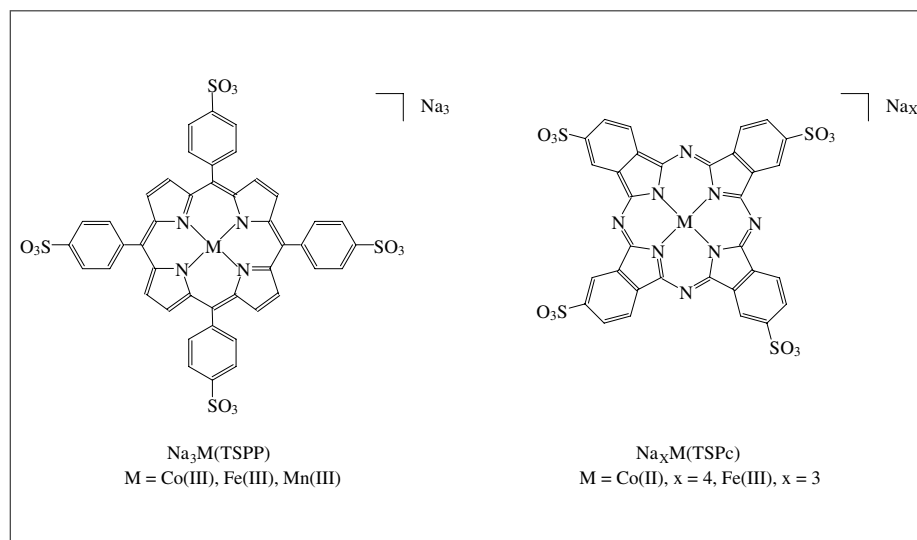

Scheme 2: The α-Keggin structure of the 12-series heteropolyanion (HPA) in polyhedral-filling representation. (Poppe 1983).

A mechanistic proposal and possible applications of HPA-5 have been reported by Evtuguin and coworkers (Evtuguin *et al.* 1997c), and the catalytic effect of HPA-5 for the oxygen delignification of kraft pulp has been documented (Evtuguin *et al.* 1998a). More specifically, oxygen delignification experiments with eucalyptus kraft pulp in the presence of HPA-5 showed that the degree of delignification depends on the nature of the solvent used. Water, acetone/water, and ethanol/water were examined as delignification media and the properties of the bleached pulps were compared. While the degree of delignification was highest in aqueous media the selectivity of delignification was found to increase with the addition of organic solvent (ethanol). This effort defined the optimal delignification conditions as a reaction time of 2 hr at

Scheme 3: Water-soluble metal porphyrin and phthalocyanine complexes as potential oxygen delignification catalysts (Perng et al. 1994).

90°C, with a solvent composition of 50% ethanol and 50% water at a pH of 1.8, and a HPA-5 concentration of 2mmol/L. No significant changes in the efficiency of the catalyst were observed after recycling the same material up to 10 times. The use of polyoxometalates has also been extended to elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching sequences (Evtuguin and Pascoal Neto 1998b). Pulps of high brightness, acceptable strength properties and reduced requirements of ClO_2 have been claimed. POM systems were also reported to activate peroxide and ozone bleaching stages of eucalyptus kraft pulp under acidic conditions (Evtuguin and Pascoal Neto 1998b).

While HPA-5 was found to catalyze peroxide delignification, the low pH's used resulted in significant pulp viscosity losses.

Perng and coworkers examined the effect of water-soluble metal porphyrins toward improving the rate and selectivity of oxygen delignification for softwood kraft pulp (Perng *et al.* 1994). Amongst the cobalt, iron and manganese complexes of meso(terasulfonatophenyl) porphyrin (TSPP) and tetrasulfopthalocyanine (TSPc), only Mn(TSPP) showed catalytic activity by promoting delignification and suppressing cellulose degradation (Scheme 3). The iron complexes appeared to suppress cellulose degradation, while the cobalt complexes were found to promote it with no effect on the delignification efficiency.

Transition metals and transition metal complexes have also been investigated as potential additives acting as catalysts or activators for oxygen delignification of kraft pulps (Hall *et al.* 1996, 1997). Ni^{2+} ions in the presence of sodium tartrate were found to increase the delignification selectivity and similar effects were observed when the tartrate was substituted with equal amounts of sodium oxalate or sodium citrate. The enhanced selectivity was attributed mainly to reduced carbohydrate degradation since

the extent of oxygen delignification was only marginally increased.

Agnemo recently showed that molybdate addition to an acidic (pH~5) softwood oxygen delignification stage resulted in increased kappa number reduction (Agnemo 1997). More specifically, a pulp of kappa number of 11.2 was obtained when 300 ppm of molybdate ions were added during the delignification as opposed to a kappa 16.8 obtained for the control.

Pulp pretreatment prior to oxygen delignification

A number of investigators have reported on the beneficial effects of kraft pulp pretreatment prior to an oxygen delignification stage. Pretreatments with compounds such as nitrogen dioxide (Abrahamsson *et al.* 1981; Lindqvist *et al.* 1986; Samuelson and Öjteg 1987 and 1994), chlorine (Fossum and Marklund 1988; Lachenal *et al.* 1989; Lachenal and Muguet 1991), chlorine dioxide (Fossum and Marklund 1988; Lachenal *et al.* 1989), and hydrogen peroxide (Fossum and Marklund 1988) were shown to improve oxygen delignification by increasing the selectivity of the delignification allowing for extending the delignification without significant losses in pulp quality.

Pretreatment of kraft pulp with nitrogen dioxide has been shown to promote oxygen delignification to a very low lignin content without causing extensive depolymerization of cellulose. Early efforts by Abrahamsson and coworkers have shown that nitrogen dioxide pretreatment of kraft pulp causes partial demethylation of the lignin (Abrahamsson *et al.* 1981). In addition, model compound work by Lindeberg and Walding has shown that NO_2 treatment caused the fragmentation of ether bonds within residual lignin with the consequent formation of new free phenolic groups (Lindeberg and Walding 1987). These reactions are expected to increase the reactivity of the lignin and decrease the possibility of cellulose being attacked by oxygen and radical species. In addition these reactions are thought to contribute to the alkali solubility of the lignin, in a sodium hydroxide impregnation stage, prior to oxygen delignification (Abrahamsson *et al.* 1981). At an applied front, work by Lindqvist and coworkers showed that the

nitrogen dioxide pretreatment significantly assisted an oxygen delignification stage by reducing the kappa number while retaining pulp viscosity (Lindqvist *et al.* 1986). Samuelson and Öjteg showed a dramatic increase in the efficiency and the selectivity of oxygen delignification when softwood kraft pulp (kappa 3.5) was subjected to a two-stage NO_2 pretreatment process, followed by an oxygen delignification stage (Samuelson and Öjteg 1987). It is worth mentioning at this point that, the nitrogen dioxide pretreatment described above has actually been evaluated and implemented on a pilot scale in Sweden (Simonson *et al.* 1987).

Interesting carbohydrate protection effects have been noted when kraft pulp was pretreated with a low charge (<2%) of chlorine. Up to 75% of the residual kraft lignin was found to be removed in a subsequent oxygen stage, while the pulp properties were maintained. Several investigators have independently confirmed the beneficial effects of such a chlorine pretreatment allowing for extensive delignification (kappa number below 10) in a subsequent oxygen delignification stage (Lachenal and de Choudens 1986b; Soteland 1988; Fossum and Marklund 1988). The hypothesis offered to rationalize for these data was that chlorine causes the generation of new phenolic groups, which would allow for a more selective reaction of oxygen with lignin. Chlorine dioxide showed similar effects at a given active chlorine charge (Fossum and Marklund 1988). This is possibly a more attractive option from an environmental and a technological point of view, since chlorine dioxide produces only one fifth of the chlorides usually produced by an equivalent amount of chlorine. Chlorine dioxide is also considerably less corrosive than chlorine. However, both of these chlorine containing activation systems add significant environmental load to the process of oxygen delignification since chloride ions are introduced in the effluent, prohibiting its recovery.

The activating effect of ozone was also studied by Lachenal and de Choudens (Lachenal and de Choudens 1986b) as a pretreatment to oxygen delignification. While these authors reported small improvements, Fossum and Marklund found no synergistic effects operating on

the selectivity between the ozone pretreatment and the oxygen stage (Fossum and Marklund 1988).

Pulp pretreatment with acidic hydrogen peroxide has been documented to offer benefits as far as the selectivity of an oxygen delignification stage is concerned, although the effect was always lower than that of NO_2 or chlorine. Applying the peroxide under neutral conditions significantly reduced these effects (Fossum and Marklund 1988).

Pretreatments with sulfur dioxide, sodium sulfite, and sodium hypochlorite have also been examined by Fossum and Marklund, but no significant effect on the selectivity of subsequent oxygen delignification stages was observed (Fossum and Marklund 1988). Improved selectivity was however, observed by Andrews and coworkers after sulphide containing green liquor was used as a pretreatment of kraft pulp prior to oxygen delignification (Andrews *et al.* 1983). Fossum and Marklund, however, showed that no selectivity improvements were apparent when sulphide was used as a pretreatment compared to conventional oxygen delignification (Fossum and Marklund 1988).

The use of peroxyformic acid, generated *in-situ* from a mixture of formic acid and hydrogen peroxide, prior to oxygen delignification allowed a total degree of delignification of 83.4% to be attained without any serious drop in viscosity (Poppius *et al.* 1989). Kappa numbers as low as 4-6 were obtained for both pine and birch kraft pulps after the (PFA)O stage. Prior to the process, however, metals had to be removed in order to prevent the decomposition of the peroxyformic acid. The reasoning behind this impressive degree of delignification was rationalized by Poppius *et al.* as being due to increased reactivity of the residual lignin toward oxygen delignification, allowing for a substantial decrease in the kappa number in the oxygen stage.

Springer and McSweeny found that peroxymonosulfuric acid pretreatment prior to oxygen delignification was equally effective to that of chlorine provided that the transition metals were removed prior to the treatment (Springer and McSweeny 1993a). Suss and Helmling invoked oxidation and hydroxylation reactions occuring between peroxymonosulfuric acid and the aromatic

rings of lignin. These reactions are thought to increase the number of free phenolic groups in lignin thus increasing the number of sites available for oxygen attack during the alkaline oxygen delignification stage (Suss and Helmling 1987).

Double oxygen delignification with interstage treatment

A two-stage oxygen delignification process was designed by Kleppe and Peterson aimed at improving the delignification effectiveness of medium consistency oxygen stages, by dividing the oxygen and the alkali charge in two separate stages using two separate mixing systems. It was thus possible to increase the rate of lignin removal while preserving the degree of polymerization of the cellulose (Kleppe and Peterson 1994). The delignification efficiency of the two-stage oxygen delignification was further increased by maintaining a high pH, by adding fresh alkali and remixing the pulp before the second oxygen stage (McDonough 1995). A cumulative degree of delignification of about 70% was claimed when double stage oxygen was applied in the absence of interstage washing, compared to 53% delignification usually attained during a single oxygen stage.

A number of recent studies have shown that the structure of the residual lignin is significantly altered after oxygen delignification making the residual lignin less reactive to another oxygen stage (Argyropoulos and Liu 1999, Asgari and Argyropoulos 1998, Akim and Argyropoulos 1999). Efforts to increase the extent of delignification during the second oxygen stage, have been centred around modifications of the residual lignin aimed at increasing its reactivity toward oxygen. In addition, various pretreatments aimed to activate the lignin prior to oxygen delignification have been reported with marked improvements in selectivity. These pretreatments include nitrogen dioxide (Abrahamsson et al. 1981), ozone and peroxide (Fossum and Marklund 1988), sulfur dioxide, sulfite, and sulphide (Fossum and Marklund 1988), hypochlorite (Fossum and Marklund 1988), chlorine and chlorine dioxide (Lachenal et al. 1989), peracids (Liebergott 1994), and even enzymes (Nelson et al. 1995).

In an attempt to combine the benefits of lignin activation with the benefits of a two-stage oxygen delignification process, a two-stage oxygen delignification with an interstage chlorine (X) treatment, was proposed by Lachenal et al. in 1989 (Lachenal et al. 1989). The OXO process was more extensively studied and optimized two years later by Lachenal and Muguet (Lachenal and Muguet 1991). In actual fact, the presence of chlorine (1.5%, active chlorine) between the two oxygen stages provided a well delignified softwood kraft pulp with improved strength properties since the selectivity of the second oxygen stage was significantly improved. The efficiency of chlorine and chlorine dioxide as activating stages was also compared. Chlorine was found to be more efficient than chlorine dioxide in inducing the sought activation. Finally, a mill-scale implementation of the OxO process was reported in 1990 (Muguet et al. 1990). Despite the advantages enumerated above the use of chlorine is accompanied by the formation of organochlorines and corrosive chlorides in the process effluent, making the process less attractive from an environmental point of view.

Allison and McGrouther attempted to further improve the two-stage oxygen delignification process using an interstage treatment with peroxymonosulfuric acid (Px) (Allison and McGrouther 1995). A charge of 2% of peroxymonosulfuric acid was found to improve the overall selectivity of an OPxO sequence. Using this combination of chemicals it became possible to delignify the pulp at a 70% level with better viscosity than a comparable pulp delignified at the same kappa number with a conventional OO sequence. The Px treatment was effective under both acidic (pH 4) and alkaline (pH 10) conditions at moderate temperatures (75°C) at contact times of about 30 min. By adding hydrogen peroxide in the product solution of an on-site generated peroxymonosulfuric acid it was found that it enhanced the overall selectivity of the process. The presence of hydrogen peroxide was actually found to be synergistic with peroxymonosulfuric acid. Interstage treatment with peroxide alone had no effect on selectivity, and treatment with peroxymonosulfuric acid alone (in the form of triple salt of potassium peroxymonosulfate) improved the selectivity but not to the same extent as the treatment with the combination of both oxidants. Allison and coworkers (Allison et al. 1994) reported a more detailed study of the effect of hydrogen peroxide on OPxO. The authors showed that no benefits to the overall process selectivity were observed when hydrogen peroxide was present in the Px stage. The presence of peroxide in the final oxygen stage of the OPxO process, however, was found to be beneficial. This contradiction to the conclusion of the earlier work of Allison and McGrouther (Allison and McGrouther 1995) has been caused by residual chemical carryover. Most of the original hydrogen peroxide in interstage treatment mixture survived the short Px interstage and was thus present during the final oxygen delignification stage. Subsequently, the presence of hydrogen peroxide in the second stage improved the overall delignification efficiency of the OPxO process, not the presence of hydrogen peroxide in the Px interstage itself.

Also studied was the effect of metal ions on the selectivity of the treatment. Metal ions were found to catalyze the reactions causing cellulose degradation when present in peroxymonosulfuric acid treatments. Direct addition of the chelating agent to the Px stage did not, however, minimize the adverse effects of the metal ions. As such it was concluded that metals must be removed (an ethylenediaminetetracetic acid—EDTA pretreatment followed by wash) prior to the Px treatment. The ideal operating conditions of the OPxO bleaching sequence were found to be metal removal prior to the peroxide free Px treatment, washing after the Px interstage, and peroxide reinforcement of the second oxygen delignification stage. Initial pilot scale trials confirmed that very low kappa numbers for hardwood and softwood kraft pulps could be obtained via an OQPx(OP) sequence. However, careful control of the peroxymonosulfuric acid reactions is required since extensive reaction during the Px stage could reduce the overall selectivity of the process.

In an another modification, McGrouther and Allison studied the addition of acetone to the peroxymonosulfuric interstage treatment with the aim to further increase the two-stage oxygen delignification selectivity (McGrouther and Allison 1995). It was found that the addition of acetone was beneficial only at

HSO_5^- charges higher than 2.5%. Below these levels the peroxymonosulfate reaction with acetone, known to *in situ* form Dimethyldioxirane (DMD), appeared to be unable to compete effectively with the peroxymonosulfate reactions with the pulp. McGrouther and Allison also examined the effect that acetone addition has on the brightness development of the OPxO bleaching sequence, since earlier studies showed that peroxymonosulfate effectively delignified the pulp without, however, promoting subsequent brightening stages (McGrouther and Allison 1994). An interstage treatment with Px(5%)/acetone(4%), followed by a second oxygen delignification stage with 3% NaOH, resulted in an increased final pulp brightness when compared to the control OPxO pulp. This impressive data was rationalized on the basis that *in situ* produced DMD was able to eliminate chromophores to a greater extent than peroxymonosulfuric acid. In addition to these studies Allison's team also examined the effect of enzyme pretreatment prior to the Px stage on the overall OPxO effectiveness and selectivity (Allison *et al.* 1996). More specifically, in this study, oxygen delignified kraft pulp was pretreated with combinations of a commercial xylanase enzyme and a chelating agent prior to the peroxymonosulfate treatment and the oxygen stage. The data showed that the use of enzyme increased the efficiency of the subsequent peroxymonosulfate delignification stage with little viscosity loss. The resulting increase in the overall OPxO selectivity allowed a decrease of up to 25% in the peroxymonosulfate charge required to obtain an OPxO pulp of a given kappa number and viscosity.

Hunt and Lee examined dimethydioxirane (T) as an interstage treatment preceding the second oxygen delignification stage in an OTO bleaching sequence and compared the efficiency of DMD with chlorine dioxide in the ODO bleaching sequence (Hunt and Lee 1995). DMD was found to significantly enhance the kappa number reduction in the second oxygen stage. It was also shown that DMD is of the same selectivity as chlorine dioxide. As an interstage treatment, DMD showed a greater brightness gain per kappa unit reduction than chlorine dioxide. Despite various claims to the contrary the major drawback of this process remains the

need of using acetone in a pulp mill.

Rost and coworkers studied the potential of using an ozone treatment as an activating stage between two oxygen bleaching stages (Rost *et al.* 1993). The interstage ozone treatment resulted in lower kappa numbers as a function of the ozone charge. A second oxygen stage, after an OZ sequence, reduced the kappa number by approximately 5 units, independent of the ozone charge. The selectivity of the OZO bleaching sequence was found to be better when compared to the OO bleaching sequence. The efficiency of ozone was found to decrease with increasing pH and temperature. At low charges (0.2%) and at 50°C and pH of 4-5, ozone can be used as an activator between two oxygen stages without negatively affecting the selectivity of the process.

Li and coworkers compared the efficiency of peroxymonosulfuric acid (Px), peroxyacetic acid (Paa) and ozone (Z) as interstage activating agents for a two-stage oxygen delignification of softwood kraft pulp (Li *et al.* 1995). The conditions of the Paa and Px stages were optimized. Under optimized conditions, the OPaaO sequence showed the best delignification efficiency and selectivity. The viscosity of the OPaaO and OPxO pulps were found to be superior to those obtained by OO and the OZO bleaching sequences. An examination of the molecular mass distributions of lignin dissolved in the acidic Paa, Px or Z stages, and of the lignin dissolved in the ensuing alkaline oxygen stages, demonstrated the depolymerizing effects of peroxyacids and ozone, which were held responsible for the lower kappa numbers obtained after the activated two-stage bleaching sequences.

Nelson and coworkers studied the use of xylanase as an interstage treatment in a two-stage oxygen delignification process (Nelson *et al.* 1995). The data showed that in the presence of the enzyme, at least 15% more lignin was removed, and the resulting pulps were of higher viscosity. The precise mechanism of the action of xylanase on the pulp fiber has not yet been fully elucidated. A number of propositions do exist, however, including that these enzymes act mainly on the removal of some alkali-resistant reprecipitated or reabsorbed xylans; thus promoting the extractability of lignin.

(Kantelinen *et al.* 1991 and 1993; Buchert 1993)

Activation and catalysis of peroxide delignification

Hydrogen peroxide has always been a technologically attractive oxidant to the pulp and paper industry. Due to its limited reactivity toward residual lignin, peroxide is unable to fully replace chlorine containing bleaching agents. Under alkaline conditions, high temperature accelerates the decomposition of hydrogen peroxide, which not only reduces the amount of peroxide available for bleaching (Troughton and Sarot 1992), but also increases the amount of radicals formed, which have a detrimental effect on carbohydrates (Francis *et al.* 1998). Under acidic conditions, low pH and high temperatures could result in severe cellulose degradation due to the acid hydrolysis of cellulose.

Extensive investigations have been carried out on the stabilization of peroxide under conditions conventionally applied during the bleaching of chemical pulps. The effect of transition metals on peroxide decomposition, and the necessity of their efficient removal before peroxide treatment have been well documented (Basta *et al.* 1991; Troughton *et al.* 1994; Devenyns *et al.* 1994; Lapierre *et al.* 1995 and 1997; Bouchard *et al.* 1995). Stabilized peroxide acts as a lignin-preserving bleaching agent, preferably removing chromophoric structures in residual lignin, but incapable of degrading the lignin network.

In efforts aimed to increase the reactivity of peroxide, harsher reaction conditions were employed (Roy *et al.* 1995; Breed *et al.* 1995; Jameel *et al.* 1996). Higher temperatures and chemical charges increased the extent of delignification, but also promoted carbohydrate degradation, especially in the presence of transition metals.

Pulp pretreatment prior to an alkaline peroxide stage offers another possibility for improving the overall selectivity of peroxide delignification. For example, softwood kraft pulp treatment with 3% nitrogen dioxide (on o.d. pulp) at 70°C and 40% consistency for 15 min, followed by washing and alkaline peroxide stage (1% H_2O_2 on the o.d. pulp) at the same temperature, removed about 60% of the residual lignin (Lachenal *et al.* 1980). It is believed that nitrogen dioxide pretreat-

ment resulted in fragmentation of ether bonds of lignin, and the formation of new phenolic groups (Lindenberg and Walding 1987), which make the lignin more reactive towards the alkaline peroxide.

Lachenal and Papadopoulos proposed a highly efficient hydrogen peroxide delignification process for kraft pulps (Lachenal and Papadopoulos 1988). It consists of an activation stage - pulp pretreatment by Cl_2, NO_2 or O_3, and a peroxide delignification stage at high temperature (90ºC). In this manner, 50% to 80% delignification was attained using unbleached softwood and hardwood kraft pulps with only a 1% peroxide charge. After the peroxide stage, the degree of polymerization of the cellulose within the pretreated pulps (Cl_2, NO_2 or O_3) was found to be higher when compared to the peroxide bleached pulp without the pretreatment. The rationalization proposed to explain the increased delignification efficiency of peroxide was the formation of new phenolic hydroxyl groups possibly occurring *via* lignin demethylation reactions.

Pretreating kraft pulps with peracids (peracetic, Caro's, or mixed peracids) followed by a washing stage has been shown to increase the delignification effectiveness and brightness gains of an ensuing peroxide stage (Geng *et al.* 1993; Devenyns *et al.* 1993a). More specifically, the use of peroxyformic acid prior to a peroxide stage, has been described by Poppius and coworkers (Poppius *et al*. 1989). Prebleaching pine kraft pulp with peroxyformic acid reduced the kappa number by 25-80%, depending on the amount of hydrogen peroxide applied, the concentration of formic acid and the temperature of the treatment. Such prebleached pulps attained a brightness of 80-85% in the subsequent alkaline peroxide bleaching sequence. The increased reactivity of the kraft residual lignin toward alkaline hydrogen peroxide was held responsible for the brightness gains observed (Poppius-Levlin *et al*. 1991).
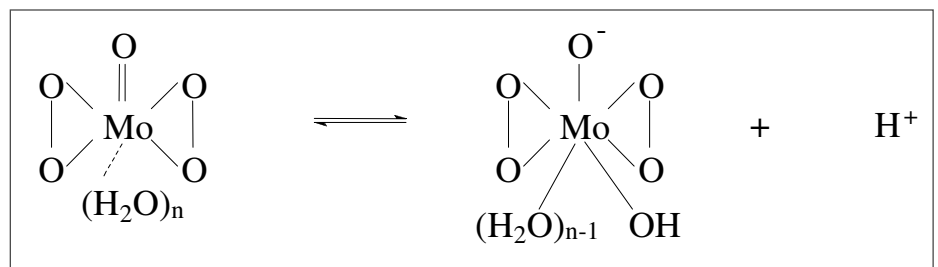
Transition metal centred peroxide activators

Various approaches aimed at overcoming the low capacity of hydrogen peroxide to selectively degrade lignin structures have been centred around its activation. The addition of an activator or catalyst direct-

ly to the peroxide stage, which by interaction with the peroxide would generate a more potent oxidants *in-situ*, allowed improved delignification with minor or no carbohydrate degradation. In this respect, a number of peroxide activators of a variety of structures, involving different activation mechanisms have been examined.

The delignification of kraft pulps with hydrogen peroxide catalyzed by transition metals was initially proposed and patented by Eckert (Eckert 1982). An acidic peroxide delignification stage was shown to be improved by the addition of transition metals selected from the group of tungsten molybdenum, chromium, osmium, and selenium. As one of the examples, in the original patent, tungsten ion catalyzed acidic peroxide delignification of hardwood kraft pulp was compared with alkaline peroxide bleaching. While the brightness gains and pulp viscosities were similar, the degree of delignification for the tungsten assisted acidic peroxide delignification stage was reported to be higher. The rationale behind the effectiveness of these systems was that the transition metal oxides, under acidic conditions reacted with peroxide to form transition metal peroxocomplexes, which are stronger oxidants than peroxide itself.

The ability of molybdate metal oxides to catalyze the acidic peroxide delignification of kraft pulps was confirmed a few years latter by Kubelka *et al.* (Kubelka *et al.* 1992). The catalytic effect of molybdate was attributed to its ability to form, under acidic conditions, reactive diperoxo complexes with peroxide (Bortolini *et al.* 1986).

The data of Kubelka coworkers showed that under acidic conditions (pH 5) and a 2% peroxide charge, the addition of 500 ppm of sodium molybdate reduced the kappa number by approximately 10 units. Acidic peroxide alone, in the absence of molybdate reduced the

kappa number of the same pulp by only 3 units. Unfortunately, however, the pronounced delignification observed, was accompanied by serious viscosity losses (Kubelka *et al.* 1992). On the same topic, Agnemo used ammonium molybdate to activate peroxide delignification (Agnemo 1997). Using only peroxide at pH ~ 5, Agnemo showed that no delignification was possible, however, addition of molybdate ions resulted in significant delignification.

Scheme 4: Diperoxo molybdenum complexes formed from the interaction of molybdenum ions and acidic peroxide (Bortolini et al. 1986).

In 1995, Jakara and coworkers studied the effect of silicomolybdate activated peroxide for ECF and TCF bleaching sequences (Jakara *et al*. 1995a). Under acidic conditions, silicomolybdate ions were invoked to react with peroxide to form silicoperoxomolybdates. Such ions, under optimal conditions are anticipated to be selective delignifying agents. Mill trials with such systems showed that 40-60% delignification could be obtained without any adverse effects on pulp quality. A fully bleached (89% ISO) softwood kraft pulp was obtained, both in the laboratory and during the mill-scale trials, by using only oxygen and activated peroxide as the bleaching agent. Jakara and coworkers compared the delignification efficiency of silicomolybdate activated hydrogen peroxide with peracetic acid (distilled and equilibrium) (Jakara *et al*. 1995b). Under optimum conditions, similar kappa number reductions and viscosity values were obtained. Both, peracetic acid (2.5% charge) and molybdate (450 ppm, calculated as Mo) were found to activate hydrogen peroxide (1.5% charge) and reduce the kappa number of softwood kraft pulp from an initial value of 16 to approximately 9. While the

molybdate activated peroxide systems offered somewhat lower brightening efficiencies compared to peracetic acid, they were claimed to offer the possibility of regeneration *via* filtrate recirculation.

In an effort to demonstrate that transition metal peroxo-complexes were responsible for the activation of peroxide, Suchy and Argyropoulos studied the effect of a transition metal peroxo complex on an alkaline peroxide delignification (Suchy and Argyropoulos 1998). Ammonium triperoxo-phenanthroline vanadate was initially synthesized and then added to the alkaline peroxide stage. At 0.5% activator charge, the kappa number of oxygen delignified pine kraft pulp was reduced from 16.2 to 6.3 (61% delignification) using a single alkaline peroxide stage. At the same time, the brightness of the pulp was increased by 5.7% ISO when compared to an alkaline peroxide bleaching stage at the same conditions in the absence of the activator.

Recently, tungstate, molybdate and vanadate based polyoxometalates have been identified as activators of acidic peroxide delignification (Bianchi *et al.* 1998; Evtuguin et al. 1998c). Bianchi and coworkers investigated various types of heteropolyacids (HPA) of Keggin type as potential catalyst of acidic peroxide delignification (Bianchi *et al.* 1998). Using 0.5 mmol/L $H_3PMo_{12}O_{40}$ and 0.1% H_2O_2 an 70°C for 4 hours, a hardwood kraft pulp with a kappa number of 2.1 and viscosity higher than control trials under the same conditions without employing a HPA as a catalyst, can be achieved. However, the use of HPAs as catalysts was found not effective for softwood pulp delignification. Evtuguin and coworkers have examined the potential of heptamolybdopentavanadophopsphate heteropolyanion - HPA-5 toward activating an acidic peroxide delignification stage (Evtuguin *et al.* 1998c). Despite an excellent delignification efficiency demonstrated by the system (from kappa 15.9 to 6), a significant reduction in pulp viscosity was also apparent. The latter was most likely caused by the extensive decomposition of hydrogen peroxide and hydroxyl radical attack of the cellulose.

Metal oxides such as tungstate, molybdate, methyltrioxorhenium, as well as some tungstate and molybdate based polyoxometalates, were evaluated as potential catalysts of acidic peroxide delignification (AP) by Chen and coworkers (Chen *et al.* 1998). The catalyzed acidic peroxide stage increased the degree of delignification of oxygen delignified softwood kraft pulp with increased selectivity compared to the non-catalyzed control bleaching. Simple metal oxides (tungstate, molybdate) were found to be equally as effective as their polyoxometalate counterparts in catalyzing acidic peroxide bleaching. Methyltrioxorhenium was found to be inactive in acidic peroxide bleaching of kraft pulps.

Patt demonstrated improved delignification efficiency of peroxide catalyzed by metal complexes. These catalysts were single or multiple nuclear metal complexes of manganese or iron, which can be present in the oxidation states II, III, IV, or V or in mixture of these states. Other parts of the complexes were various ligands (Patt 1997). Catalyzed P-stage resulted in improved delignification and selectivity of the peroxide bleaching stage. The metal complexes were also tested in peroxide reinforced oxygen delignification and were shown to be capable of increasing the delignification rate of the process.

A bi-nuclear manganese complex in which the manganese ions are present in the +IV and +III oxidation states, linked *via*

an acetate and two oxygen bridges (Scheme 5) was shown to selectively improve peroxide delignification.

Scheme 5: Chemical structure of the nucleus and the ligands of the selected manganese based catalytic activating peroxide system. (Patt et al. 1998).
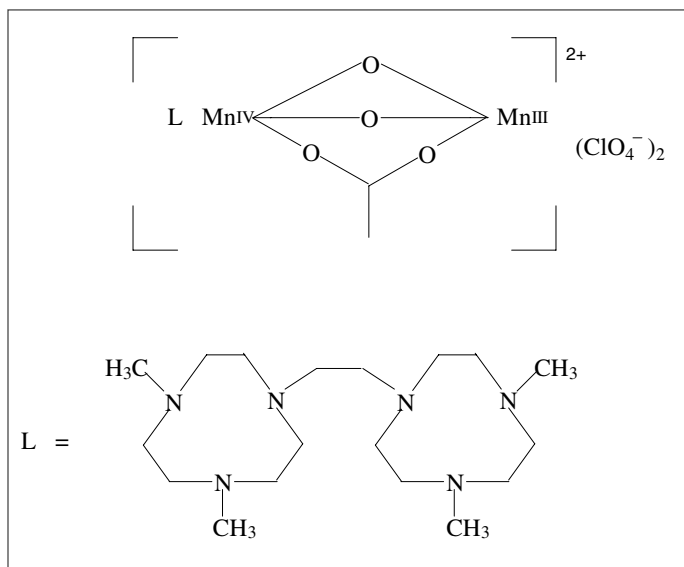
Patt and Mielisch and Patt and coworkers using an OQ(OP)P bleaching sequence demonstrated the effectiveness of the proposed system for the production of a fully bleached TCF softwood kraft pulp. Amongst the various parameters examined, the authors showed that this system may activate peroxide at the relatively low temperature of 50°C, while higher temperatures offered significantly reduced retention times. The proposed catalyst was shown that it could be applied either in one or two P stages. When applied at a level of 20 ppm, during the OP stage, a brightness of 88% ISO was obtained. When the catalyst was also applied in the ensuing P-stage, a brightness of 90% ISO was obtained at elevated temperatures (Patt and Mielisch 1997 and Patt *et al.* 1998).

Scheme 6: Proposed redox cycle of a catalyst with two manganese nuclei. The oxidized complex is oxidizing lignin, whereby it is reduced, and then the cycle is reinitiated. (Patt et al. 1998)
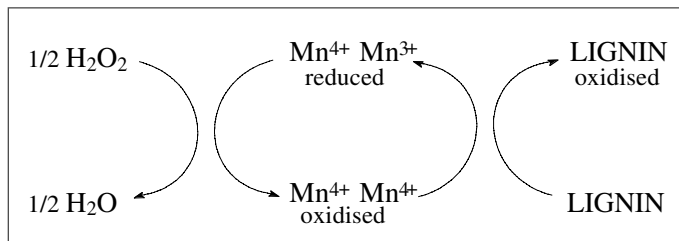
Cui and coworkers investigated the reactivity of lignin toward hydrogen peroxide catalyzed by binuclear manganese complex,

[LMn(IV)(m-O)$_3$Mn(IV)]$^{2+}$(abbreviated as Mn(IV)-Me$_4$DTNE) where L stand for 1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane (Cui *et al.* 1998). Based on the model compounds reaction studies, it was suggested, that hydrogen peroxide catalyzed by Mn(IV)-Me$_4$DTNE would be capable of oxidizing the a-hydroxyl groups and conjugated C-C double bonds in the residual lignin of chemical pulps. The resulting carbonyls and epoxides would be then susceptible to nucleophilic attack leading to further degradation and fragmentation of the residual lignin (Cui *et al.* 1998; 1999). Also examined was the efficiency of Mn(IV)-Me$_4$DTNE catalyzed hydrogen peroxide in the delignification of a pine kraft pulp. More specifically, an addition of Mn(IV)-Me$_4$DTNE (60 ppm on o.d. pulp) to the peroxide bleaching stage at 80ºC with a charge of 4% peroxide at 10% consistency for 120 min significantly improved the degree of delignification from 25 to 46%, compared to the non catalyzed delignification under the same reaction conditions (Cui *et al.* 1999).

Recently, Collins and coworkers developed a new class of peroxide activators (Collins *et al.* 1998). The research of this team was focused at resolving the incompatibility issue that most ligands have with strongly oxidizing metal ions or media. Consequently, the team has proposed a new class of iron (III) complexes involving macrocyclic tetraamides. These complexes were shown to catalytically activate aqueous hydrogen peroxide offering a variety of oxidation reactions.

Using softwood kraft pulp, Collins *et al.* demonstrated that the aforementioned systems could catalytically activate peroxide rapidly bleaching kraft pulp under mild conditions in basic aqueous media. Micromolar concentrations of the proposed compounds, at temperatures ranging from ambient to 90ºC were claimed to selectively direct the oxidation ability of peroxide toward the lignin. More specifically, a 1 hr peroxide bleaching stage at 90ºC with a charge of 4% peroxide (on o.d. pulp) and 80 ppm of activator reduced the kappa number of a softwood kraft pulp from 21.5 to 7.8, while its viscosity was maintained at an acceptable level.

Nitrogen centered peroxide activators

The literature contains a number of accounts in which various peroxide activators containing nitrogen have been examined. Amongst them cyanamide and its dimer, dicyandiamide occupy a prominent position. The cyanamide activated peroxide bleaching process of chemical pulps was initially proposed and patented by Hammer *et al.* and Sturm (Hammer *et al.* 1991; Sturm 1991). Alkaline hydrogen peroxide was thought to react with cyanamide to form a peroxyimidic acid intermediate. Since such a species is ought to have a higher oxidation potential than peroxide, its effectiveness should be greater (Sturm and Kuchler 1993).

Scheme 8: Showing the interaction of cyanamide with alkaline hydrogen peroxide, generating peroxyimidic acid (Sturm and Kuchler 1993).
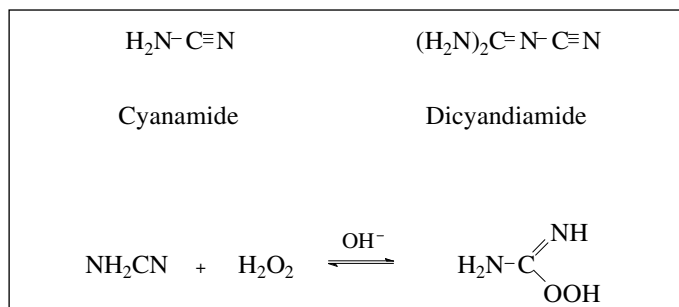
When compared to control runs, cyanamide activated alkaline peroxide bleaching stages produced pulps of higher brightness (by nearly 10 ISO units) with comparable viscosities (Hammer *et al.* 1991; Sturm 1991).

Research by Chen, showed that dicyanediamide, the dimeric form of cyanamide, is a more effective peroxide activator allowing oxygen delignified kraft pulps to be efficiently bleached (Chen 1997), most likely proceeding with a mechanism similar to that of cyanamide.

In contrast to the proposition of Sturm and Kuchler (Sturm and Kuchler 1993), recent work by Kadla and coworkers, on the reactions of lignin and lignin model compounds with cyanamide activated peroxide, demonstrated the involvement of superoxide anion radicals during the reaction (Kadla *et al*. 1998a). The data provided evidence for two competing reaction systems, radical and ionic, in which the majority of the chemistry proceeds via a radical mechanism. The reactions were found to be strongly dependent on pH, with optimum reactivity at pH 9-10 when equimolar amounts of cyanamide and peroxide are used. Further examination of the interaction of cyanamide with alkaline hydrogen peroxide confirmed the presence of a radical intermediate, perhydroxyl radical from peroxide and the corresponding radical cation emerging from cyanamide (Kadla *et al.* 1998b). Four main reaction pathways were thus invoked; aromatic hydroxylation, oxidative demethylation, oxidative coupling and aromatic ring opening with subsequent fragmentation reactions. Oxidation reactions involving
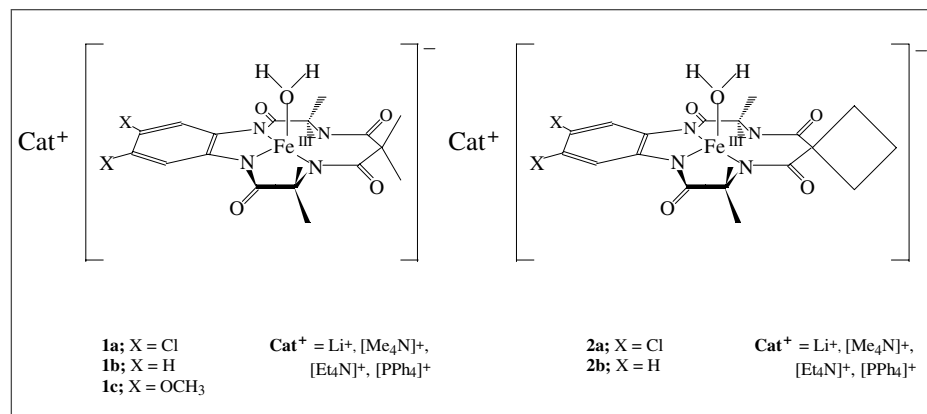
*Scheme 7: Iron based macrocyclic tetraamide activators of hydrogen peroxide (Collins et al. 1998)*

radical intermediates were thought to predominate over radical coupling reactions.

Kang and coworkers have examined the effect of adding cyanamide and molybdate ions in a neutral peroxide delignification of oxygen delignified softwood kraft pulp (Kang *et al.* 1998). A neutral peroxide stage in the absence of an activator produced only 4.1% delignification, while the addition of 2% of cyanamide increased the delignification to 23.5%, while the addition of 500 ppm of Mo^{6+} ions increased the delignification to 27.9%. The simultaneous addition of cyanamide and Mo^{6+} further improved the delignification to 36.9% with no decrease in the viscosity of the resulting pulp. The effect of other metal additives (W^{6+}, V^{5+}) in the cyanamide/metal activated peroxide system were also studied and compared. W^{6+} showed similar results to those of Mo^{6+}, while V^{5+} was totally ineffective.

Tetra acetyl ethylene diamine (TAED) was shown to increase the brightening potential of peroxide by generating peracetic acid *in-situ* as a result of the interaction of TAED with peroxide (Croud and Mathews 1996).

Scheme 9: Tetra acetyl ethylene diamine (TAED) (Croud and Mathews 1996).
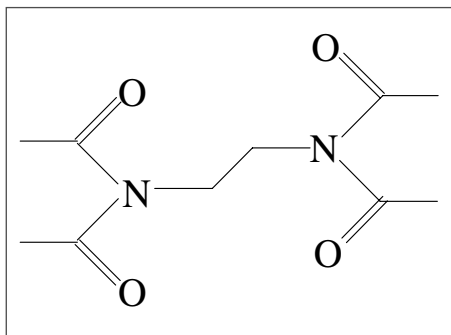
Depending on the pH of the bleaching stage, TAED is thought to react with peroxide to produce peracetic acid or peracetate anion. Both species are stronger oxidants than hydrogen peroxide. In addition, generating peracetic acid *in-situ* avoids handling and capital investment complexities involved when using peracetic acids solutions.

Scheme 10: The reaction of TAED with hydrogen peroxide under alkaline conditions. (Croud and Mathews 1996).
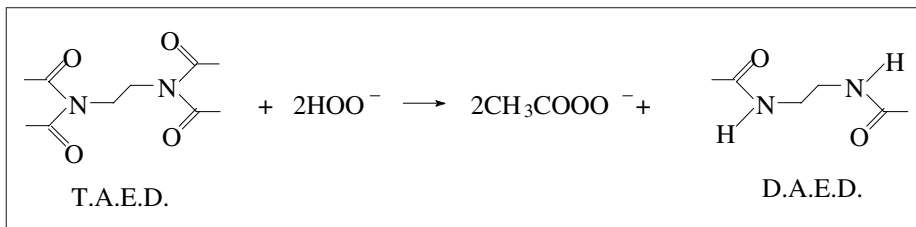
Under alkaline conditions, (pH 9-10) TAED reacts with peroxide rapidly. For example, at 20ºC the reaction is complete within 10-15 min. At pH's higher than 10 the reaction rate increases but the stability of the peracetate anion and the rate of side reactions, involving hydroxide and TAED also increase. In general, the optimum pH of TAED assisted alkaline peroxide delignification is lower than that used in conventional alkaline peroxide stages. TAED also reacts with peroxide under neutral and even acidic conditions while under such conditions peroxide alone is practically ineffective as a delignifying agent. In general, Croud and Mathews state, that this system offers an environmentally benign way of activating peroxide by decreasing the bleaching reaction time without the need of silicate stabilizers, providing possible chemical and cost savings. In addition, Turner and Mathews claim that the use of TAED can readily and safely be incorporated into ECF and TCF bleaching sequences for a number of pulp types (Turner and Mathews 1998).

Nitrogen heterocyclic compounds, containing an a,a'-diimine group as part of the aromatic system, is another potential set of peroxide activators. Such a group is that of polypyridines. Jaschinski and Patt in 1998 showed that delignification and brightness of chelated oxygen delignified softwood kraft pulps, can be significantly improved by adding polypyridines into an alkaline peroxide stage (Jaschinski and Patt 1998). Charges of 4-methyl-1,10-phenenanthroline as low as 0.025%, showed significant brightness gains (11%ISO) when compared to control experiments, with minimum viscosity losses. A significant brightness improvement was also observed when a peroxide stage was carried out at high temperatures. In general the brightness gains were found to be dependent on the dose of polypyridine applied. Amongst the compounds examined, 4-methyl-1,10-phenanthroline 1,10-phenanthroline and 2,2'-bipyridine were found to be the most effective.

1,10-phenanthroline

2,2'-bipyrydine

4-methyl-1,10-phenanthroline

2,4,7,8-tetramethyl-1,10-phenanthroline
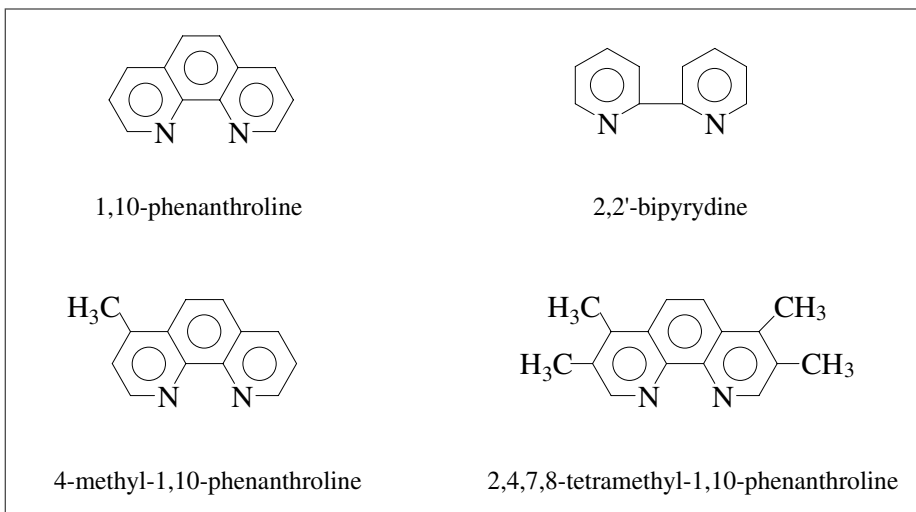
Scheme 11: Polypyridines containing an a,a'-diimine group as part of an aromatic system applied in various bleaching trials. (Jaschinski and Patt 1998).
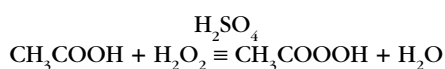
Peracids

Peracids, which are essentially derivatives of peroxides, are substantially stronger oxidizing agents than alkaline oxygen or peroxide. From this point view, bleaching with peracids can be considered as a form of activated peroxide delignification. The oxidizing power of peracids is similar to that of chlorine dioxide and chlorine and as such their delignifying and bleaching potential should be similar to chlorine and chlorine dioxide, with the obvious advantage of being chlorine free.

The ability of peracids to delignify under neutral and/or acidic conditions, coupled with environmental pressures for replacing chlorine and chlorine containing bleaching agents, makes these compounds promising alternative oxidizing agents for chemical pulp bleaching. Peracids have been examined as potential agents for replacing an initial chlorination stage or immediately following an oxygen delignification stage. They have even been applied in the final brightening stages of a bleaching sequence and as activators before or between two oxygen or peroxide stages (Thomasfolk *et al.* 1996). Their proven versatility, therefore, dictates that a close attention be paid to them in this review.

Peracetic acid

The potential of using peracetic acid for chemical pulp delignification was realized as early as the 1950s (Rapson 1956). However, its high cost coupled with its transportation complexities prevented its wider industrial utilization. In 1966, Bailey and Dence described the use of peracetic acid as a brightening and a delignification agent of chemical pulp. These authors compared the Kappa number and the optical and strength properties of the emerging pulps with those obtained from conventional bleaching and delignifying reagents (Bailey and Dence 1966). Despite the fact that peracetic acid showed great promise as a delignification agent, its cost and poor selectivity prohibited its industrial applicability. The peracetic acid used in these early studies was an equilibrium product prepared by mixing appropriate amounts of acetic acid and peroxide in the presence of sulfuric acid as a catalyst.

$$CH_3COOH + H_2O_2 \overset{H_2SO_4}{\equiv} CH_3COOOH + H_2O$$

As implied by the above equilibrium and under conditions that promote it, peracetic acid typically contains high concentrations of acetic acid and hydrogen peroxide. The low amounts of peracid present in the equilibrium mixture severely affected the economics of the process. The peroxide present in the mixture together with transition metal ions impurities of the pulp also may cause serious viscosity losses (Sinkey and Thompson 1974).

In an effort to reduce the chemical costs associated with the process, Christiansen and coworkers investigated the possibility of *in-situ* generating peracetic acid during a bleaching stage (Christiansen *et al.* 1966). In their efforts peracetic acid was formed *in situ* by reacting hydrogen peroxide and acetic anhydride. Bleaching kraft pulp with peracetic acid formed *in situ,* under optimum conditions, resulted in brightness levels similar to those obtained by chlorine dioxide at the same oxidation equivalent. However, the strength of the pulp was significantly lower and its production costs significantly higher when compared to the chlorine dioxide bleached pulp.

Several approaches aimed at improving the selectivity of peracetic acid have been suggested. Hill and coworkers focused their efforts on transition metal control, aimed at reducing the radical decomposition of the unreacted peroxide (Hill *et al.* 1992) and of peracetic acid (Yuan *et al.* 1997). Other efforts involved the removal of peroxide from the peracetic acid equilibrium mixture by distillation (Hill et al. 1992). Distilled peracetic acid can actually be prepared by vacuum distillation of a mixture of acetic acid, hydrogen peroxide and sulfuric acid (Devenyns *et al.* 1993b, Basta *et al* 1994). This process offers a high conversion of peroxide to peracid and the excess acetic acid, peroxide and sulfuric acid are removed. As such, the peroxide responsible for cellulose damage is eliminated and the cost of the peracetic acid is reduced since the excess chemicals may now be recycled.

Jakara and coworkers have compared the delignification efficiencies of equilibrium (e)Paa with distilled (d)Paa delignification stages in TCF bleaching sequences of softwood kraft pulp (Jakara *et al.* 1995b). It was thus confirmed that different optimal initial pH's for ePaa (pH 4.5) and dPaa (pH 5-7) were required. The delignification efficiency of the ePaa and the dPaa stages showed little difference. However, as anticipated, considerable differences were observed in the total amount of chemical required.

Vuorenvirta and coworkers recently compared the efficiency of using equilibrium and distilled peracetic acids in TCF softwood pulp bleaching (Vuorenvirta *et al.* 1998). Their data confirmed the fact that equilibrium and distilled peracetic acids have different optimum pH operating ranges. The optimum initial pH for ePaa proved to be 4-5, and for dPaa 5-8. However, the delignification achieved with distilled and equilibrium peracetic acids were the same when the bleaching was carried out under optimized pH conditions. These authors also investigated the possibility of reducing the consumption of Paa by applying an acid stage before bleaching. Their data showed that the final kappa numbers of the acid washed and chelated pulp were about the same. However, there was a significant drop in chemical consumption if the reaction time of the acid stage was long enough (120 min).

Jaaskelainen and Poppius-Levlin studied the factors affecting the kinetics of oxygen-treated pine kraft pulp delignification with peroxyacetic acid (Jaaskelainen and Poppius-Levlin 1999). They confirmed that equilibrium and distilled Paa gave equally high delignification rates and pulp viscosity, while ePaa led to slightly better pulp brightness, most likely due to the presence of peroxide in the ePaa mixture. Jaaskelainen and Poppius-Levlin concluded that the most important factors affecting the kinetics of delignification in the Paa stage were Paa concentration, temperature, and pH.

A full-scale mill trial using peracetic acid was carried out in Sweden in 1994 and in 1995, the first mill in the world started to use peracetic acid for TCF pulp production (Thomasfolk *et al*. 1996). Selective delignification, good pulp strengths and low investment costs were amongst the advantages claimed for this process when compared to other TCF sequences. However, production costs were higher.

The possibility of using distilled peracetic acid was examined in various mill-

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scale trials in Finland (Ruohoniemi *et al.* 1998). This effort lead to the conclusion that peracetic acid could be used for both brightening and delignifying purposes. In ECF bleaching, the advantage of Paa is a high brightness level and the reduced need for active chlorine in bleaching. The use of Paa in TCF bleaching resulted in a pulp with low kappa number and high brightness with good stability. Various economic disadvantages were still obvious.

Caro's acid and other peracids

Growing interests in non-chlorine bleaching agents have promoted attention to peroxy acids, other than peracetic acid, as possible delignification and bleaching agents. Peroxymonosulfuric acid, its salts and more recently performic acid, have all been reported as effective oxidizing agents for delignifying and bleaching chemical pulps (Poppius *et al.* 1989; Song *et al.* 1993; Geng *et al.* 1993; Springer and McSweeny 1993b).

Peroxymonosulfuric acid, also known as Caro's acid, is another powerful oxidizing agent belonging to the group of peracids, prepared from the interaction of hydrogen peroxide with sulfuric acid. This is also an equilibrium reaction similar to the one that describes the formation of peracetic acid.

$$H_2SO_4 + H_2O_2 \equiv H_2SO_5 + H_2O$$
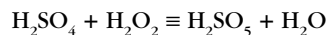
The amount of water present in the reaction mixture affects the conversion of peroxide to Caro's acid. Its concentration reaches a maximum at about 45% conversion, when an excess of 99% sulfuric acid and 50% hydrogen peroxide (1.5:1.0 mole ratio) is used. The conversion of the process can be increased by minimizing the amount of water or by using more concentrated peroxide (70%) and sulfuric acid (oleum) (Szegda 1994). Both of these routes, however, have aroused serious safety concerns (Amini and Webster 1994). Despite these, mill trials using Caro's acid have been conducted yielding high brightness softwood and hardwood kraft pulps (Seccombe *et al.* 1994).

Geng and coworkers have described another means of increasing the peroxide conversion to the peracid (Geng *et al.* 1993). By adding acetic acid to the equilibrium mixture of Caro's acid a mixture of peracetic and peroxymonosulfuric acids is formed. This permits the high conversion of peroxide to the peracids without using excessively high peroxide and sulfuric acid concentrations.

$$H_2SO_4 + H_2O_2 \equiv H_2SO_5 + H_2O_2 +$$
$$CH_3COOH + H_2O_2 \equiv CH_3COOOH +$$
$$H_2O$$
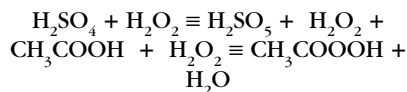
The work of Song and coworkers essentially confirmed the effort of Geng *et al.* They reported that by adding one mole of acetic acid to the Caro's acid mixture increased the conversion of peroxide to peracids to a 94% level (Song *et al.* 1993). The role and possible application of Caro's acid (Px) and mixed peracids (Pxa) in ECF and TCF bleaching sequences were also investigated in the following efforts (Geng *et al.* 1993; Song *et al.* 1993; Brasileiro *et al.* 1997).

Devenyns and coworkers have shown that they were able to obtain fully bleached softwood kraft pulp by using a peroxygen based bleaching sequence (Devenyns *et al.* 1993a). Oxygen delignified and chelated pulp was prebleached with peroxide followed by a peracid stage (peracetic, Paa and Caro's Px acids). The final brightening was obtained by applying a P* stage (alkaline hydrogen peroxide at high consistency with particular attention being paid to transition metal removal and stabilization). Using the described OQPPPaaP* and OQPPPxP* sequences, fully bleached TCF kraft pulp was produced with adequate mechanical properties.

A TCF bleaching sequence composed of an acid pretreatment, acidic peroxymonosulfate, oxygen delignification, and alkaline peroxymonosulfate brightening was described by Springer and McSweeny (Springer and McSweeny 1993b). Under the optimal bleaching conditions, the sequence produced a final brightness of 83% ISO in pine kraft pulp. When the same sequence was applied to an aspen kraft pulp a final brightness of 86% ISO was obtained.

Amini and Webster compared the delignification efficiency of mixed peracids (Pxa) with oxygen (Amini and Webster 1994). A comparison of oxygen delignification and mixed peracids stages followed by Eop, showed that both reduced the kappa number of pine kraft pulp (kappa 34) by half. The PxaEop stage, however, gave in higher brightness. Experiments with eucalyptus kraft pulp (kappa number 20) showed an even better performance for peracids. A single Pxa stage was shown to have a higher delignification efficiency than a single oxygen delignification stage. The combination of Pxa and Eop stages resulted in 60% delignification. This is substantially more than the delignification obtained after the single oxygen. When a PxaEop sequence was applied after an oxygen stage, the kappa number was reduced from 12 (after the oxygen stage) to 5.1, and the brightness reached 69% ISO. By comparing the delignifying and brightening efficiencies of peracetic acid, Caro's acid and mixed peracids, the researchers concluded that for a variety of conditions, equal amounts of peracid (equal active oxygen in its peracid form, or equal molar amounts of peracid) gives similar delignifying and brightening performance.

Basta and coworkers (Basta *et al.* 1994) also compared peracetic acid and Caro's acid. Oxygen delignified softwood kraft pulp bleached with a sequence composed of a peracid treatment, followed by a chelating stage and a final alkaline peroxide stage, showed superior selectivity when peracids (for peracetic acid both dPaa and ePaa were used) were compared to Caro's acid. A similar comparison with ozone in a QPZP bleaching sequence again proved the higher selectivity of dPaa.

Troughton and coworkers examined the effect of inserting a peracid stage into a TCF bleach sequence, consisting of a metal controlling Q-stage, followed by several alkaline peroxide stages (Troughton *et al.* 1995). By inserting a peracid stage into the QPPP sequence it was found that the pulp brightness may be increased by 5-10 ISO points without pulp strength losses. When the delignification efficiencies for the various sequences were compared, the effect of the peracid stage was found to be due to a more extended delignification. For example, when a softwood oxygen delignified kraft pulp was bleached by a QPPxP sequence its kappa number was reduced to 2.4. However, a somewhat better delignification was obtained when Caro's acid was replaced by peracetic acid. The final kappa number, after the QPPPaaP sequence was 2.1. Equivalent

bleaching, using only peroxide (QPP) was found to reduce the kappa number to only 5.7.
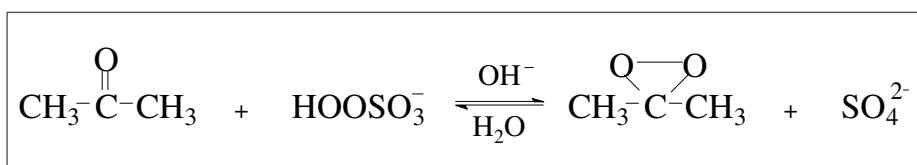
Liebergott showed that by applying a peracetic acid pretreatment on an unbleached softwood kraft pulp, followed by an Eop stage can increase the delignification from 35% (QEop) to 48.9% (PaEop) (Liebergott 1996). Similar results were observed when an oxygen delignified softwood kraft pulp was used. The Pa treatment increased the extent of delignification after an Eop stage from 20% (for an OQEop sequence) to 40% (for an OPaEop sequence). The kappa number was reduced from 16.4 (after oxygen delignification) to 9.8.

Poppius and coworkers reported the use of peroxyformic acid in TCF bleaching (Poppius *et al.* 1989). The degree of delignification of a pine kraft pulp achieved with peroxyformic acid and hydrogen peroxide was 25-80%, depending on the concentration of formic acid, amount of peroxide and the temperature of the treatment. Subsequent alkaline peroxide bleaching stages raised the brightness to 80-85% ISO. In addition, the same team showed that peroxyformic acid may also increase the efficiency of an oxygen delignification stage by ensuring a substantial decrease in the incoming kappa number prior to the oxygen stage (Poppius-Levlin *et al.* 1991). Kappa numbers as low as 4-6 were obtained for pine and birch kraft pulps after the (PFA)O sequence. Consequently, brightness values of 90% ISO were reached for both the pine and birch kraft pulps predelignified with peroxyformic acid and bleached with a sequence using oxygen, ozone and alkaline peroxide.

Springer examined peroxymonophosphoric acid as a possible delignification agent for wood and kraft pulp (Springer 1997). Pine kraft pulp was delignified with a dilute aqueous solution of peroxymonophosphoric acid and its delignification selectivity was compared with peroxymonosulfuric acid. This exploratory study showed that, under identical reaction conditions, peroxymonophosphoric acid delignified more rapidly and more selectively than peroxymonosulfuric acid. However, the incompatibility of the phosphates with current mill recovery systems is a major drawback.

Dioxiranes

Dioxiranes have recently been identified as a novel and selective class of non-chlorine bleaching agents for chemical pulps (Lee *et al.* 1994). This is a class of powerful electrophilic oxidants efficiently transferring oxygen onto aromatic and/or unsaturated substrates. The major feature of such compounds is their effectiveness to transfer a single activated oxygen atom onto an aromatic substrate. Consequently, this class of oxidants was termed "*activated oxygen*" (AO), in reference to its use in a bleaching sequence. Dimethyldioxirane (DMD) represents the simplest member of this series. This cyclic organic peroxide can be generated by the interaction of peroxymonosulfuric (Caro's) acid with acetone (Edwards et al. 1979). The potential

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \; + \; HOOSO_3^- \; \underset{H_2O}{\overset{OH^-}{\rightleftharpoons}} \; CH_3-\overset{\overset{\displaystyle O-O}{|\quad\;|}}{C}-CH_3 \; + \; SO_4^{2-}$$

Scheme 13: Synthesis of dimethyldioxirane (DMD) from acetone and peroxymonosulfuric acid. (Lee et al. 1994)

of DMD for pulp bleaching purposes was initially recognized, patented and reported by Lee and coworkers at PAPRICAN and latter was confirmed by Ragauskas (Lee 1991; Lee *et al.* 1992; Ragauskas 1993).
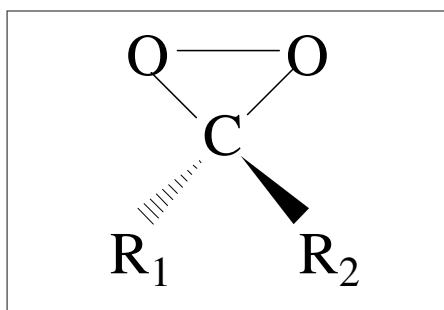
Scheme 12: Chemical structures of dioxiranes. R1 and R2 can be the same or different, and may be linked to form cyclic compounds. (Lee et al. 1994).

Lee and coworkers initially studied the bleaching efficiency of isolated DMD (Lee 1991) and latter of *in-situ* generated DMD (Lee *et al.* 1992). A one-stage treatment of a hardwood kraft pulp with isolated DMD (0.55% as AO, calculated as 1

activated oxygen per molecule of DMD, or 2.5% isolated DMD) for 1 hr, reduced the kappa number from 16.4 to 3.4 (79% delignification) (Lee et al. 1993). The yield of activated oxygen, however, in the isolated form, based on the charge of monoperoxysulfate was found to be extremely low, seriously precluding the potential of the process for industrial application. Bleaching with *in-situ* generated AO was carried out by mixing the pulp slurry with acetone in an aqueous slurry. Sodium bicarbonate was added to control the pH (7-7.5) and then monoperoxysulfate was added to the pulp slurry. The reaction of acetone with monoperoxysulfate at a near neutral pH, generated AO *in-situ*, which subsequently bleached the pulp.

Delignification of softwood kraft pulp with *in situ* generated DMD (2.7% AO, 12.5% DMD) followed by an alkaline extraction stage, reduced the kappa number from 31.5 to 5.4 (83% delignification). Lee's data were latter confirmed by Ragauskas who bleached a softwood kraft pulp with a 5% isolated DMD charge (Ragauskas 1993). The initial kappa number of 39.5 was reduced to 12.5 (68% delignification). Both groups defined DMD as a very selective delignification agent either in its isolated form or generated *in situ* within the pulp slurry.

Further work was carried out latter by McDonough and coworkers who studied the efficiency of DMD in bleaching oxygen delignified kraft pulp, and its effects in a TCF bleaching sequence using with oxygen and peroxide (McDonough *et al.* 1994). Oxygen delignified softwood kraft pulp was sown to be effectively delignified by treating it with a 4% DMD charge. The kappa number was reduced from 14.1 to 5.8. Amongst various TCF bleaching sequences examined, O(AO)QP was

found to be the most successful. When a DMD stage was added at the end of the bleaching sequence (OQP(AO)) the final brightness and viscosity were lower. DMD was not found to be an ineffective brightening agent because it introduces chromophores into the remaining lignin. It was found, however, to have a positive effect on the brightening power of a subsequent peroxide stage. DMD charges of up to 2% had virtually no effect on viscosity while charges of 4% and above resulted in noticeable viscosity losses. This effect was rationalized on the basis that, at low lignin contents, the excess DMD was not consumed, increasing the possibility of it oxidatively attacking the cellulose.

Lee and coworkers also examined the efficiency of DMD in the bleaching of oxygen delignified kraft pulp (Lee *et al*. 1994). A DMD treatment (AO charge 2.5%) of an oxygen delignified softwood kraft pulp followed by oxygen-peroxide-reinforced extraction (Eop) reduced the kappa number from 12.6 to 2.0. Viscosity and strength properties were the same as those observed after an O(C+D)Eop sequence. Since AO was shown to delignify kraft pulps to kappa numbers as low as 3 or less, the researchers thought it would be possible to produce fully bleached TCF softwood kraft pulp by a single peroxide brightening stage preceded by a chelating treatment (Q). An OAEopQP bleaching sequence using a 2.5% AO charge was shown to yield a pulp of 90.9% ISO brightness with a severe viscosity loss at the peroxide stage.

In an effort to shed more light on the effectiveness of dioxiranes toward their demonstrated bleaching efficiency, Argyropoulos and coworkers have studied the reactions of DMD with lignin model compounds (Argyropoulos *et al*. 1996). DMD was found to electrophilically oxidize the aromatic rings of both etherified and non-etherified softwood lignin model compounds. This is an advantage that DMD has over other bleaching agents (ClO_2, H_2O_2, O_2, etc.) since other agents require free phenolic hydroxyl groups to act upon. On the same front, Bouchard and coworkers studied the stability of DMD under kraft pulp bleaching conditions (Bouchard *et al*. 1996). This work showed that the decomposition of DMD was accelerated by the presence of transition metals. However, the fast reaction rate of DMD with the pulp was found to partially counteract the deteriorating effects of such metals.

Concluding remarks

Exploratory attempts to improve the delignification and bleaching efficiency of oxygen and/or hydrogen peroxide commenced almost as soon as their delignification and brightening potential was realized. During the early efforts, the imposing limitations were economic and safety issues associated with the improvements of a particular process. During the past decade, however, environmental issues and regulatory forces have seriously altered the way we view such improvements. Despite the renewed interest in developments in this area and our new outlook, many processes, activators, and catalysts that showed significant potential for application in oxygen or peroxide delignification fail to see widespread industrial applicability because the same economic and safety considerations still apply. More specifically, while peracetic acid and various other agents have been documented to efficiently delignify and bleach pulps, their high cost, relative instability, and sometimes their incompatibility with the existing energy recovery systems, still prevents their widespread industrial use. Alternatively, the potential of catalytically activating hydrogen peroxide still needs to be fully explored and realized. Promising research endeavors in this area are already underway, using novel classes of compounds and emerging principles of organic and bioinorganic chemistry. Perhaps some of the answers may lie in the way nature reduces oxygen to water, controlling the process using various enzymatic receptors. Understanding the principles of biomimetic oxidations and applying them to our industry could conceivably offer some truly revolutionary processes that may guide our industry into the new millenium. **TJ**

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